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Commodity Chemicals Derived from Glycerol, an Important Biorefinery Feedstock

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1. Introduction and Background

As our fossil raw materials irrevocably diminish and environmental pressures build, a progressive changeover of chemical industries to renewable feedstocks emerges as an inevitable necessity. Experts realistically predict the end of cheap oil in 2040 at the latest, a development that we can already witness as chemical manufacturers confront the rising cost of oil and natural gas. The transition to a more biobased production system is currently underway, and much attention has been given to the catalytic conversion of renew-

able feedstocks and chemicals. The conversion of renewable materials to hydrogen assists in the utilization of renewable energy sources, and conversion to commodity chemicals facilitates the replacement of petroleum by renewable resources. Recently, it has been proposed that renewable resources such as plant-derived sugars and other compounds be used to synthesize the compounds necessary for the production of pharmaceuticals, agricultural chemicals, plastics, and transportation fuels. Compounds that are now derived from fossil resources might be produced in future biorefineries.^{1–3}

Glycerol is a potentially important biorefinery feedstock, available as a byproduct in the production of biodiesel by transesterification of vegetable oils or animal fats.^{4–37} For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol byproduct is formed. Glycerol markets have reacted strongly to the increasing availability of glycerol: Although the global production of biodiesel is still very limited, the market price of glycerol has dropped rapidly. If the production of biodiesel increases as predicted, the supply of glycerol will be in excess of demand. On the other hand, the present cost of biodiesel is higher than diesel fuel. Some studies^{22,38} stated that the production cost of biodiesel was found to vary inversely and linearly with variations in the market value of glycerol.

Therefore, new uses for glycerol need to be found. Although glycerol can be burned as a fuel, it can also be processed into more valuable commodity chemicals. Its highly functionalized nature means that glycerol can readily be oxidized, reduced, halogenated, etherified, and esterified to obtain alternative commodity chemicals (Figure 1), such as dihydroxyacetone,^{39–44} mesoxalic acid,⁴⁵ 1, 3-propanediol,^{46–50} 1,3-dichloropropanol,^{29,48} glyceryl ethers,^{51–58} glycerol carbonate,^{52,59,60} and glyceryl esters.^{61–73}

In this review, we investigate the technical and economic aspects of producing commodity chemicals from glycerol using various chemical or biological catalysts. The aim is to provide a connection between glycerol from renewable feedstocks and commodity chemicals.

2. Glycerol, an Important Biorefinery Feedstock

Glycerol is the simplest triol and is a component of all natural fats and oils in the form of fatty acid esters and is an important intermediate in the metabolism of living organisms. It is obtained in yields of up to 90% by the splitting of triglycerides. It is the most important byproduct of oleochemistry, and its supply is increasing with accelerated oleochemical production. Glycerol can also be produced by fermentation and chemical synthesis.

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Yuguo Zheng was born in Xiangshan, Zhejiang, China, in 1961. He received his B.E. and M.E. in chemical process machinery and Ph.D. in biochemical engineering. Presently, he is Professor of Biochemical Engineering in Zhejiang University of Technology. His research interests are biochemical engineering and biotransformation and biocatalysis.



Xiaolong Chen was born in Xianju, Zhejiang, China, in 1970. After graduation, he worked as a researcher and teacher at Zhejiang University of Technology. He started his doctorate degree in 2004 at Zhejiang University of Technology. In 1999, he began to study natural products, such as valienamine, valioline, validamine, and tautomycin. His research field interests are the production of natural products and their structure modifications.

Microbial production of glycerol has been known for 150 years. During World War I, glycerol was produced commercially with microbes. A number of microorganisms are capable of producing glycerol by fermentation, including yeasts such as *Saccharomyces cerevisiae*, *Candida magnoliae*, *Pichia farinose*, and *Candida glycerinogenes*, bacteria such as *Bacillus subtilis*, and algae such as *Dunaliella tertiolecta*.

Overexpression of the genes associated with glycerol formation has been attempted in efforts to improve glycerol synthesis by microorganisms, which is based on channeling the glycolytic flux toward glycerol formation and on decreasing the activities of the pathways for dissimilation of glycerol. Triose phosphate isomerase is a key enzyme in the glycolysis that directs dihydroxyacetone phosphate to glyceraldehyde-3-phosphate after the split of fructose-1,6-bisphosphate. When the triose phosphate isomerase gene (TPI) of *S. cerevisiae* is deleted, the mutant is able to attain a high glycerol yield from glucose (80–90% of the theoretical yield) and glycerol productivity [1.5 g/(L h)] without the need for a steering agent.⁷⁴ However, the mutant strain grows poorly due to an energy deficiency and shows genetic instability on the glucose medium.



Yinchu Shen was born in Shengzhou, Zhejiang, China, in 1938. In 1962, he obtained his undergraduate degree from Fudan University. In the same year, he began to study his graduate courses. He worked in Shanghai Institute of Pesticide and Shanghai Research Center of Biochemical Engineering subject to China Chemical Engineering Department in 1964. He was voted as an academicien to the Chinese Academy of Engineering in 1998. Then, he moved to Zhejiang University of Technology as the professor of Biochemical Engineering. In 2000, he acted as the president of the university. His major research fields are the products of Biochemical Engineering.

The NAD⁺-dependent glycerol-3-phosphate dehydrogenase is a key enzyme for glycerol formation in *S. cerevisiae* and many other yeast strains, and the overexpression of the GPD1 gene in yeast increases glycerol production. In a strain of *S. cerevisiae*, the glycerol yield exhibiting 20-fold increased Gpd1p activity resulting from overexpression of GPD1 gene was 6.5 times of that the wild type.⁷⁵ Overexpression or disruption of GPD1 could also modulate glycerol and ethanol yields during alcoholic fermentation in *S. cerevisiae*.^{75,76} Mutants with *gpd1D* exhibited a 50% decrease in glycerol production and increased ethanol yield. On the other hand, overexpression of GPD1 in strains resulted in a substantial increase in glycerol production at the expense of ethanol in broth containing 200 g/L glucose. In 2001, a review was reported about the glycerol production with microbial fermentation.⁷⁷

New energy resources such as biodiesel fuel have grown in importance in recent years. Biodiesel (composed of fatty acid methyl esters) is an efficient, clean, 100% natural energy alternative to petroleum fuels. The many favorable aspects of biodiesel fuel include the following: It is safe for use in all conventional diesel engines, it offers the same performance and engine durability as petroleum diesel fuel, it is nonflammable and nontoxic, and it reduces tailpipe emissions, visible smoke, and noxious fumes and odors. Biodiesel is obtained from natural, renewable sources such as new and used vegetable oils and animal fats. On the basis of these advantages, biodiesel technology is making the transition from a research endeavor to a worldwide commercial enterprise.

In support of this increasing consumption, there have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. Europe and the United States are the leading biodiesel producers at this time, with European production in 2003 estimated at 1.7×10^9 L (450 million gal) (data from European Biodiesel Board, 2004) and U.S. production in 2004 estimated at 114 million L (30 million gal) (data from McCoy, 2005). This growth is the result of the construction of new production plants and the expansion of existing ones.

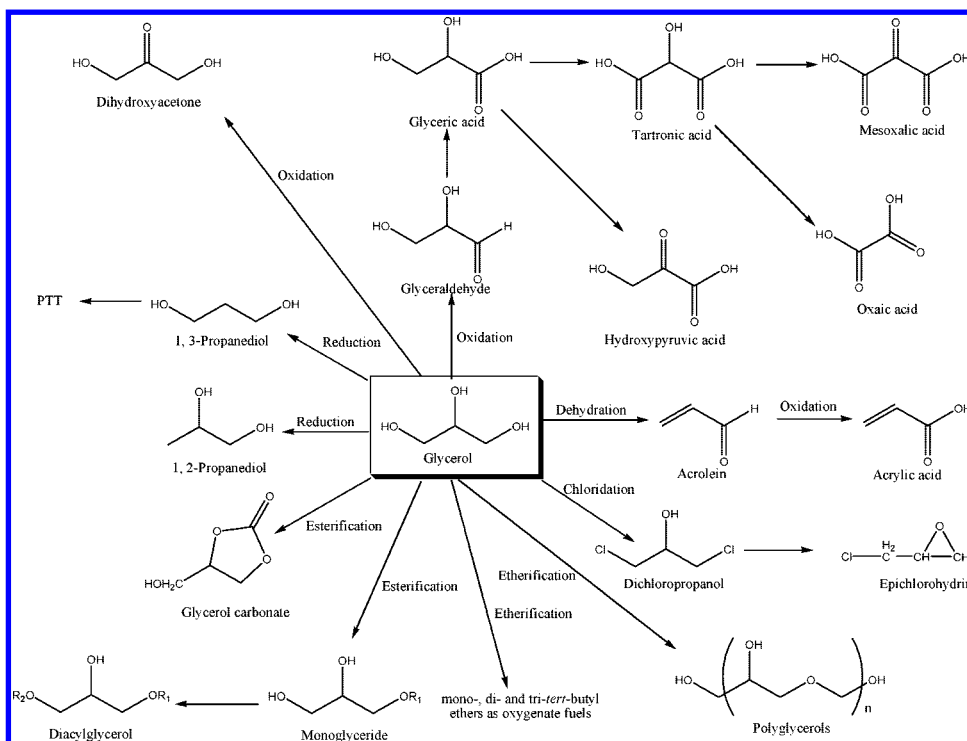


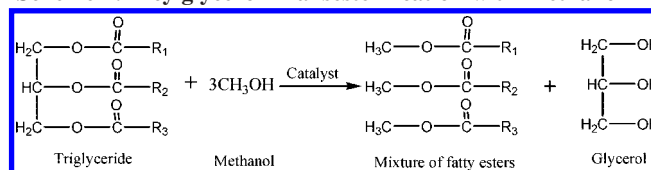
Figure 1. Commodity chemicals from glycerol.

Biodiesel can be produced from any material that contains fatty acids, whether they are free acids or linked to other molecules. Thus, various vegetable fats and oils, animal fats, waste greases, and edible oil-processing wastes can be used as feedstocks for biodiesel production. The choice of feedstock is based on such variables as local availability, cost, government support, and performance as a fuel.

A variety of reaction configurations can be employed in biodiesel synthesis, involving inorganic acid, inorganic base or enzymatic catalysis, biphasic or monophasic reaction systems, and ambient or elevated pressures and temperatures. The choice of which chemical technology to employ in a production plant depends on the type of feedstock and its quality. The choice of conversion technology will in turn influence costs. The scale of operation will also bear upon construction and operating costs. In any case, individuals considering the construction or modification of a biodiesel production facility need a means of estimating the cost of biodiesel production based on the components of the operation and construction costs. A review⁷⁸ of 12 economic feasibility studies shows that the projected cost for biodiesel from oilseed or animal fats ranges from U.S. \$0.30–0.69/L, including meal and glycerol credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added to an existing grain or tallow facility. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, U.S. \$0.54–0.62/L and U.S. \$0.34–0.42/L. With pretax diesel priced at U.S. \$0.18/L in the United States and U.S. \$0.20–0.24/L in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed.⁷⁹

During triglyceride transesterification, glycerol separates from the oil phase as the reaction proceeds (Scheme 1). The glycerol liberated during transesterification has substantial commercial value if purified to USP grade. As a rough rule of thumb, about 1 kg of glycerol is produced for every 9 kg

Scheme 1. Acylglycerol Transesterification with Methanol



of fatty acid methyl ester. Therefore, increased biodiesel production results in the accumulation of glycerol, which leads to a price decline. The effect is that the sale of glycerol is becoming the bottleneck of biodiesel production enhancement. Figure 2 is a forecast of the development of global glycerol production.⁸⁰ The model was based on the production and sale of 80% glycerol by mass, assigning it a value of U.S. \$0.33/kg consistent with recent prices for this material. The model predicted an inverse linear relationship between the production cost of biodiesel and the variations in the market value of glycerol, increasing by U.S. \$0.0022/L for every U.S. \$0.022/kg reduction in glycerol value. To

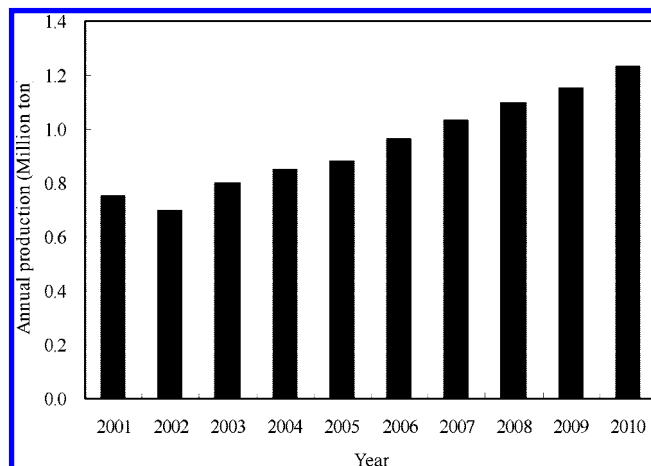


Figure 2. Projection of the global glycerol production.

expand biodiesel production, economical utilization pathways for the glycerol byproduct must be developed.

3. Commodity Chemicals Derived from Glycerol

The development of new applications for glycerol would be enthusiastically welcomed by the entire glycerol industry. The broadest-based opportunity for the effective consumption of glycerol will arise from its use as a primary chemical building block. Because of price and availability, many current uses of glycerol do not employ further transformation of its structure. Once it is recognized that a ready source of low cost glycerol is available from the biodiesel unit operation, glycerol could be positioned within the biorefinery as a primary renewable building block analogous to those of the petrochemical industry (methane, ethylene, BTX, etc.). As the price of glycerol drops and its availability rises, glycerol ceases to become an “additive” for a fragmented list of small volume products and assumes a position as the starting point for the production of a smaller number of high-volume materials. When the cost of a chemical drops, its range of industrial utility broadens, and the ability to absorb the cost of additional chemical transformations increases. Glycerol would transition from its current state as an advanced intermediate or chemical end product to a starting material for a large family of compounds.

A number of opportunities for glycerol consumption have been identified and are summarized in Figure 1. The intent of this figure is not to imply that all areas should receive simultaneous R&D effort but rather to provide an overview analogous to similar diagrams developed for petrochemical unit operations. The petrochemical industry describes the families of products arising from their most basic building blocks as the “ethylene family” or the “BTX family”. Within the context of the biorefinery, Figure 1 is suggested as a starting point for a definition of the “glycerol family”. Success in the development of an effective glycerol operation will have a synergistic effect on the production of biodiesel. Finding higher value, large volume uses for glycerol will help offset the low value of biodiesel, resulting in a profitable integrated biodiesel/byproducts unit operation. From a technical standpoint, glycerol’s multifunctional structure can be exploited by several different means, as shown by the potential glycerol product family in Figure 1.

3.1. Oxidation of Glycerol

Glycerol’s structure lends itself well to catalytic oxidative processes using inexpensive oxidizing agents such as air, oxygen, hydrogen peroxide, or bleach. A combination of these inexpensive oxidizing agents with an inexpensive source of glycerol will allow the production of a number of new derivatives. A range of possible products can be formed by oxidizing glycerol, such as dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid, hydroxypyruvic acid, mesoxalic acid, oxalic acid, and tartronic acid, as shown in Figure 3. Dihydroxyacetone is used as a tanning agent in the cosmetics industry and as a synthon in organic synthesis. Dihydroxyacetone and hydroxypyruvic acid are possible starting materials for D,L-serine synthesis.⁸¹ The highly functionalized molecule mesoxalic acid has potential for use as a complexing agent and as a precursor in organic synthesis and recently was found to show activity as an anti-HIV agent.⁸² Hydroxypyruvic acid is a flavor component⁸³ in cheese and has previously been used for synchronization of

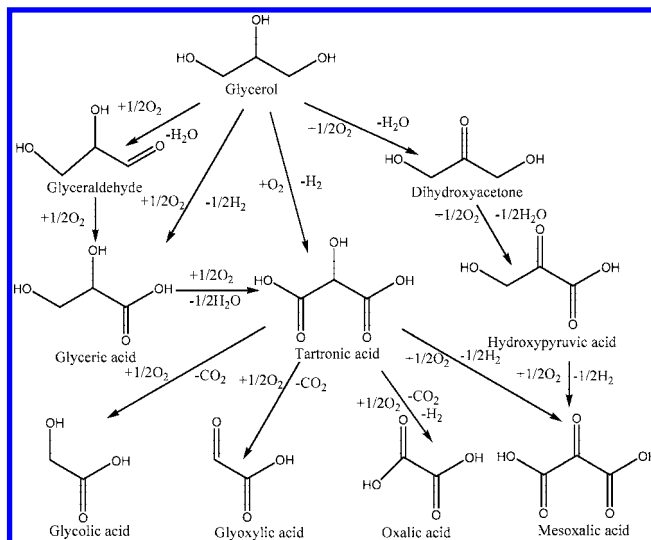


Figure 3. Reaction network of the glycerol oxidation.

fruit maturation.⁸⁴ At present, the market for these chemicals has not developed because of the high cost of their current production methods. Oxidation of aqueous solutions of glycerol using air and recyclable catalysts provides a low-cost, environmentally friendly route to these compounds.

3.1.1. Oxidation of Glycerol with Chemical Catalysts

A range of possible products (Figure 3) can be obtained from the oxidation of glycerol using chemical catalysts or electrochemical methods. Thus, crucial research targets include control of selectivity for the desired product and prevention of overoxidation. It has been shown that by using monometallic or bimetallic catalysts based on Au, Pd, and Pt metals provides tunable selectivity.^{45,81,83,85–97} Furthermore, the temperature, the pH, and the particle size of the metal^{88,98,99} conditions are very crucial for the formation of the desired product.

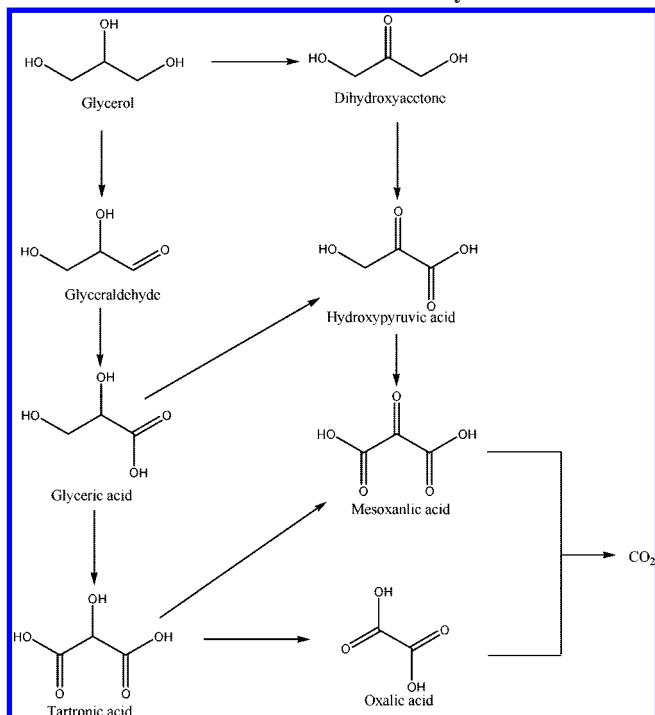
Selective Oxidation of Glycerol with Metal Catalysts.

The selective oxidation of glycerol with oxygen using mono- and bimetallic catalysts based on Au, Pd, and Pt metals were investigated by researchers, including Hutchings,^{87–89,100} Prati,^{98,101–108} Gallezot,^{45,85,85,94,95} Kimura,^{81,90,91,93,109–114} Claus,^{115,116} and Davis.^{96,97,99}

Hutchings Research Group. Supported gold nanoparticles produced 100% selectivity in the oxidation of glycerol to sodium glycerate when the reaction was carried out in NaOH,^{87–89} in spite of the large number of products that can be formed from glycerol oxidation (Scheme 2). Characterization using TEM reveals that the active Au/graphite catalysts comprise gold nanoparticles 50 nm in diameter with a broad size distribution, whereas an inactive Au/graphite catalyst displays significantly larger particle diameters (> 50 nm) with a narrower size distribution.

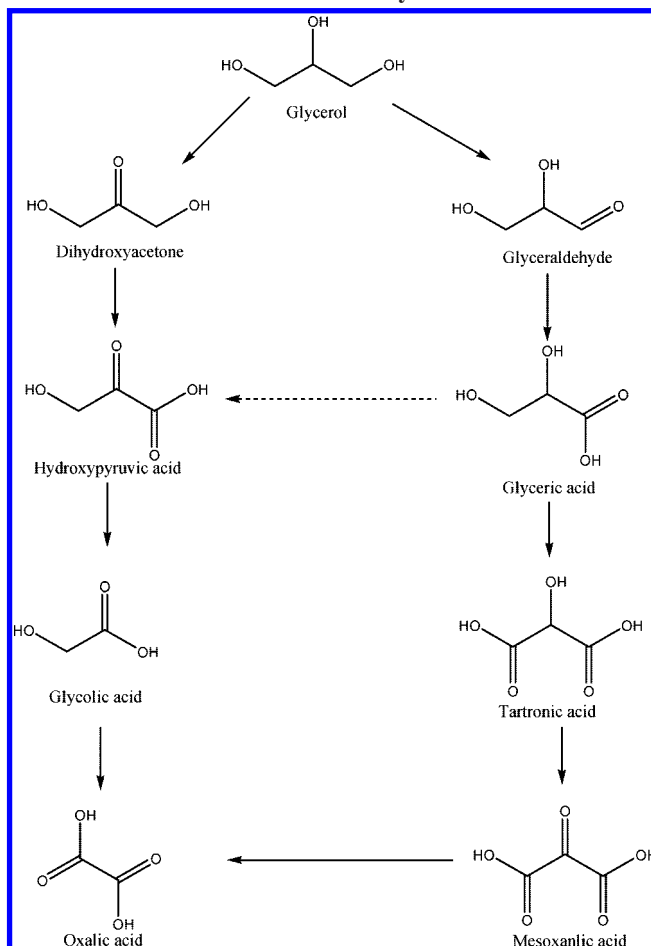
Prati Research Group. The liquid phase selective oxidation of glycerol with oxygen using mono- and bimetallic catalysts of Au, Pt, and Pd on carbon or graphite was studied, including the behavior of Pt(0)/carbon and Pt(0)/Au(0)/carbon catalysts. Under optimal conditions, 92% selectivity to glycerate at full conversion was obtained by oxidizing glycerol using an Au/carbon catalyst at 30 °C, with a NaOH/glycerol ratio of 4, a glycerol/Au ratio of 500, and 0.3 M concentration.⁹⁸ Comparison of Au and Pd monometallics supported on the graphite showed a similar behavior in terms of selectivity, with Pd showing a higher activity, and

Scheme 2. Products from Oxidation of Glycerol



bimetallic catalysts showed a higher activity with respect to monometallic catalysts, which indicates a synergetic effect between the two metals.¹⁰⁵ This effect was especially significant in the case of Pt as the monometallic was poisoned before reaching full conversion. In terms of selectivity to glyceric acid, (Au–Pd) catalysts in general showed better selectivity than (Au–Pt) catalysts, with Pd serving mainly to promote the formation of tartronic acid and Pt to glycolic acid. The overall selectivity to glyceric acid increased using bimetallic (Au–Pd)/C catalysts relative to monometallics.¹⁰¹ The influence of metal particle size in monometallic and bimetallic supported catalysts (Au, Pd, A–Pd)/C was studied using the liquid phase oxidation of glycerol as a model reaction.¹⁰⁴ By tuning the metal particle size from 2 to 16 nm, a progressive decrease of activity and simultaneous increase in selectivity to sodium glycerate was observed. The effect of temperature was also investigated, and it was found that at elevated temperatures, the product glycerate was retained only with larger catalyst particles, while smaller particles led to overoxidation to tartronate. Finally, the behavior of Pt(0)/carbon and Pt(0)/Au(0)/carbon catalysts in the oxidation of glycerol with molecular oxygen in water was investigated.¹¹⁷ The activity and the distribution of products in the liquid phase were significantly influenced by the nature of the Pt precursor (“fresh” vs “aged”) and reducing agent (NaBH₄, N₂H₄, and H₂) for monometallic Pt/C catalysts. In the case of “fresh” Pt/C catalysts, reduction by H₂ was the most effective in terms of activity and selectivity to glyceric acid, whereas for “aged” Pt/C catalysts, NaBH₄ produced a more selective catalyst, suggesting that different nanoparticles can be produced by tuning the reduction method. However, in all monometallic Pt/C catalysts, a deactivation process took place during the reaction. When the catalysts were modified by addition of Au, the activity was significantly enhanced, reaching full conversion with both fresh and aged catalysts. The most active bimetallic catalyst was obtained when H₂ was the reducing agent for

Scheme 3. General Reaction Pathways



the Pt precursor. Scheme 3 illustrates a proposed reaction pathway for the glycerol oxidation, based on the observed products.

Kimura Research Group. The Kimura research group reported the oxidation of glycerol to glyceric acid, dihydroxyacetone, and other important chemical intermediates. In 1993, during the catalytic oxidation of glycerol over a 0.9% Ce, 1.2% Bi, and 3% Pd/C catalyst^{81,90,91,93} for the preparation of tartronic acid disodium salt, traces (0.2%) of polymeric materials with high molecular weights (1000000) were discovered by gel permeation chromatography analysis.^{112,113} By increasing Bi loading to 3%, the content of polymeric materials increased to 1.4%. However, this was the maximum value at that time as long as a palladium-based oxidation catalyst was used. The tartronic acid was further oxidized to mesoxalic acid. Later, the research group investigated the oxidation of glycerol to mesoxalic acid directly.^{109–111,114}

Gallezot Research Group. Gallezot et al. studied the selective oxidation of glycerol^{45,94,95} or the intermediates^{45,85,86} from the oxidation of glycerol with air on platinum metals or bismuth-promoted platinum metals.^{85,86} In the liquid-phase oxidation of glycerol to glyceric acid or dihydroxyacetone using air and platinum catalysts, the effects of pH (pH range 2.0–11.0) and type of metal catalyst were investigated. The selectivity to glyceric acid was as high as 70% at 100% conversion on Pd/C at pH 11.0. On a Pt/C catalyst, glyceric acid was still the main product (55% selectivity), but the deposition of bismuth on platinum particles moved the selectivity toward the oxidation of the secondary hydroxyl

group to yield dihydroxyacetone with a selectivity of 50% at 70% conversion.⁹⁵ In the selective catalytic oxidation of glyceric acid to tartronic and hydroxypyruvic acids,⁴⁵ platinum catalyst yielded the tartronate salt (61% yield at 94% conversion, pH 10.0–11.0), and slightly higher yields were obtained on bismuth-promoted platinum (83% yield at 90% conversion, pH 10.0–11.0). Hydroxypyruvic acid was obtained on bismuth-promoted platinum under acidic conditions (64% yield at 75% conversion, pH 3.0–4.0). In the catalytic oxidation with air of tartronic acid to mesoxalic acid on bismuth-promoted platinum,^{85,86} by increasing the pH, using a higher catalyst/substrate ratio, or increasing the temperature, higher yields could be obtained (maximum yield obtained of 65% at 80% conversion).

Claus Research Group. The Claus research group at Darmstadt University of Technology in Germany^{115,117} reported the heterogeneously catalyzed liquid-phase oxidation of glycerol over nanosized carbon-supported gold catalysts. The gold catalysts displayed high activity, and the nanosized carbon support was more active than activated carbon or graphite. Comparing the catalytic behavior of Au/C catalysts with mean gold particle sizes ranging from 2.7 to 42 nm, it could be shown that the glycerol oxidation is structure-sensitive. The selectivity to glyceric acid was increased to 75% as the particle size was reduced to an optimum value of 3.7 nm. With a smaller mean gold particle size (2.7 nm), the selectivity to glyceric acid decreased to 40%, while the glycolic acid selectivity increased from 15 to 36%. Consequently, the metal particle size of the Au/C catalyst plays a major role in the oxidation of glyceric acid. The promontory effect of platinum on Au/C catalysts was also examined, and it could be shown that the presence of Pt increased not only the catalyst activity but also the selectivity. By blending the gold catalysts with platinum, the selectivity to dihydroxyacetone could be increased from 26 (Au/C) to 36% (Au–Pt/C).

Davis Research Group. Davis et al.^{96,97,99} at University of Virginia investigated carbon-supported AuPd bimetallic nanoparticles, which were characterized and evaluated as catalysts in the aqueous-phase selective oxidation of glycerol. Measurement of glycerol oxidation rates (0.3 M glycerol, 0.6 M NaOH, 10 atm O₂, 333 K) in a semibatch reactor gave a turnover frequency (TOF) of 17 s^{−1} for monometallic Au and 1 s^{−1} for monometallic Pd, with Pd exhibiting a higher selectivity to glyceric acid. Although the activity of the bimetallic Au/Pd catalysts depended on the amount of Au present, none of them had a TOF greater than that of the monometallic Au catalyst. However, the AuPd catalysts had higher selectivity to glyceric acid as compared with the monometallic Au. They also studied the effects of particle size and hydroxyl on the catalysis. Large Au particles (> 20 nm) were more selective to glyceric acid.

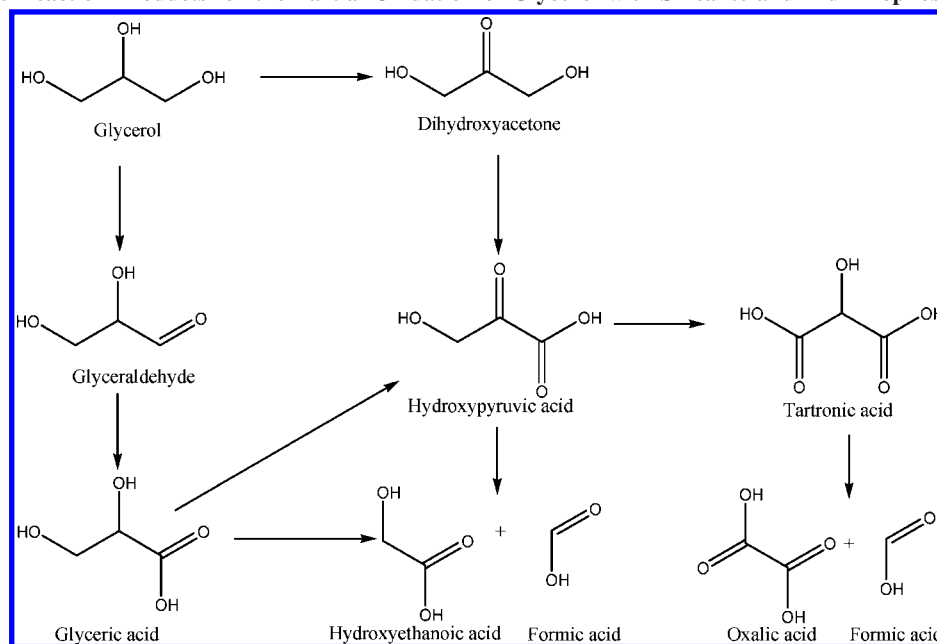
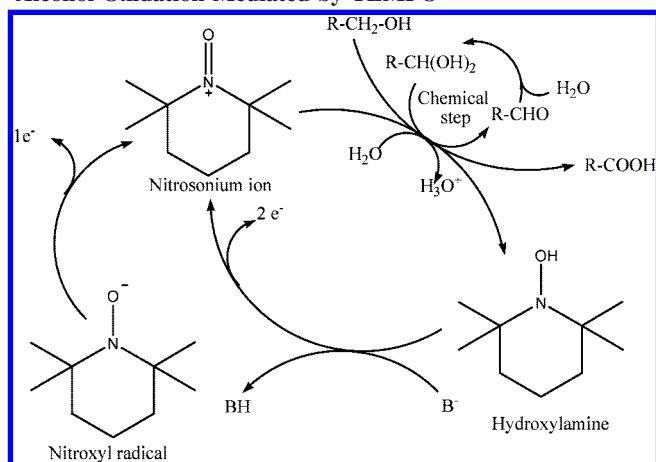
The production of hydroxypyruvic acid by heterogeneous catalytic liquid-phase oxidation of glycerol and derivatives over a bismuth-modified platinum catalyst using air as terminal oxidant was reported by Abbadi et al.⁸³ A convenient preparative method is described using sodium glycerate as the starting material under weakly acidic conditions (pH 5.0–6.0). A selectivity of 93% toward hydroxypyruvic acid at a conversion of sodium glycerate of 95% could be achieved. However, dihydroxyacetone as well as glycerol were found to be not a suitable starting material for the preparation of the title compound. Oxidation of these two substrates under the above conditions yields mainly oxalic

acid. In the process, the glyceric acid can be prepared by oxidation of glycerol with oxygen over Pd/C catalyst under alkaline conditions (pH 10.0) or by liquid-phase catalytic oxidation of solketal with oxygen over Pt/C catalyst and subsequent removal of the protecting isopropylidene group in acidic medium.

Selective Oxidation of Glycerol with Silicalite and Aluminophosphate Catalysts. Hutchings and his co-workers¹¹⁸ reported the oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts. A range of metallosilicates (TS-1, FeS-1, and VS-1) with pore size ca. 0.5 nm and aluminophosphates with the AlPO-5 framework (pore size ca. 0.8 nm, containing V, Cr, Mn, and Co) were all found to give similar products for this reaction. Regardless of conversion levels or reaction conditions, the major products were not the desired partial oxidation products but instead were formic acid and formate esters of glycerol. They also observed that the catalyst pore size was the most important parameter determining the selectivity of the products observed. As the pore size for Ti-containing catalysts increased from ca. 0.5 nm for TS-1 to 15 nm for the titania-silica cogels, the selectivity to the formate ester decreased, and glyceraldehydes, dihydroxyacetone, and glyceric acid were observed as products (Scheme 4).

Selective Oxidation of Glycerol with Electrocatalysts. Venancio et al.¹¹⁹ have probed the electrochemical oxidation of glycerol on gold and platinum electrodes. They reported that platinum electrodes are active in acidic media, whereas both gold and platinum are active in alkaline media. Grace et al.¹²⁰ have further explored the effect of second adatom viz. Pd and Ru nanoparticles to Pt toward the efficiency of glycerol oxidation. The electrodes were modified using three types of nanoparticles catalysts, Pt nanoparticles [Pt(0)], Pt–Pd bimetallic nanoparticles [Pt–Pd(0)], and Ru nanoparticles added to Pt–Pd(0) also called as Pt–Pd(0)/Ru(0) nanoparticles, which will be denoted as ITO/polyaniline/Pt(0), ITO/polyaniline/Pt–Pd(0) and ITO/polyaniline/Pt(0)/Ru(0). Polyaniline was used as a host matrix for the deposition of metal nanoparticles. The results show that the improvement of electrocatalytic activity on Pt was observed by modifying Pt with other metals. The oxidation of glycerol showed much less significant electrode poisoning when Ru nanoparticles were added to Pt–Pd bimetallic nanoparticles. The higher activity and stability of the composite electrodes could be due to the stabilization of metal nanoparticles in the polymeric environment, and the presence of Pd and Ru nanoparticles in addition to Pt may inhibit the formation of strongly adsorbed CO species. The activity toward the oxidation of glycerol was found to be in the order ITO/polyaniline/Pt(0)/Ru(0) > ITO/polyaniline/Pt–Pd(0) > ITO/polyaniline/Pt(0). The micrographs and elemental composition of metal dispersed polymer films were characterized by scanning electron microscopy, energy dispersive X-ray analysis, and contact mode atomic force microscopic studies. Nanoparticles favor the stability of second metal in comparison to bulk alloy. This specific property of nanoparticles opens a wide field of research in catalysis.

The Pagliaro research group¹²¹ has investigated a one-pot aqueous Br/TEMPO-catalyzed homogeneous and heterogeneous oxidation of glycerol to ketomalonic acid using NaOCl as a regenerating oxidant. An overall 98% selectivity to ketomalonic acid with complete glycerol conversion was obtained after only 30 min with a modest amount of dihydroxyacetone (2%) as the sole byproduct.

Scheme 4. Possible Reaction Products for the Partial Oxidation of Glycerol with Silicalite and Aluminophosphate Catalysts**Scheme 5. General Reaction Scheme for Electrochemical Alcohol Oxidation Mediated by TEMPO**

Recently, Ciriminna et al.¹²² reported the one-pot electrochemical oxidation of glycerol to dihydroxyacetone (Scheme 5). No additional chemical oxidants were required.

By simple application of a low voltage (1.1 V vs Ag/AgCl) to a solution of glycerol (0.05 M) buffered at pH 9.1 with bicarbonate (0.2 M) in the presence of catalytic TEMPO (0.0075 M), glycerol was selectively converted to dihydroxyacetone at the anode. Prolonging the reaction time resulted in the formation of hydroxypyruvic acid (Scheme 6).

3.1.2. Oxidation of Glycerol with Biocatalysts

Glycerol can also be oxidized with the biocatalysts, such as enzymes and microorganisms. The common chemical product is dihydroxyacetone.^{41,123–126}

Applications of Dihydroxyacetone. Dihydroxyacetone is a widespread chemical product that is used extensively in the cosmetic industry for making artificial suntans. Fair-skinned people should limit their exposure to sun because of the hazardous consequences related to suntan, for example, malignant melanoma, increase in wrinkles, immune suppression, cataract, etc. A natural suntan could lead to skin cancer by the activation and deactivation of various downstream

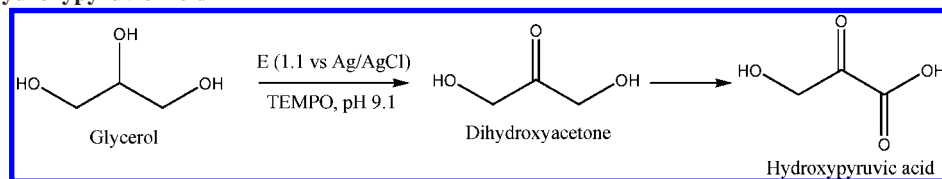
signals, which finally lead to tumorigenesis. Therefore, a natural suntan is undesirable due to the risk of skin cancer associated with it. However, it can be noticed that there is an increasing demand of artificial suntan. These artificial suntans are based on dihydroxyacetone as an active ingredient.¹²⁷ Dihydroxyacetone gives the same tanning effect as the natural suntan, but the difference lies in the mechanism of action, due to which dihydroxyacetone gives a tanned look without the risk of skin cancer. Depending on the darkness of the tan required and the place of application, sunless tanning products usually contain 2–5% dihydroxyacetone, although these artificial suntans cause only temporary darkening of skin and need to be applied at regular intervals to maintain the tanned look.

Dihydroxyacetone is also applied as an important precursor for the synthesis of various fine chemicals and precursors of pharmaceuticals.¹²⁴ With the potential capacity of dihydroxyacetone to cause pigmentation, it is also used for the treatment of vitiligo, an autoimmune disease in which pigment cells (melanocytes) are destroyed, resulting in irregularly shaped white patches on the skin. This method of vitiligo treatment is practical and well-accepted.¹²⁸

Another application of dihydroxyacetone is for protection against a disease called variegate porphyria;¹²⁹ such patients can benefit by its use-based products as their skin is overly sensitive to sunlight and dihydroxyacetone can provide some protection against UVA. Because of its nontoxic nature, dihydroxyacetone has also been proposed to be involved in weight augmentation and fat loss, antioxidant activity, and increasing endurance capacity,¹³⁰ and various other claims are made, but currently, no experimental evidence is available.¹³¹

Microbial Sources for Dihydroxyacetone Production.

Bertrand first observed the production of dihydroxyacetone from glycerol through a bacterial route in 1898. *Sorbose bacillus* was used and was able to oxidize certain secondary alcohols to their corresponding ketone. Later, *S. bacillus* was found to be identical with the acetic acid bacterium *Bacillus xylinum*. Dihydroxyacetone was produced due to the enzymatic activity of the dihydroxyacetone synthase (DHAS) in

Scheme 6. Electrochemical Oxidation of Glycerol Mediated by TEMPO in Water Affords Dihydroxyacetone and, after Longer Reaction Times, Hydroxypyruvic Acid**Table 1. Glycerol-Oxidizing Activity of Intact Cells of *Acetobacter* and *Gluconobacter***

microorganism	total activity (μmol per min per mL of broth)	specific activity (μmol per min per mg of cells)
<i>A. suboxydans</i> ATCC 621	6.20	1.02
<i>A. xylinum</i> A-9	7.95	1.07
<i>G. melanogenus</i> IFO 3293	4.99	0.66
<i>G. melanogenus</i> IFO 3294	4.21	0.64

a carboxydobacterium, *Acinetobacter* sp. strains jc1 Dsm 3803, when it was grown in methanol.¹³²

Intact cells of the following microorganisms, *Acetobacter suboxydans* ATCC 621, *Acetobacter xylinum* a-9, *Gluconobacter melanogenus* IFO 3293, and *G. melanogenus* IFO 3294, were studied for their glycerol oxidizing activity.⁴¹ *A. xylinum* A-9 showed the highest activity out of them (Table 1). A mutant of methanol-utilizing yeast, *Hansenula polymorpha* CBS 4732, can produce a significant amount of dihydroxyacetone using methanol as a substrate,¹³³ in a resting-cell reaction. This mutant is impaired in its ability to synthesize the enzyme dihydroxyacetone kinase.

Gluconobacter oxidans formerly called as *A. suboxydans*¹³⁴ is the most extensively used microorganism in the present-day research for dihydroxyacetone production. It is a Gram-negative bacterium, obligate aerobe belonging to family Acetobacteraceae (found only on flowers and fruits).¹³⁵ It produces dihydroxyacetone via incomplete oxidation of glycerol with the activity of glycerol dehydrogenase.^{41,44,123–126,136–140} Recently, Gatgens and Degner¹⁴¹ have genetically manipulated the DHA-producing *G. oxidans* strains to overproduce the glycerol dehydrogenase and then to improve DHA production. Now, dihydroxyacetone is produced in large scale through this method.

3.2. Reduction of Glycerol

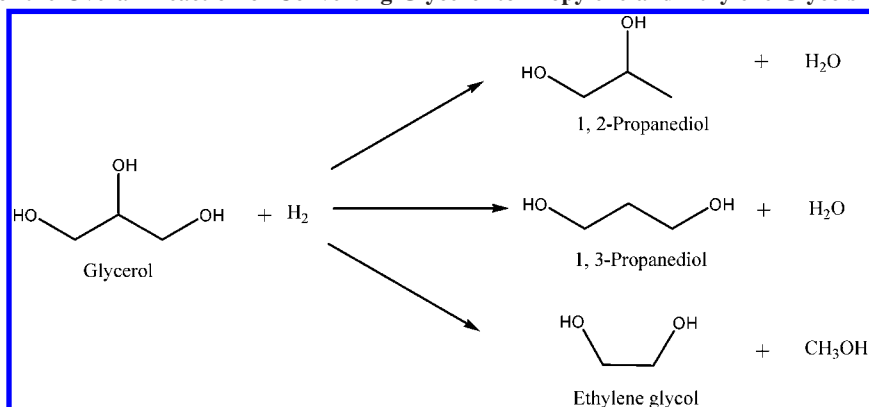
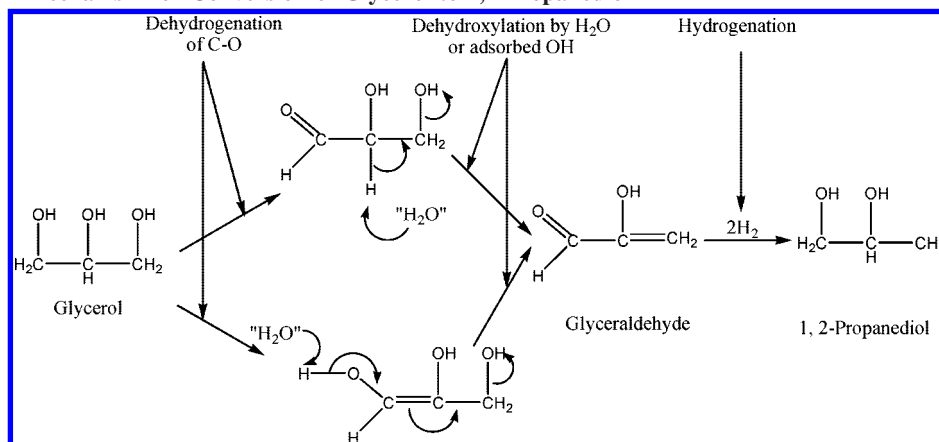
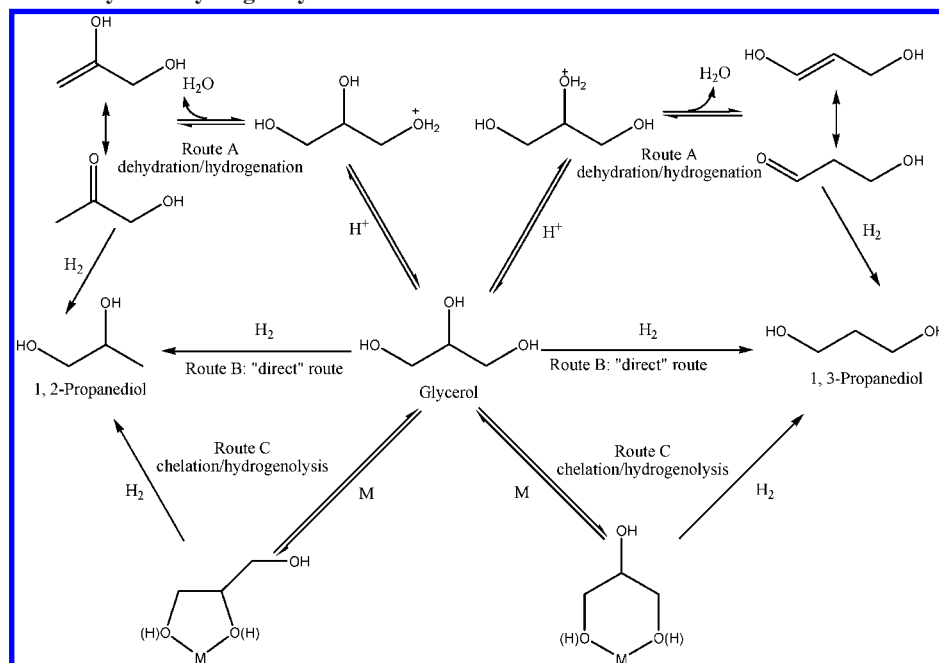
The main products arising from the reduction of glycerol are 1,3-propanediol and 1,2-propanediol. 1,3-Propanediol is copolymerized with terephthalic acid to produce the polyester known as SORONA from DuPont and CORTERRA from Shell, used in the manufacture of carpet and textile fibers exhibiting unique properties in terms of chemical resistance, light stability, elastic recovery, and dyeability.¹⁴² Currently, 1,3-propanediol is produced from petroleum derivatives such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route) using chemical catalysts.^{143,144} 1,2-Propanediol is an important commodity chemical derived from propylene oxide. These diols can be produced by an alternative route involving selective dehydroxylation of glycerol through chemical hydrogenolysis or biocatalytic reduction.

3.2.1. Reduction of Glycerol with Chemical Catalysts

Scheme 7 summarizes the overall reaction of converting glycerol to 1,2-propanediols. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to 1,2-

propanediol (1,2-propanediol), 1,3-propanediol, or ethylene glycol. In 1985, Celanese¹⁴⁵ patented the hydrogenolysis of glycerol water solution under 300 bar of syngas at 200 °C in the presence of a homogeneous rhodium complex $[\text{Rh}(\text{CO})_2(\text{acac})]$ and tungstic acid. 1,3-Propanediol and 1,2-propanediol were produced with 20 and 23% yield, respectively. Shell^{146,147} developed the use of homogeneous palladium complex in a water–sulfolane mixture in the presence of methane sulfuric acid. After 10 h of reaction, 1-propanol, 1,2-propanediol, and 1,3-propanediol were detected in a 47:22:31 ratio. Schlaf et al.¹⁴⁸ described the dehydroxylation of glycerol in sulfolane catalyzed by a homogeneous complex of ruthenium. The reaction proceeded under milder conditions (52 bar, 110 °C), but very low yields of 1,2-propanediol and 1,3-propanediol were achieved (<5%). Hydrogenolysis on solid catalysts was also attempted. The treatment of glycerol under hydrogen in the presence of copper–chromium-based catalysts yielded only 1,2-propanediol.¹⁴⁹ Montassier et al.¹⁵⁰ reported that the hydrogenolysis of glycerol under 300 bar H_2 at 260 °C in the presence of Raney nickel, Ru, Rh, and Ir catalysts yielded mainly methane, but in the presence of Raney copper, 1,2-propanediol was the main reaction product. They also proposed the reaction mechanism for the conversion (Scheme 8). Werpy¹⁵¹ patented the hydrogenolysis of glycerol and other polyols over Ni/Re catalyst. After 4 h at 230 °C under 82 bar H_2 , 44% of 1,2-propanediol and 5% of 1,3-propanediol were obtained together with 13% of ethylene glycol.

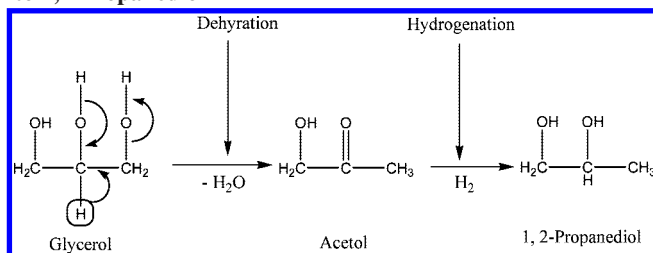
Glycerol hydrogenolysis on heterogeneous catalysts under 80 bar H_2 pressure at 180 °C was investigated by Chaminand et al.¹⁵² Various metals (Cu, Pd, and Rh), supports (ZnO , C, and Al_2O_3), solvents (H_2O , sulfolane, and dioxane), and additives (H_2WO_4) were tested to improve the reaction rate and selectivity. The best selectivity (100%) for 1,2-propanediol was obtained by hydrogenolysis of a water solution of glycerol in the presence of CuO/ZnO catalysts. To improve the selectivity to 1,3-propanediol, the reaction was conducted with rhodium catalysts, and tungstic acid was added to the reaction medium. The best result in terms of conversion and selectivity to 1,3-propanediol (1,3-propanediol/1,2-propanediol = 2) was achieved by operating in sulfolane. The presence of iron dissolved in the reaction medium was also beneficial in selection for 1,3-propanediol. In view of these results, a general mechanism was proposed to account for the effect of these parameters (Scheme 9). The formation of the diols can proceed via several routes, and the presence of tungstic acid increased the reaction rate. The acid can promote the dehydration route (route A) via protonation of the hydroxyl groups and loss of water. The keto group formed as an intermediate can be easily reduced under the reaction conditions. However, the use of an alternative acid (HCl) yielded low conversion, suggesting that the acidity of H_2WO_4 was not the dominant catalytic property for this reaction. Furthermore, the formation of a Rh–W catalyst cannot be excluded and would affect the selectivity and the activity of the hydrogenolysis. The addition of a second metal

Scheme 7. Summary of the Overall Reaction of Converting Glycerol to Propylene and Ethylene Glycols**Scheme 8. Reaction Mechanism for Conversion of Glycerol to 1,2-Propanediol****Scheme 9. Mechanism of Glycerol Hydrogenolysis**

(Fe or Cu) in the reaction medium reduced the activity as if poisoning the rhodium catalyst. Iron can also be chelated by a diol and thus modifies the selectivity of the hydrogenolysis (route C). In sulfolane, which may favor the dehydration via an E1-like mechanism (route A), the selectivity for 1,3-propanediol was two times larger than 1,2-propanediol. In water, 1,2-propanediol was the primary product, but the presence of a second metal improved the

selectivity toward 1,3-propanediol. It is evident that many parameters influence the activity and the selectivity of this reaction.

Dasari et al.¹⁵³ studied the low-pressure hydrogenolysis of glycerol to 1,2-propanediol using nickel, palladium, platinum, copper, and copper-chromite catalysts. At a temperature above 200 °C and hydrogen pressure of 13.8 bar, the selectivity to 1,2-propanediol decreased due to excessive

Scheme 10. Reaction Mechanism for Conversion of Glycerol to 1,2-Propanediol

hydrogenolysis of the 1,2-propanediol. Their proposed mechanism is outlined in Scheme 10. The preliminary reactions were conducted in two steps. In step 1, relatively pure acetol was isolated from glycerol at 200 °C at 0.65 bar pressure in the presence of copper-chromite catalyst. In step 2, the acetol formed in step 1 was further hydrogenated to 1,2-propanediol at 200 °C and 13.8 bar hydrogen pressure using a catalyst similar to that used for the formation of acetol.

Lahr et al.^{154,155} at Iowa State University reported glycerol hydrogenolysis to ethylene glycol and 1,2-propanediol with ruthenium catalysts. The work mainly investigated the effect of sulfur and temperature on the reaction. Chiu et al.²² at the University of Missouri studied the formation of 1,2-propanediol by hydrogenolysis of crude glycerol prepared during biodiesel processing.

Regarding to the addition of solid acids to metal catalysts, Tomishige et al. in Japan recently published a series of works concerning glycerol hydrogenolysis using Ru/C and an ion-exchange resin (Amberlyst) under mild reaction conditions (120 °C, 80 bar). The dehydration of glycerol to acetol is catalyzed by the acid resin. The subsequent hydrogenation of acetol on the metal catalysts gives 1,2-propanediol. The activity of the metal catalyst + Amberlyst in glycerol hydrogenolysis can be related to that of acetol hydrogenation over the metal catalysts. Regarding acid catalysts, $\text{H}_2\text{SO}_4(\text{aq})$ shows lower glycerol dehydration activity than Amberlyst, and $\text{HCl}(\text{aq})$ strongly decreases the activity of acetol hydrogenation on Ru/C. In addition, the OH group on Ru/C can also catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which can then be converted to 1,3-propanediol through subsequent hydrogenation and other degradation products. According to their results, the combination of Ru/C + Amberlyst is effective for glycerol hydrogenolysis in terms of activity and selectivity. However, the formation of 1-propanol and 2-propanol was observed on both Ru/C + Amberlyst and Ru/C in the glycerol reaction. It is characteristic that the selectivity of 1-propanol was much higher than that of 2-propanol. The similar tendency in these selectivities can be observed in the reaction of 1,3-propanediol. On the other hand, in the reaction of 1, 2-propanediol, the selectivity of 1-propanol was comparable to that of 2-propanol, and the tendency is different. These results indicate that 1-propanol and 2-propanol can be formed mainly via 1,3-propanediol in glycerol hydrogenolysis. On the basis of the above results, a reaction mechanism was proposed by them as shown in Scheme 11.

Recently, they investigated hydrogenolysis of glycerol with various SiO_2 supported noble metal catalysts.¹⁵⁶ In the catalysts, Rh/ SiO_2 is effective in the reaction of glycerol under H_2 . They found that Rh/ SiO_2 exhibited higher activity and selectivity to hydrogenolysis products in the reaction of glycerol than the conventional catalyst Ru/C. In particular, under higher H_2 pressure and higher concentration of

glycerol, Rh/ SiO_2 was much more effective than Ru/C. The consecutive hydrogenolysis of propanediols to propanols in the glycerol reaction can proceed mainly via 1,3-propanediol on Ru/C, while the consecutive reactions can proceed mainly via 1,2-propanediol on Rh/ SiO_2 .

The Davis research group at University of Virginia studied hydrogenolysis of glycerol over carbon-supported Ru, Pt, and bimetallic PtRu and AuRu catalysts.^{157,158} The activity and selectivity of Ru/C and Pt/C catalysts were compared for the hydrogenolysis of glycerol. The effects of NaOH and CaO addition on the reaction rates were used to help elucidate metal-catalyzed vs base-catalyzed routes in the mechanism of glycerol hydrogenolysis. The presence of both 0.8 M NaOH and CaO enhanced the rate of glycerol hydrogenolysis over both catalysts; however, the extent of enhancement is greater over Pt/C than Ru/C. This trend is consistent with the observation by others that the rate of alcohol dehydrogenation over Pt is enhanced by base to greater extent than over Ru. Because the dehydrogenation of glycerol to glyceraldehydes is proposed to be the first step in the mechanism of glycerol hydrogenolysis, the activity of Pt/C is enhanced more than Ru/C with the addition of NaOH and CaO. In the absence of base, Ru/C was more active than Pt/C for the hydrogenolysis of glycerol. Under neutral conditions, Ru favors the formation of ethylene glycol over 1,2-propanediol. Because the rate of ethylene glycol formation was not enhanced significantly in the presence of base, C–C cleavage is thought to occur over Ru primarily via a metal-catalyzed reaction. The addition of Cl^- to the system resulted in decreased selectivity to ethylene glycol. Ethylene glycol is proposed to form through base-catalyzed retro-aldol reaction because Pt is a less effective C–C cleavage catalyst.

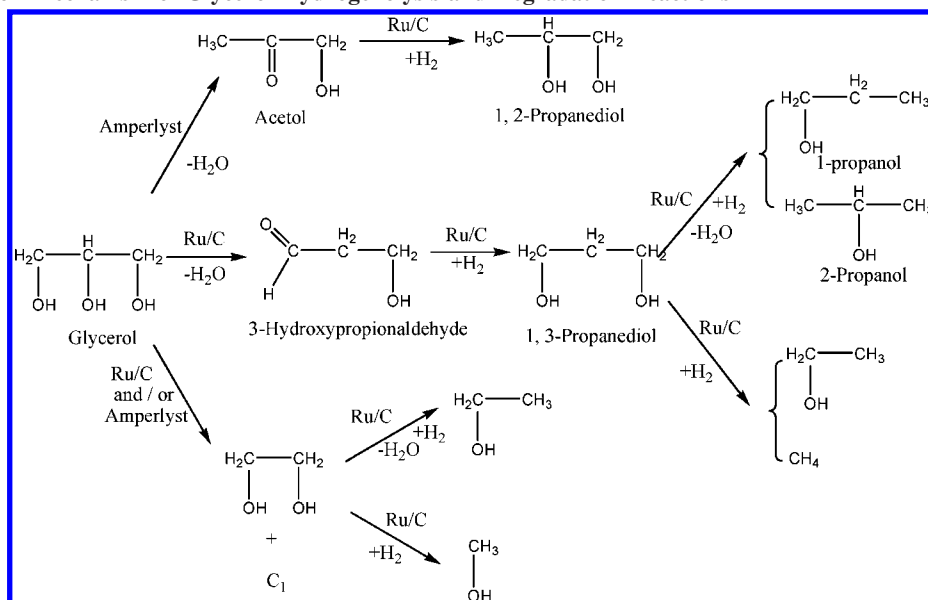
Bimetallic PtRu and AuRu catalysts were prepared by a surface redox method in which Pt or Au was deposited onto the surface of carbon-supported Ru nanoparticles with an average diameter of 2–3 nm. The bimetallic particles were applied in the aqueous-phase hydrogenolysis of glycerol at 473 K and 40 bar H_2 at neutral and elevated pH. Although monometallic Pt and Ru exhibited different activities and selectivities to products, the bimetallic PtRu catalyst functioned more like Ru. A similar result was obtained for the AuRu bimetallic catalyst. The PtRu catalyst appeared to be stable under the aqueous-phase reaction conditions, whereas the AuRu catalyst was altered by the harsh conditions. Gold appeared to migrate off the Ru and agglomerate on the carbon during the reaction in liquid water.

Feng et al.^{159,160} also reported hydrogenolysis of glycerol under mild reaction conditions (170 °C, 3 MPa). Glycerol is hydrogenolyzed to 1,2-propanediol using Ru/ TiO_2 as a catalyst in basic aqueous solution. The base aids the initial dehydrogenation of glycerol to glyceraldehyde and promotes the dehydration of glyceraldehyde to 2-hydroxyacrolein.

3.2.2. Selective Dehydroxylation of Glycerol

In 2003, Wang et al.⁵⁰ reported that a new approach to the production of 1,3-propanediol from glycerol via selective dehydroxylation. The concrete process is to selectively transform the middle hydroxyl group of glycerol into a tosyloxyl group and then remove the transformed group by catalytic hydrogenolysis. The new glycerol dehydroxylation approach is illustrated in Scheme 12. It consists of three steps: acetalization, tosylation, and detosyloxylation. The aim is to selectively transform the second hydroxyl group of glycerol into a tosyloxyl group (tosylation) and then remove

Scheme 11. Reaction Mechanism of Glycerol Hydrogenolysis and Degradation Reactions



the tosyloxy group by catalytic hydrogenolysis (detosyloxylation). As compared to the hydroxyl group, the tosyloxy group is a better leaving group and is easier to replace with a hydride ion.

The first step in the conversion of glycerol to 1,3-propanediol is to acetalize the glycerol with benzaldehyde. The purpose is to protect the first and third hydroxyl groups of glycerol, so that only the middle one can be tosylated in the second step and subsequently removed in the third step. The condensation between glycerol and benzaldehyde is an equilibrium reaction, but it can be driven to completion by removing the water formed in the reaction. The second step of the conversion is tosylation of the unprotected hydroxyl group of the acetalized glycerol, so as to transform it into a good leaving group. This step is a fairly straightforward process. The final step of the conversion is a detosyloxylation reaction proceeded or followed by a hydrolysis reaction. The detosyloxylation reaction removes the tosylated middle hydroxyl group, while the hydrolysis reaction removes the protection on the first and third hydroxyl groups. The detosyloxylation reaction shown in Scheme 12 is basically a hydrogenolysis reaction. According to the proposed conversion approach, this reaction is to be done with molecular hydrogen in the presence of a transition metal catalyst.

3.2.3. Reduction of Glycerol with Biocatalysts

Microbial production of 1,3-propanediol has been widely researched and considered as a competitor to the traditional petrochemical routes. It is an example of a socially beneficial method for obtaining bulk chemicals from renewable resources. Only a small number of microorganisms in nature are able to produce 1,3-propanediol via glycerol fermentation, including *Klebsiella pneumoniae*,^{38,161–163} *Enterobacter agglomerans*, *Citrobacter freundii*, *Clostridium acetobutylicum*, *Clostridium butyricum*,^{46,161} *Clostridium pasteurianum*, *Lactobacillus brevis*, and *Lactobacillus buchneri*.^{164,165} Among them, more attention has been directed at *K. pneumoniae*, *C. freundii*, and *C. butyricum* because of their appreciable substrate tolerance, yield, and productivity in 1,3-propanediol production. The biosynthesis of 1,3-propanediol under anaerobic conditions takes place via the following

biochemical reactions: Some of the glycerol is oxidized to dihydroxyacetone by an NAD-dependent glycerol dehydrogenase, while the remainder is dehydrated to 3-hydroxypropionaldehyde by a vitamin B12-dependent dehydratase. The product of the dehydration reaction, 3-hydroxypropionaldehyde, is reduced to 1,3-propanediol by an NAD-dependent oxidoreductase. In this case, the final acceptor of the electrons is the 3-hydroxypropionaldehyde. However, several studies found that 3-hydroxypropionaldehyde would inhibit 1,3-propanediol synthesis.^{166,167–169} The gene sequences of these three enzymes as well as dihydroxyacetone kinase are encoded in the same regulon (DHA) and have been cloned and sequenced for *K. pneumoniae*¹⁷⁰ and *C. freundii*.¹⁷¹

3.3. Dehydration of Glycerol

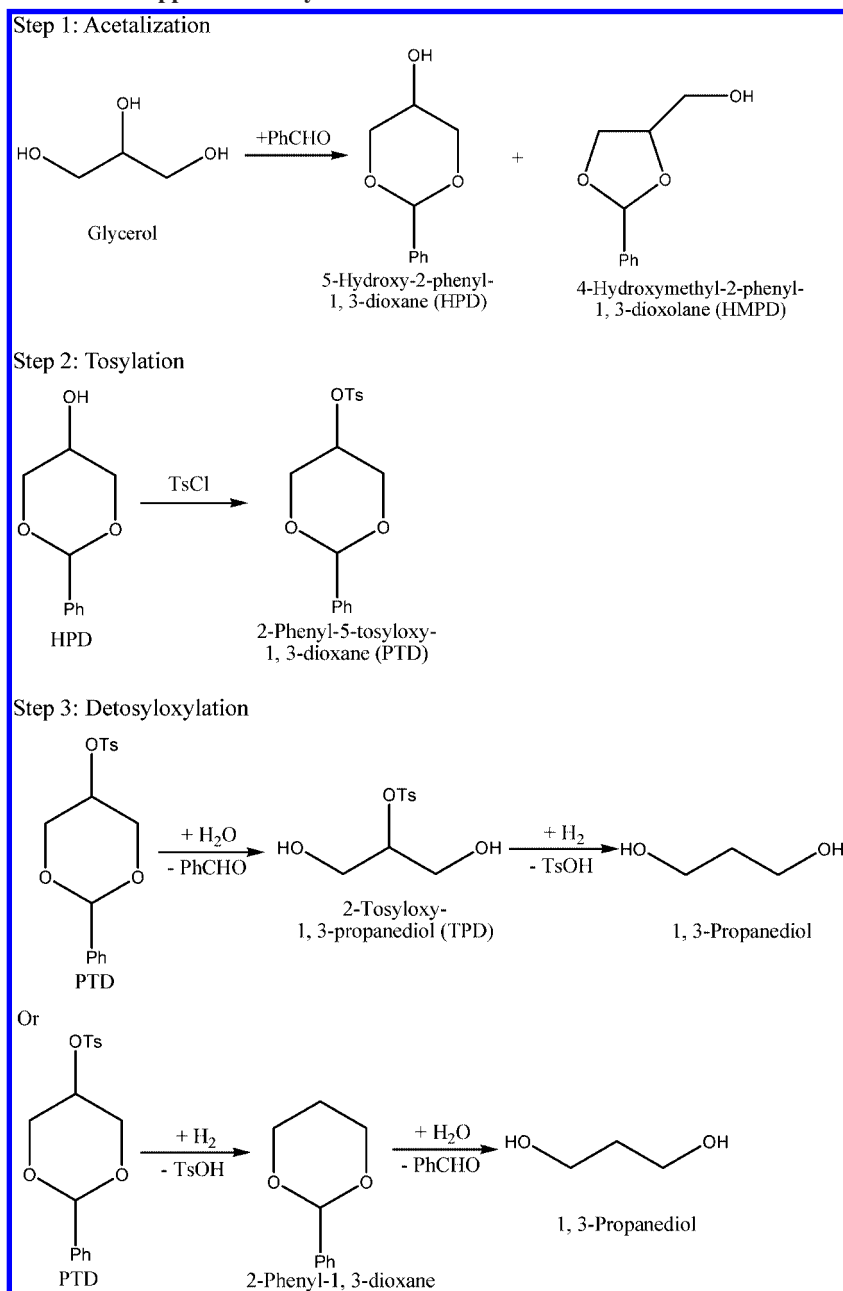
Two important chemicals can be produced directly by dehydration of glycerol, acrolein, and 3-hydroxypropionaldehyde. Acrolein is an important bulk chemical used as a feedstock for acrylic acid production, pharmaceuticals, fiber treatments, and other uses. The most significant direct application of acrolein is as an herbicide to control the growth of aquatic plants. It kills plant cells by reaction with biological molecules and the destruction of cell membrane integrity, as well as by its affinity for sulfhydryl groups, causing the denaturation of vital enzymes. 3-Hydroxypropionaldehyde is a precursor for many modern chemicals including acrolein, acrylic acid, and 1,3-propanediol and is used for polymer production (Figure 4).

3.3.1. Dehydration of Glycerol to Acrolein

The current method for manufacturing acrolein is based on oxidation of propylene or propane derived from petroleum,^{172–180} suggesting that carbon-neutral processes for producing acrolein from glycerol^{80,181–185} (Scheme 13) will lead to lower oil consumption and reduced environmental damage.

In 1987, Ramayya et al.¹⁸⁵ reported that acrolein was obtained with high selectivity (84% selectivity of acrolein at 40% conversion of glycerol) by adding 5 mM H₂SO₄ into water at 623 K and 34.5 MPa. Buhler et al.¹⁸⁴ conducted the experiments of glycerol reactions using a flow apparatus

Scheme 12. Illustrations of the New Approach to Glycerol Conversion



in near- and supercritical water at 622–748 K and 25–45 MPa without additive and also analyzed the experimental data using the detail kinetic model. Through these experimental and mathematical modelings, they suggested that the glycerol reactions in hot-compressed water competitively progressed both through ionic and radical reactions. The predominance of the ionic or radical could be controlled by temperature and pressure: The ionic reaction preferred subcritical water below the critical temperature (liquid state), and the radical was relatively favored at supercritical region. The kinetic model also indicated that glycerol dehydration into acrolein mainly occurred through ionic reactions, whereas the other dehydration into allyl alcohol and the bond scission into acetaldehyde and formaldehyde preferably underwent through radical reactions. Ott et al.⁸⁰ found that zinc sulfate is effective catalyst for the acrolein synthesis from glycerol in sub- and supercritical water (573–663 K, 25–34 MPa, and 10–60 s), and the maximum selectivity of acrolein was 75% at 50% of glycerol conversion. They

also suggested that the glycerol dehydration into acrolein was ionic reaction. Dubios et al.^{181,182} reported a process for manufacturing acrolein by gas-phase dehydration of glycerol in the presence of strongly acidic solid catalysts with a Hammett acidity H_0 of between –10 and –16. Tsukuda et al.¹⁸⁶ investigated the production of acrolein from glycerol over silica-supported heteropoly acids. In the study, silicotungstic acid supported on silica with mesopores of 10 nm showed the highest catalytic activity with the acrolein selectivity of <85 mol % at 548 K and an ambient pressure. They also supposed a probable reaction routes for the reaction (Scheme 14). Recently, acrolein synthesis from glycerol in hot-compressed water was studied by Watanabe et al.¹⁸³ Glycerol conversion was conducted in pressurized hot water (573–673 K, 25–34.5 MPa) using both a batch and a flow apparatus. Approximately 80% selectivity for acrolein was obtained at 90% glycerol conversion using an acid catalyst under supercritical conditions (673 K and 34.5 MPa). The rate constant of acrolein decomposition was always higher

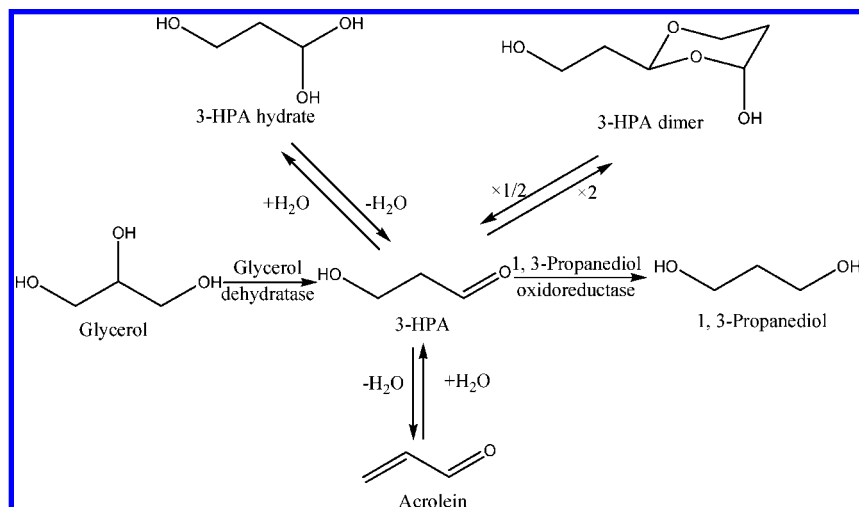
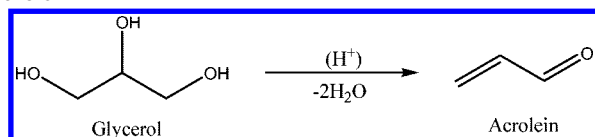


Figure 4. Formation of 3-hydroxypropionaldehyde (3-HPA), 1,3-propanediol, and acrolein.

Scheme 13. Acid-Induced Dehydration of Glycerol to Acrolein



than that of acrolein formation in the absence of acid catalyst; the presence of the acid catalyst reversed this.

Recently, Chai et al. at Tsinghua University^{187,188} reported sustainable production of acrolein with solid acid–base catalysts for gas-phase dehydration of glycerol. With solid acid–base catalysts, the most selective acid–base catalysts for the production of acrolein by gas-phase glycerol dehydration are those having the strongest acid strength in the range of $-8.2 \leq H_0 \leq -3.0$; the highest steady acrolein selectivity obtained was 70 mol %. The catalysts having further stronger acid sites ($H_0 \leq -8.2$) produce a lower acrolein selectivity (40–50 mol %) due to more severe catalyst coking. Bronsted acid sites seem to be superior to Lewis acid sites for the acrolein production. Solid base catalysts are basically not effective for the formation of acrolein. On the basis of the reaction products, they proposed the reaction mechanism as shown in Scheme 15. The reaction of glycerol would be initiated by the dehydration involving either the central $-\text{OH}$ (Step I) or the terminal $-\text{OH}$ (step II), which result in parallel formation of two enol intermediates. The enols would undergo rapid rearrangement to 3-hydroxypropionaldehyde or 1-hydroxyacetone, respectively. The 3-hydroxypropionaldehyde would be very unstable at the reaction temperature (315 °C) and can easily give rise to a further dehydration for the production of the desirable acrolein (step III). A secondary hydrogenation reaction of the acrolein product will lead to the formation of allyl alcohol (step VI). The unstable intermediate 3-hydroxypropionaldehyde would also decompose, according to a reversed aldol condensation (step IV), to acetaldehyde and formaldehyde; a follow up hydrogenation or decomposition of formaldehyde would result in the formation of methanol or CO and H_2 (steps VII and VIII).

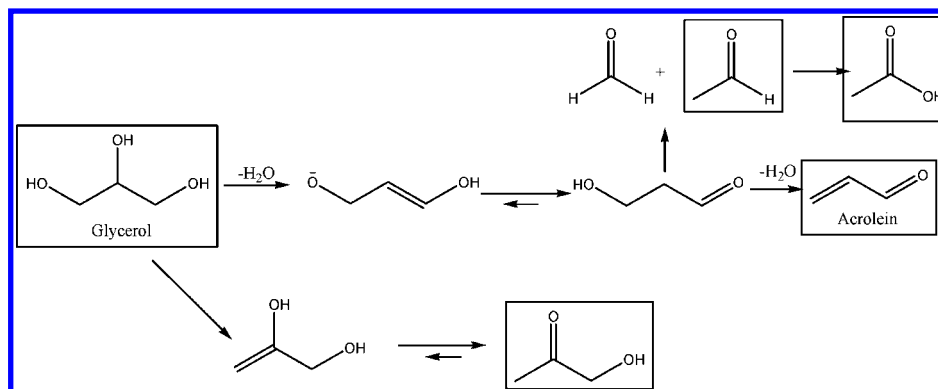
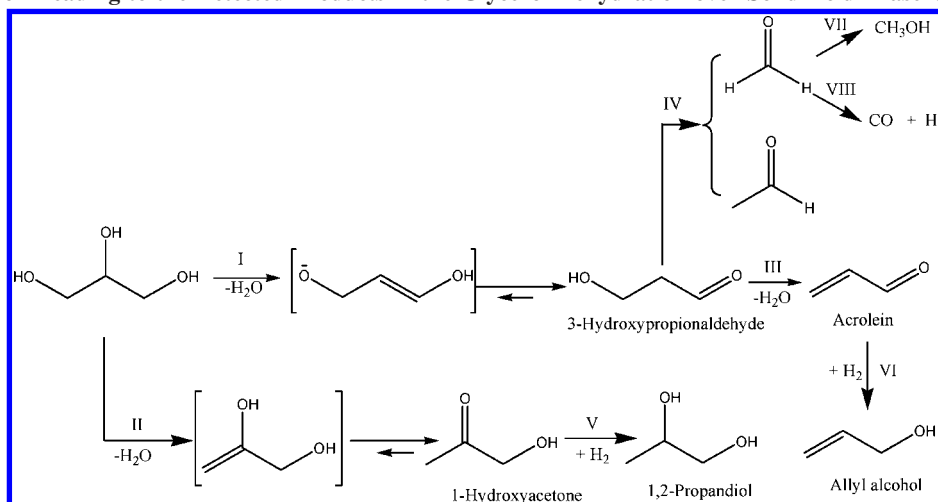
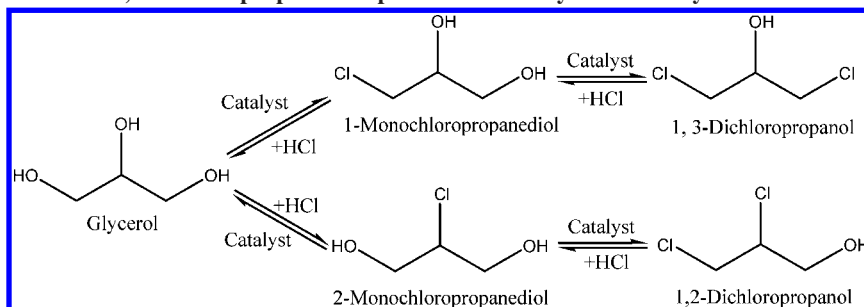
3.3.2. Dehydration of Glycerol to 3-Hydroxypropionaldehyde

Typically, 3-hydroxypropionaldehyde is produced by synthesis from petrochemicals. Two chemical processes are

known to produce 3-hydroxypropionaldehyde as an intermediate in 1,3-propanediol production: the Degussa and Shell processes.¹⁸⁹ The Degussa process begins with the catalytic transformation of propylene into acrolein, which is hydrated to 3-hydroxypropionaldehyde and further reduced to 1,3-propanediol. Although propylene is inexpensive, the separation of the different molecules is expensive, and acrolein is toxic. The 1,3-propanediol yield of this process is only 43%. The Shell process begins with ethylene, forming ethylene oxide, which is transformed by a hydroformylation reaction under high pressure (150 bar) with syngas to 3-hydroxypropionaldehyde. Ethylene is inexpensive, and the intermediate products are not toxic, but 3-hydroxypropionaldehyde has to be extracted from the organic phase. The 1,3-propanediol yield is about 80%. No information on the yields for 3-hydroxypropionaldehyde production is available in the literature.

3-Hydroxypropionaldehyde can also be produced from the renewable resources. Biotechnological production has several advantages as compared to the chemical process. First, 3-hydroxypropionaldehyde production can be carried out in glycerol-containing aqueous solution at room temperature or at 37 °C under normal pressure. The transformation from glycerol to 3-hydroxypropionaldehyde is a one-step enzymatic catalysis, and the yields (85–87% mol 3-hydroxypropionaldehyde/mol glycerol) have been shown to be higher than those achieved by chemical synthesis.^{189–201} To date, six genera of bacteria that are able to ferment glycerol into 3-hydroxypropionaldehyde have been identified as follows: *Bacillus*, *Klebsiella* (*Aerobacter*), *Citrobacter*, *Enterobacter*, *Clostridium*, and *Lactobacillus*. The enzyme responsible for the formation of 3-hydroxypropionaldehyde from glycerol, glycerol dehydratase, is known to be cobamide-dependent.²⁰² 3-HPA is normally an intracellular intermediate that does not accumulate but is reduced by an NAD^+ -dependent oxidoreductase to 1,3-propanediol, the end product of glycerol fermentation.²⁰³

However, biotechnological production of 3-hydroxypropionaldehyde should be performed without glucose, to favor accumulation of 3-hydroxypropionaldehyde.^{204,205} At high concentrations, 3-hydroxypropionaldehyde is secreted into the medium and can easily be concentrated by lyophilization. Furthermore, the toxicity of 3-hydroxypropionaldehyde toward bacteria limits the accumulation of this compound in the fermentation broth medium.^{189,190} Two methods have

Scheme 14. Probable Reaction Routes (Chemicals Surrounded with a Flame Are the Representative Products Detected in the Work)**Scheme 15. Reaction Leading to the Detected Products in the Glycerol Dehydration over Solid Acid–Base Catalysts****Scheme 16. Reaction Scheme of 1,3-Dichloropropanol Preparation from Glycerol and Hydrochloric Acid**

been attempted to overcome this toxicity and increase the yield for biotechnological production. In the first method, 3-hydroxypropionaldehyde is entrapped by semicarbazide,¹⁹⁴ such that 3-hydroxypropionaldehyde becomes unavailable. This reduces its toxic affect and prevents its further reduction to 1,3-propanediol, increasing the yield of 3-hydroxypropionaldehyde production. The recovery of 3-hydroxypropionaldehyde has never been reported, although the method is very promising. The second method uses *Lactobacillus reuteri*, a species shown to sustain large amounts of 3-hydroxypropionaldehyde produced from glycerol. However, although *L. reuteri* is very resistant to high concentrations of 3-hydroxypropionaldehyde, its viability does decrease when 3-hydroxypropionaldehyde is produced in large quantities.¹⁹⁰ To date, there is no report about the bulk production of 3-hydroxypropionaldehyde using microbial conversion from glycerol.

3.4. Halogenation of Glycerol

Studies of glycerol halogenation have focused on production of 1,3-dichloropropanol,^{206–218} an intermediate in epichlorohydrin synthesis. Epichlorohydrin is an important raw material for the production of materials such as epoxide resins, synthetic elastomers, and sizing agents for the paper-making industry. The global reaction pathway for preparing 1,3-dichloropropanol from glycerol is depicted in Scheme 16.

The reaction proceeds by means of a first chlorination of the glycerol, primarily forming 1-monochloropropanediol and water along with small quantities of 2-monochloropropanediol. This is followed by a second chlorination from which 1,3-dichloropropanol is obtained, combined with modest quantities of 1,2-dichloropropanol as a byproduct.

Traditional processes^{211–218} performed starting from glycerol, which are rather old, provide for the reaction of the glycerol with hydrochloric acid in solution, in the presence of acetic acid as a catalyst, at the temperature of approximately 80–100 °C. Several patents describe processes using an inert organic solvent not miscible with water and in which 1,3-dichloropropanol is soluble. The reaction is performed at the boiling point of the mixture; therefore, the temperature varies depending on the particular solvent. Other patents describe reactions followed by complicated neutralizations, extractions, and distillations to recover 1,3-dichloropropanol. These traditional processes starting from glycerol suffer from considerable drawbacks: the loss of catalyst during the reaction, due to the low boiling point of acetic acid; the slowing of the reaction caused by the introduction of water into the reaction mixture in the form of aqueous hydrochloric acid and failure to remove the water that forms as a consequence of the reaction; and the difficult separation of the 1,3-dichloropropanol from the reaction mixture. These drawbacks, together with the high cost of glycerol as a raw material, have prevented this process from becoming established. The method currently used employs propylene as a starting material and yields a mixture of 30% 1,2-dichloropropanol and 70% 1,3-dichloropropanol. The high percentage of 1,2-dichloropropanol causes difficulties, since this substance reacts much more slowly than 1,3-dichloropropanol in producing epichlorohydrin in subsequent dehydrochlorination reactions. This has repercussions on the sizing of plants and reduces the yield by promoting the formation of byproducts. Recently, Siano et al.²⁰⁶ patented a process for production of 1,3-dichloropropanol from glycerol and preferable gaseous anhydrous hydrochloric acid in the presence of low volatility organic acids as catalysts with a boiling point of more than 120 °C. The process for producing 1,3-dichloropropanol is performed starting from pure or unprocessed glycerol as obtained as a byproduct in the process for producing biodiesel, with gaseous hydrochloric acid, in the presence of various organic acids (monocarboxylic acids with 3–10 carbon atoms or ditricarboxylic acids with a number of carbon atoms between 2 and 10) as catalysts. The reaction temperature is controlled between 80 and 180 °C and the pressure of gaseous hydrochloric acid under 0.5 MPa. The increasing production of biodiesel makes this reaction starting from glycerol particularly advantageous, given the large quantities of glycerol this reaction could consume.

3.5. Etherification of Glycerol

Glycerol ethers of interest include the compounds resulting from reaction with isobutylene or *tert*-butanol, polyglycerols, and glycosyl glycerol.

3.5.1. Butylation of Glycerol

The glycerol ethers are excellent oxygen additives for diesel fuel.^{54,58,219} Oxygenated diesel fuels are of importance for both environmental compliance and efficiency of diesel engines.¹² One potential application of glycerol is in the preparation of glycerol alkyl ethers by etherification (*O*-alkylation) by alkenes, particularly isobutylene or the C₄ fraction obtained from pyrolysis and FCC. Mixtures of mono-, di-, and trialkyl glycerols are suitable for use as oxygenates in diesel fuels. The addition of these ethers has a positive effect on the final quality of the diesel fuel (high CN) and aids in the reduction of fumes and particulate matter,

carbon oxides, and carbonyl compounds in engine exhaust. A limitation on the use of vegetable oil or animal fat methyl esters is the cloud point, which is –16 °C for petroleum diesel fuels and around 0 °C for biodiesel. The addition of ethers such as glycerol ethers decreases the cloud point of diesel fuels.

A mixture of alkyl ethers of glycerol can be prepared by etherification of glycerol by alkenes and preferentially by isobutylene at molar ratio of glycerol/isobutylene = 1:2 and up, at the temperature from 50 to 150 °C on strongly acidic catex Amberlyst. The mixture of alkylethers is added to original diesel fuel with biodiesel or separately. The reduction of carbon oxide, hydrocarbons, aldehydes, and particulate matters after application of alkyl ethers of glycerol to diesel fuel has been proved.^{54,58,219} *p*-Toluene sulfonic acid is catalyst for etherification of glycerol. The etherifications are carried out at the temperatures from 50 to 100 °C at the surplus of isobutylene. The manufacture of *tert*-butyl ethers of glycerol is realized by etherification of glycerol with isobutylene in the liquid phase at the presence of large-porous zeolite catalyst at temperatures from 80 to 120 °C, at a pressure between 0.6 and 2.1 MPa, and at the molar ratio of glycerol/alkene from 1:1 to 1:5. The conversion of glycerol was near 99%. Macho et al. studied possibilities of utilization of isobutylene from the C₄ fraction for etherification of different more hydroxylic aliphatic compounds. They studied etherification glycol and glycerol at the presence of different acidic catalysts. Ostion catex was a very active catalyst for this section. Authors studied kinetics of this reaction and also the formation of secondary products.

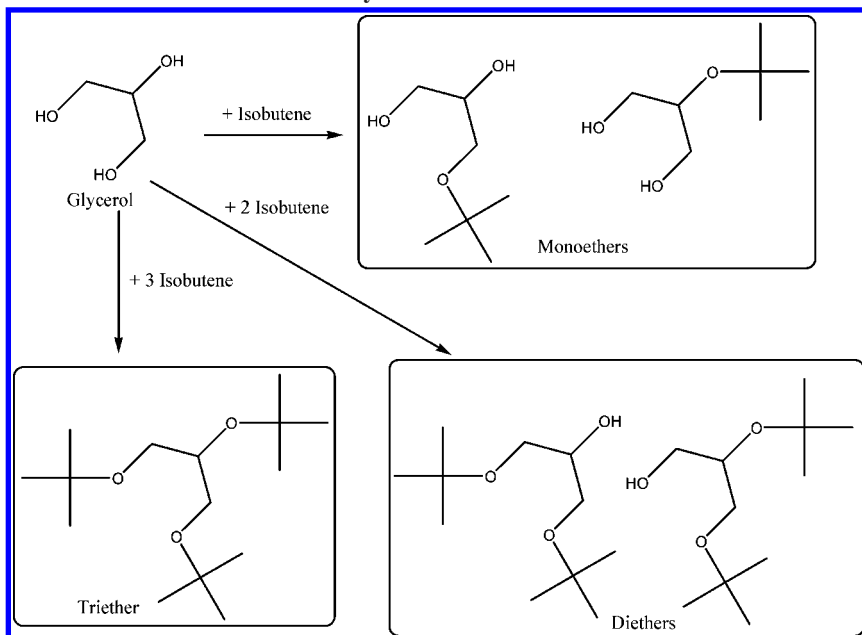
Klepacova et al.^{220–223} reported the etherification of glycerol with *tert*-butanol with strong acid ion-exchange, Amberlyst type resins and two large pore zeolites, H-Y and H- β , as catalysts. The maximum conversion of glycerol 100% was achieved over a strong acid macroreticular ion-exchange resin Amberlyst 35 at a temperature of 60 °C. A higher temperature (90 °C) causes a considerable drop in conversion and yield of desired di- and triethers, mainly in the case of acid ion-exchange resins Amberlyst-35 (39.2%). Zeolites H-Y and H- β provide lower selectivity than ion-exchange resins.

Recently, the butylation of glycerol using isobutene in liquid phase with acidic ion-exchange resin catalyst was investigated by Karinen et al.²²⁴ Five product ethers were achieved in the process. The effect of the reaction conditions on the system was studied, and conditions for optimal selectivity toward ethers were discovered with a near isobutene/glycerol molar ratio of 3 at 80 °C. Scheme 17 describes their proposed reaction mechanism. The mono-, di-, and tri-*tert*-butyl ether reaction products were characterized using MS, NMR, IR, and Raman molecular spectroscopy.²²⁵

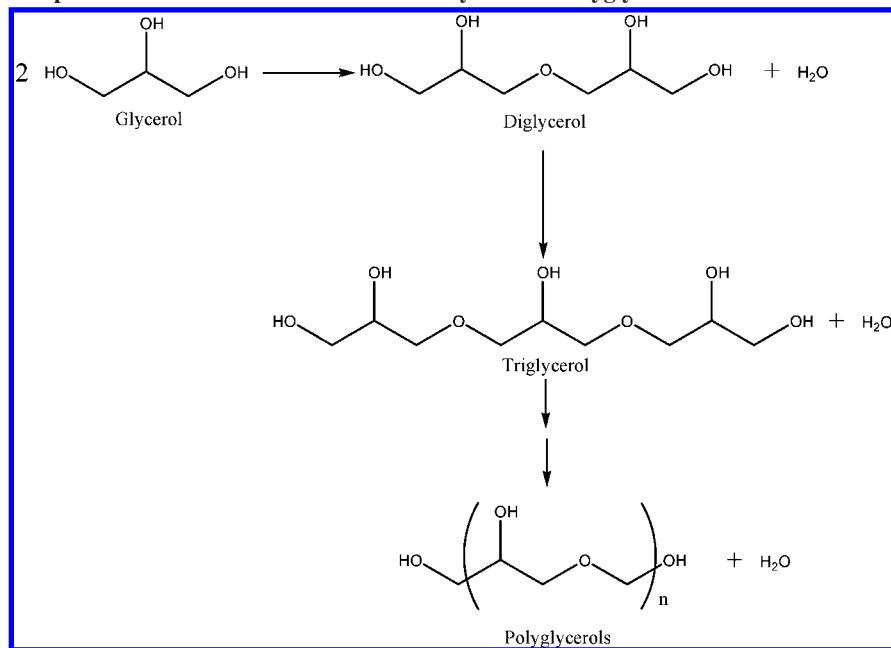
3.5.2. Polymerization of Glycerol

At present, polyglycerols and polyglycerol esters are gaining prominence in products such as surfactants, lubricants, cosmetics, and food additives. Polyglycerol esters exhibit multifunctional properties and a wide range of formulating options, provided it is possible to control (i) the length of the polyglycerol chain, (ii) the degree of esterification, and (iii) the fatty acid molecular weight. Control of these properties presents an interesting challenge for shape-selective catalytic processes. The etherification of glycerol to form polyglycerols is demonstrated in Scheme 18. The

Scheme 17. Reaction Scheme for the Etherification of Glycerol with Isobutene



Scheme 18. Schematic Representation of the Etherification of Glycerol to Polyglycerols



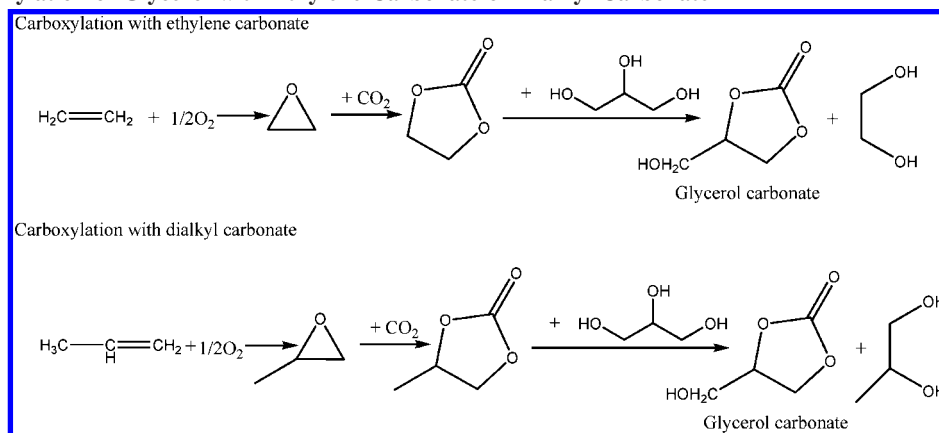
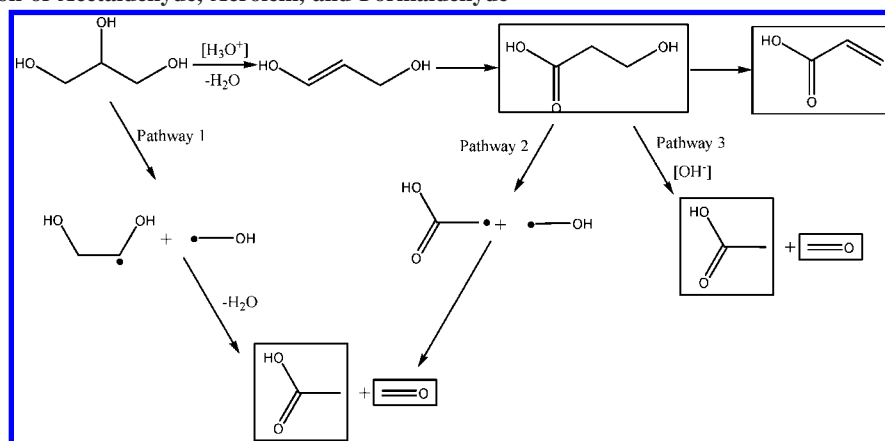
reaction was catalyzed with Na_2CO_3 or MCM-41 type mesoporous materials using alkaline-exchanged zeolites or cesium-exchanged X zeolite.^{51,53,56,63} Experiments have indicated that a higher selectivity to diglycerol is possible with the latter catalysts than with the former catalysts.

3.5.3. Glycosylation of Glycerol

O- α -D-Glucosyl glycerol (Glc-GL) is found in Japanese traditional fermented foods such as sake, miso, and mirin.²²⁶ For example, Glc-GL contributes to the flavor of sake, which contains approximately 0.5% of this compound. Glc-GL is a nonreducing glucoside exhibiting about half the sweetness of sucrose, high-thermal stability, low heat colorability, low Maillard reactivity, low hygroscopicity, high water-holding capacity, noncariogenicity, and low digestibility. Its use in foods, beverages, and cosmetics is expected to increase.^{226–228} Glc-GL was also reported to suppress the action of rat

intestinal disaccharidases and may prove useful in decreasing caloric intake.

Glc-GL is produced by an enzymatic process first described in detail by Sawai and Hehre.²²⁹ The process uses *Candida tropicalis* α -glucosidase to transfer the Glc residue of starch and dextrans to the 1- (or 3-) position of glycerol. The Glc-GL in the above-mentioned foods is thought to be a transglucosylation product of Kojimold α -glucosidase, and the preparative synthesis from glycerol and maltose by *Aspergillus niger* α -glucosidase was reported by Takenaka and Uchiyama.²²⁸ Nakano et al.²³⁰ found cyclodextrin glucanotransferases (EC 2.4.1.19) to be useful catalysts for the transglycosylation of glycerol. When starch was used as the donor substrate in this process, the enzymes synthesized not only Glc-GL but also products with a series of maltooligosaccharide residues. Among the enzymes tested, those from *Geobacillus stearothermophilus* and *Thermoanaero-*

Scheme 19. Carboxylation of Glycerol with Ethylene Carbonate or Dialkyl Carbonate**Scheme 20. Formation of Acetaldehyde, Acrolein, and Formaldehyde**

bacter sp. were suitable for the transglycosylation. Several products composed of glucose and a series of α -1,4-linked maltooligosyl residues bound with glycerol were isolated. Concentrations of 30% (w/v) glycerol and 20% (w/v) soluble starch were most effective in ensuring efficient transglycosylation. The reaction mixture contained much lower levels of reducing sugars than the conventional α -glucosidase-catalyzed process. The study also described the inhibitory effect of glycosylated glycerols against porcine pancreas α -amylase. Significant inhibition was observed only for transfer products with multiple glucose units, whereas Glc-GL exhibited only weak inhibition.

3.6. Esterification of Glycerol

In recent years, esterification of glycerol has been a particularly active area of research. Processes employing both chemical catalysts and enzymes such as lipases have been reported. Glycerol esterification reactions can be divided into three types: esterification with carboxylic acids, carboxylation, and nitration.

3.6.1. Esterification with Carboxylic Acid

Esterification of glycerol with carboxylic acid forms monoglycerides (MGs) and diacylglycerol (DAG). MGs are amphiphilic molecules useful as nonionic surfactants and emulsifiers. They are widely used in bakery products, margarines, dairy products, and sauces.²³¹ In the cosmetic industry, they are added as texturing agents for improving the consistency of creams and lotions.^{232,233} In addition, because of their excellent lubricant and plasticizing proper-

ties, MGs are used in textile processing and formulation of oils for various types of machinery.²³⁴ In 1995, the world market for food-grade emulsifiers was estimated to be about 3×10^5 tons, of which mono-olein represented approximately 10%.²³⁵

DAG is naturally present as a minor component of edible fats and oils from various sources.²³⁶ It can exist as either 1,3-DAG or 1,2 (2,3)-DAG.²³⁷ DAG has been utilized as a cocoa butter blooming agent²³⁸ and as an intermediate in the synthesis of structural lipids.^{239,240} Recent studies on its nutritional properties and dietary effects^{241–253} suggest that DAG in which 1,3-DAG is the major component plays a role in reducing serum triacylglycerol (TAG) levels and, as a result, decreases both body weight and visceral fat mass. Consequently, oil with a high DAG content has drawn attention as being potentially useful in the prevention of obesity and other lifestyle-related diseases.^{254,255}

Production of MGs. Currently, MGs are manufactured on an industrial scale by continuous chemical glycerolysis of fats and oils at high temperature,^{220–250} employing alkaline catalysts under a nitrogen atmosphere²⁵⁶ or employing aluminum- and zirconium-containing mesoporous molecular sieves in supercritical carbon dioxide medium.²⁵⁷ The products obtained by this procedure have several drawbacks (dark color and burnt taste). Moreover, the yield is rather low. A molecular distillation step is necessary because the MGs need to be highly pure in the food industry, since they have better emulsifying properties than a mixture of different acylglycerols.^{233,258} Many approaches for the synthesis of MGs in nonconventional media by lipases have been reported. One of them is the glycerolysis of palm olein in

Table 2. Reaction Types to Be Considered in the Free Radical Part of the Reaction Mechanism

Reaction type	Example
1. Initiation reaction	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{H}_2\text{C}-\dot{\text{C}}\text{H} \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \begin{array}{c} \bullet\text{CH}_2 \\ \\ \text{OH} \end{array}$
2. β -Scission	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{O} \bullet \end{array} \longrightarrow \begin{array}{c} \text{H}_2\text{C}-\dot{\text{C}}\text{H} \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \begin{array}{c} \text{CH}_2 \\ \\ \text{O} \end{array}$
3. Hydrogen transfer	$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} + \bullet\text{H} \longrightarrow \begin{array}{c} \text{H}_2\text{C}-\dot{\text{C}}\text{H}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} + \text{H}_2$
4. Radical isomerization	$\text{H}_2\text{C}-\dot{\text{O}}\text{H} \longrightarrow \text{H}_3\text{C}-\text{O}\bullet$
5. Radical addition	$\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{C}-\dot{\text{O}}\text{H} \longrightarrow \begin{array}{c} \bullet\text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\ \\ \text{OH} \end{array}$
6. Radical dehydration	$\begin{array}{c} \text{H}_2\text{C}-\dot{\text{C}}\text{H}-\text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{H}_2\text{C}-\text{C} \\ \quad \\ \text{CH} \quad \bullet \end{array} + \text{H}_2\text{O}$
7. Radical substitution	$\text{H}_3\text{C}-\text{OH} + \bullet\text{H} \longrightarrow \text{CH}_3\bullet + \text{H}_2\text{O}$
8. Radical termination reaction	$\bullet\text{H} + \bullet\text{H} \longrightarrow \text{H}_2$

the liquid phase, which yields only 20.74% of MGs.²⁵⁹ McNeill and Yamane^{260,261} improved their system by carrying out the reactions first in liquid–liquid emulsion state. The mixture reaction was then cooled until becoming solid. The strong increase in the formation of MGs after reaching solid state was related to the crystallization of MGs from the mixture reaction. The reaction yield with this method increased to 70–99%. However, continuous production of MGs by this method was impossible. Besides, high yield of MGs can be obtained by esterification using the protected glycerol derivative 1,2-*O*-isopropylidene glycerol.²⁶² Recently, Ghamgui et al.²⁶³ reported the synthesis of MGs with immobilized *Staphylococcus simulans* lipase on CaCO_3 in a solvent-free system. Under the optimized conditions 70.6% yield of MGs was achieved. This continuous approach may be suitable for producing MGs for food use.

Production DAG. Various methods have been reported for the production of 1,3-DAG using lipases, including hydrolysis of triolein,²⁶⁴ glycerolysis of TAG,^{234,265} esterification of fatty acids, and glycerol in organic solvents^{266,267} and in a solvent-free system.²⁶⁸ In the nonsolvent esterification reaction reported by Rosu et al., a longer time (e.g., 12 h) was required to obtain a sufficiently high content of dilinolein (71.7%) since the reaction was carried out at the low temperature of 25 °C. Optimization of the reaction conditions for the efficient production of 1,3-DAG has not been reported. A high yield of 84% with a DAG purity of 90% was obtained from 1.29 mM glycerol and 2.59 mM fatty acid by conducting the reaction in a solvent-free system

at 50 °C using a 1,3-resioselective lipase with the simultaneous removal of water in a stirred-tank bioreactor.²⁶⁹ To find a suitable approach for long-term and industrial-scale production, Watanabe et al.²⁷⁰ reported the reaction in a packed bed bioreactor using a 1,3-regioselective immobilized lipase. Under the optimized conditions, a maximum 1,3-DAG content of approximately 70% was obtained when the molar ratio of fatty acid to glycerol was higher than 2.0.

3.6.2. Carboxylation of Glycerol to Glycerol Carbonate

Glycerol carbonate is a stable, colorless liquid. It is a useful solvent for plastics and resins, such as cellulose acetate, nylon, nitrocellulose, and polyacrylonitrile. It reacts readily with phenols, alcohols, and carboxylic acids when heated to form the glycerol ethers or esters of these materials, for example, polyesters, polycarbonates, polyurethanes, and polyamides.

Glycerol carbonate can be prepared by several methods. It was reported that glycerol carbonate can be formed by the reaction of epichlorohydrin with KHCO_3 carried out at 80 °C in the presence of 13-crown ether. Nevertheless, methods utilizing a renewable and cheap raw material such as glycerol are more attractive. Considering the increasing quantities of biodiesel fuel entering the market, a large amount of glycerol will be available as a side product of the transesterification of plant oils.

A typical method of obtaining carbonate derivatives of glycerol is its transesterification with ethylene carbonate or

Table 3. Reaction Types to Be Considered in the Ionic Reaction Part of the Mechanism

Reaction type	Example
1. Autoprotolysis	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
2. Protonation	$ \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \text{H}_3\text{O}^+ \rightleftharpoons \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH}_2^+ \end{array} + \text{H}_2\text{O} $
3. Deprotonation by OH ⁻ -ion	$ \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \text{OH}^- \rightleftharpoons \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{O}^- \end{array} + \text{H}_2\text{O} $
4. Dehydration	$ \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH}_2^+ \end{array} \rightleftharpoons \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \text{H}_2\text{O} $
5. Keto-enol-tautomerization	$ \begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array} \rightleftharpoons \begin{array}{c} \text{H}_2\text{C}=\text{C} \\ \\ \text{OH} \end{array} $
6. Acetalization	$ \begin{array}{c} \text{H}_2\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array} \xrightarrow{\text{H}_3\text{O}^+} \text{Cyclic acetal} + \text{H}_2\text{O} $
7. Aldol condensation	$ \begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array} \xrightarrow{\text{OH}^-} \begin{array}{c} \text{H}_2\text{C}=\text{C} \\ \quad \quad \quad \text{O} \\ \text{H} \quad \quad \quad \parallel \\ \quad \quad \quad \text{H} \end{array} + \text{H}_2\text{O} $

dialkyl carbonate (Scheme 19).²⁷¹ In a reaction with ethylene carbonate carried out at 125 °C in the presence of sodium bicarbonate, the product was formed in a yield of 81%. A recent patent reports a process in which a reaction between urea and glycerol produces glycerol carbonate with good selectivity (92%).²⁷²

Another promising method of glycerol carbonate preparation utilizes the reaction of glycerol with CO₂ or carbon monoxide and oxygen in the presence of Cu(I) catalysts.²⁷³ The reaction of glycerol with carbon dioxide was carried out in a ScCO₂ medium in the presence of zeolite and ethylene carbonate as a cosource of carbonate groups.⁵⁹ The above-mentioned methods require that the glycerol carbonate be subsequently purified by distillation under reduced pressure.

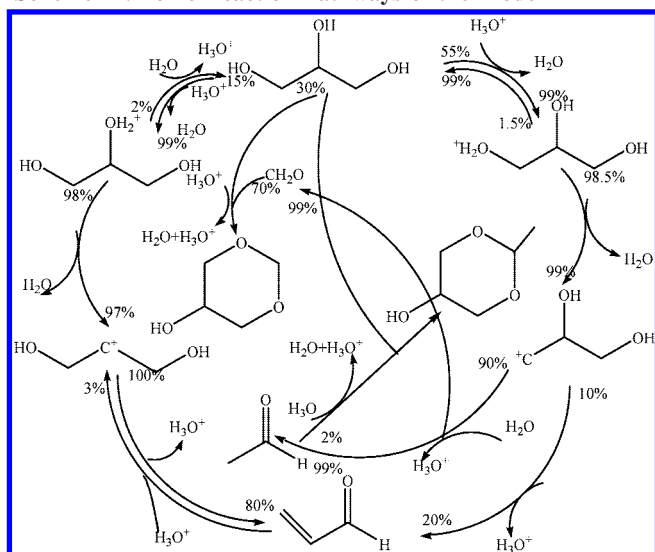
Recently, Aresta et al. reported the carboxylation of glycerol carbonate with carbon dioxide in the presence of Sn catalysts, such as *n*-Bu₂Sn(OMe)₂, *n*-Bu₂SnO, and Sn(OMe)₂, using either glycerol or tetraethylene glycerol dimethyl ether as the reaction medium.²⁷⁴ *n*-Bu₂Sn(OMe)₂ and *n*-Bu₂SnO were able to promote the direct carboxylation of glycerol into glycerol carbonate. The most active among the catalysts tested was *n*-Bu₂Sn(OMe)₂.

3.6.3. Nitration of Glycerol to Glycerol Nitrate

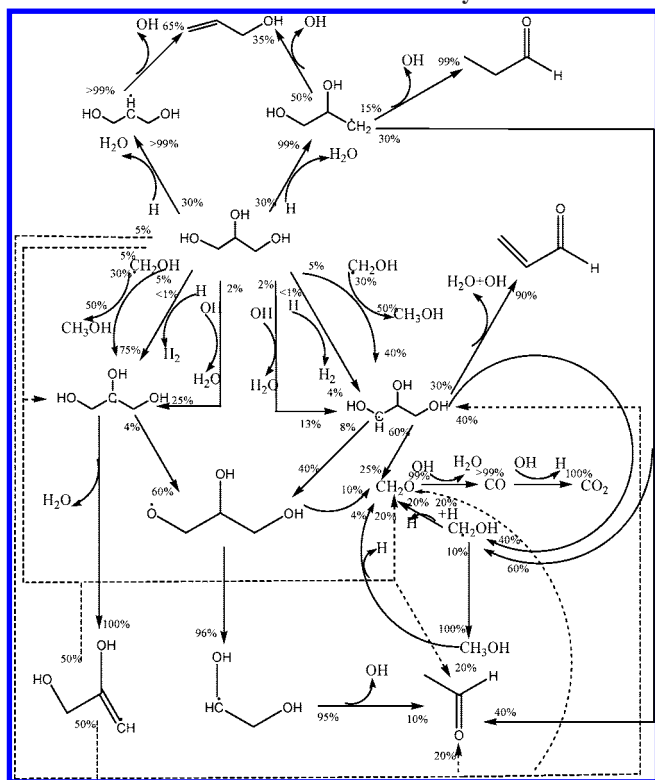
Glycerol can be treated with nitrating agents to form a solution containing dinitroglycerol. The solution is treated with a cyclizing agent to convert the dinitroglycerol into glycidyl nitrate, which is polymerized into poly(glycidyl nitrate).²⁷⁵ Poly(glycidyl nitrate) (PGN) has been recognized as an energetic polymer potentially suitable for use in propellants, explosives, gas generators, and pyrotechnics. The industrial synthesis of PGN typically follows a three-step procedure. The first step involves the nitration of epichlorohydrin, followed by a second step in which the nitrated epichlorohydrin is cyclized with a base to form glycidyl nitrate. The glycidyl nitrate is then polymerized in a third step by cationic polymerization to form PGN. In this process, the raw material is derived from petrochemicals and nonrenewable. However, it is also possible to produce PGN using glycerol obtained from renewable sources.

3.7. Pyrolysis of Glycerol

Pyrolysis of glycerol has been studied in steam^{276,277} and supercritical water^{184,185} with acrolein (2-propanal), formaldehyde (methanal), and acetaldehyde (ethanal) observed

Scheme 21. Ionic Reaction Pathways of the Model^a

^a The numbers at the arrow ends are the calculated percentages of the compound reacting via these reaction pathways. The numbers at the arrowhead are the calculated percentages of compound formed via these reaction pathways. The number on an arrow is the number of the elementary reaction (calculated for 621 K, 45 MPa, and 118 s).

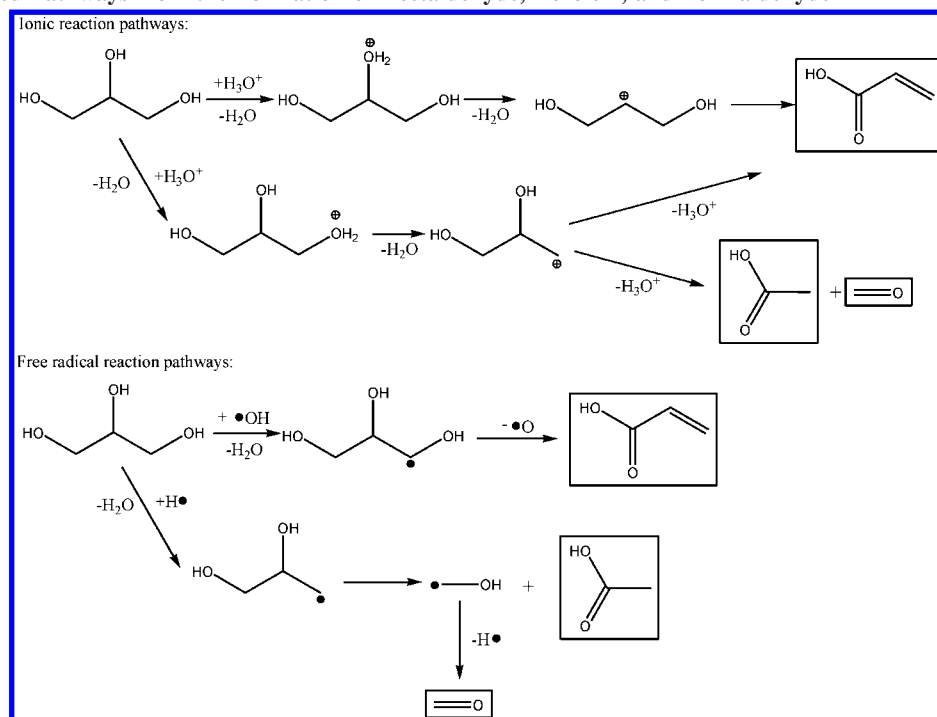
Scheme 22. Free Radical Reaction Pathways of the Model^a

^a The numbers at the arrow ends are the calculated percentages of the compound reacting via this reaction pathway. The numbers at the arrowhead are the calculated percentages of compound formed via this reaction pathway. The number on an arrow is the number of the elementary reaction (calculated for 744 K, 45 MPa, and 110 s).

as the major products at lower temperatures. These products appear to result from dehydration and fragmentation of glycerol. At higher temperature, other products such as carbon dioxide, molecular hydrogen, ethylene, and methane are observed, indicative of more complex chemistry. The reaction mechanisms of glycerol decomposition were pro-

posed by the research groups.^{184,185,276} Antal et al.²⁷⁶ first assumed the formation of acetaldehyde to be a free radical reaction. Later, they proposed it to be a retro-aldol condensation (Scheme 20).¹⁸⁵ The free radical pathways are splittings of a carbon–carbon bond. This would be an initiation step of a free radical chain reaction. The assumption of retro-aldol condensation by Antal et al. seems reasonable, and it explains the influence of different additives.

In 2002, Buhler et al.¹⁸⁴ proposed the mechanism of glycerol decomposition in near- or supercritical water in the temperature range of 622–748 K, at pressures of 25, 35, or 45 MPa, reaction times from 32 to 165 s, and different initial concentrations. For the modeling of the decomposition of glycerol in near- and supercritical water on the basis of elementary reactions, they assumed a combination of a free radical thermal decomposition model and an acid-catalyzed ionic decomposition model. The radical part of the reaction mechanism was developed similar to other radical mechanisms in supercritical water,²⁷⁸ which are only modifications of free radical mechanisms at low pressures. The reaction classes considered are initiation reactions, β -scissions, hydrogen transfer reactions, radical isomerizations, radical additions, radical dehydratizations, radical substitutions, and radical termination reactions (Table 2). The ionic part of the reaction mechanism is totally based on assumptions. They assume the following ionic reaction classes: protonations, deprotonations by OH^- ion, hydrations, keto–enol tautomerizations, acetalizations, and aldol condensations (Table 3). The model calculations were done with CHEMKIN II. A single run calculated the concentrations of all species in dependence of the reaction time for a radial homogeneous plug flow reactor and for overall isothermal conditions. In addition, sensitivity calculations and flow analysis were performed to get information about important reaction steps. The method of setting up the reaction model may be summarized by the following partially iterative schema: (i) All initial elementary reaction, which are reasonable from a chemical point of view, are included. (ii) All free radical and all ions, which can be formed by initiation of by bimolecular reaction of free radicals or ions with glycerol, are used for the set up (primary radicals and ions). (iii) All free radicals and ions resulting from unimolecular decomposition of the primary reactive species are included (secondary reactive species). (iv) Most of the unimolecular and bimolecular elementary reaction of glycerol and the primary and secondary reactive species become part of the reaction mechanism. (v) Only these reactions of the stable products (like, e.g., acrolein), which seem necessary, are included. (vi) Other elementary reactions (like, e.g., addition reactions) are built-in, using chemical reasoning. (vii) Kinetic and thermodynamic parameters are assigned. (viii) Model calculations for one set of experiments are performed. (ix) Comparison with the experimental results, flow analysis, and optimization is done: iteration. (x) Model calculation for all experimental set-ups is completed. (xi) Comparison with all experimental results, flow analysis, and optimization is done: iteration. Considering the formed products and the density dependence of product formation, a summary of elementary reaction steps for the ionic reaction pathways was built up (Scheme 21). In Scheme 21, the most important step is the protonation of glycerol. This means that the reaction rates of the ion reactions strongly depend on the self-dissociation of water. The simplified radical mechanism as shown in Scheme 22 is achieved from the flow analysis at 744 K, 45

Scheme 23. Selected Pathways from the Formation of Acetaldehyde, Acrolein, and Formaldehyde

MPa, and 110 s reaction time. Alternative pathways for the formation of acetaldehyde, acrolein, and formaldehyde were also proposed (Scheme 23).

Recently, some research groups studied the degradation of glycerol hydrogen with different catalysts. Hirai et al.²⁷⁹ investigated the production of hydrogen by steam reforming of glycerol on ruthenium catalyst on Y_2O_3 as the support. Soares et al.²⁸⁰ and Simonetti et al.^{281,282} described the production of hydrogen and carbon monoxide from glycerol over platinum-based catalysts. More recently, Zhang et al.²⁸³ in China researched hydrogen production from steam reforming of glycerol over ceria-supported metal catalysts with hydrogen selectivity of more than 85 and 100% glycerol conversion at 673 K.

3.8. Fermentation Products from Glycerol

Because of glycerol surplus in the current market, conversion of glycerol to various high value-added products attracts much interest. Except the above products, glycerol has also been used as a sole fermentation substrate to produce other valued products, such as ethanol and hydrogen²⁸⁴ or biomass and α -amylase.²⁸⁵ Organic acids have also been produced by strains using glycerol.^{286–292} Glycerol undergoes other reactions to yield important chemicals such as polyether polyols and alkyd resins, both of which are large volume commodities that could offer an opportunity to expand glycerol's utility.

4. Economy Analysis of the Derivation

Technological and political developments point to the re-emergence of a carbohydrate-based economy, in which agricultural commodities are used for not only food and fibers, but also as fuel and basic raw materials. With the worldwide development of biodiesel from vegetable oils and animal fats, large quantities of glycerol have been produced as a byproduct in the biodiesel process, causing a rapid decline in the price of glycerol. In Europe, the price has

dropped to only half of that several years ago. There is currently a glut of glycerol on the world market, and the search for new uses for glycerol is becoming urgent. With three hydroxyl groups, glycerol can be readily converted to many important commodity chemicals. The combination of renewable resources and selective catalytic processes provides a clean and economically competitive route for the production of these commodity chemicals (the “glycerol family”) from renewable carbohydrate feedstocks instead of from nonrenewable petroleum.

With the decrease of available fossil resources, the price of oil will rise rapidly, and manufacturers will seek their commodity chemicals from renewable sources rather than the petrochemical industry. The current market glut has depressed prices, and glycerol will be continued to be undervalued until new uses are found. Therefore, commodity chemicals obtained from glycerol are competitive with those from petroleum sources at present or in the near future. The conversion of glycerol to commodity chemicals can also solve the problem of surplus glycerol in the market and will help to lower the cost of biodiesel.

5. Conclusions

The diminished availability of fossil resources makes the search for biobased substitutes an urgent matter. The expanding production of biodiesel fuels has produced a market excess of glycerol as a byproduct. Glycerol, therefore, presents an ideal source for low-priced, renewable industrial feedstocks, provided researchers can meet the pressing need for alternative methods of glycerol utilization. Recent progress in catalysis makes possible the conversion of glycerol to a host of other commodity chemicals, such as acrolein, dichloropropanol, epichlorohydrin, dihydroxyacetone, 1,3-propanediol, 1,2-propanediol, glycerol carbonate, DAG, MG, oxygenate fuels, glyceric acid, tartronic acid, and mesoxalic acid. Conversion of glycerol to these important commodity chemicals leads to definition of the “glycerol

family”, analogous to the “ethylene family” and “BTX family” of the petrochemical industry. Glycerol could become a strong link between renewable feedstocks and commodity chemicals.

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7. References

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