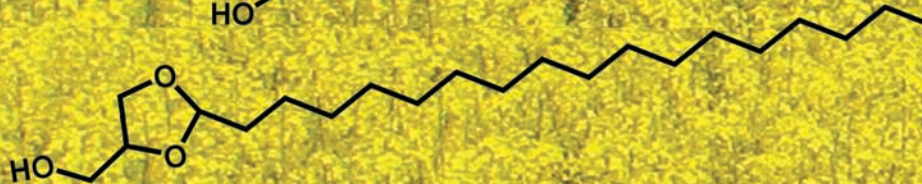
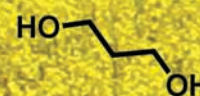
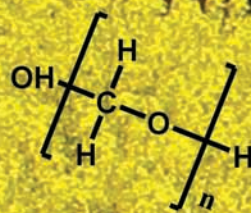
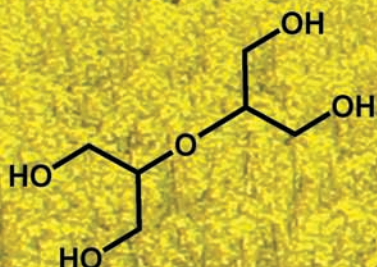
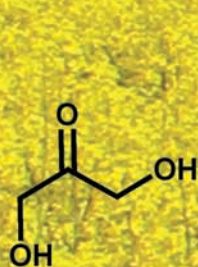
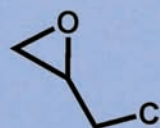
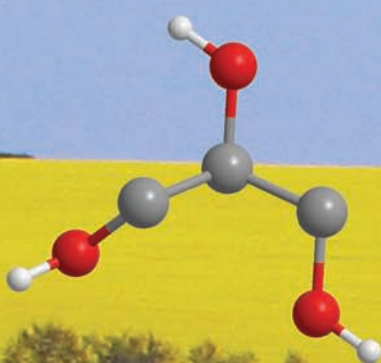
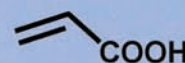
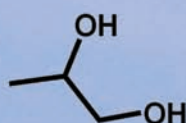
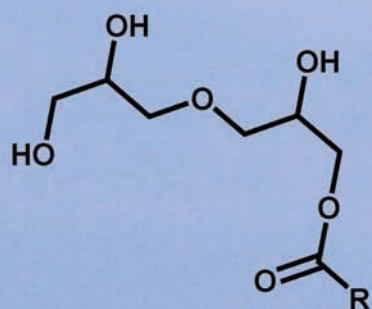


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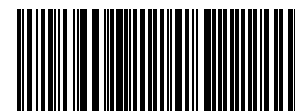
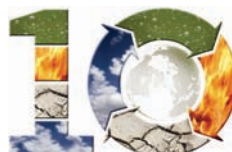


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New derivatives of glycerol

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Improved utilisation of renewable resources: New important derivatives of glycerol

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Although glycerol has been a well-known renewable chemical for centuries, its commercial relevance has increased considerably in the last few years because of its rising inevitable formation as a by-product of biodiesel production. The present review gives a broad overview on the chemistry of glycerol starting from the classic esters and oligomers to new products like glycerol carbonate, telomers, branched alkyl ethers, propanediols and epoxides. In particular, the novel possibilities to control the numerous addition, reduction and oxidation reactions *via* heterogeneous, homogeneous and biocatalysis will be presented. A benchmark will be given to determine the products which will have the best chances of entering the market and which processes are currently most developed.

1. Introduction

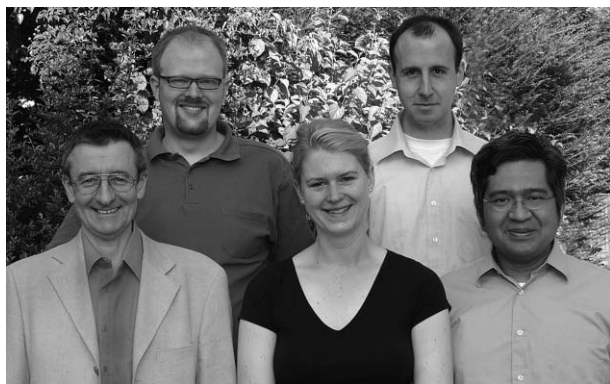
Glycerol, 1,2,3-propane triol, has been a well known chemical for more than two centuries. It was discovered in 1783 by the Swedish chemist Carl Wilhelm Scheele when treating natural oils with alkali materials. He noticed the formation of a liquid which he tasted, finding a very sweet flavour. He published his research results under the title "Experiment about a special sugar material coming from squeezed oils and fats". However, the discovery of "Scheele's sweet" had no further impact on scientific research or industrial usage for a long time. The name "glycerol" was given in 1811 by the chemist Michel

Eugene Chevreul, who deduced this name from the Greek word "glykos" (= sweet).

In 1866 the first technical usage of glycerol was the production of the trinitrate of glycerol, the so-called nitro glycerol. Dynamite is formed when nitro glycerol is adsorbed on diatomaceous earth, which can be used as an explosive, for instance, for the construction of tunnels, channels or railroad routes. Just for the construction of the Panama channel (started in 1879) 30 000 tons of dynamite were applied. At the end of the nineteenth century the processing of natural oils and fats and hence the production of glycerol increased continuously.

Nowadays the production of glycerol from fats and oils is carried out by saponification yielding glycerol and soaps (Scheme 1, $Y = \text{ONa}$), by hydrolysis yielding glycerol and fatty

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From left: Arno Behr, Jens Eilting, Julia Leschinski, Falk Lindner and Ken Irawadi

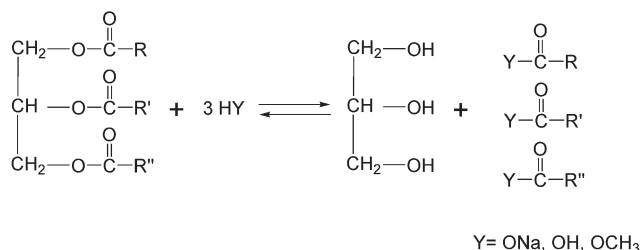
Arno Behr studied chemistry at Aachen University, Germany and did his PhD in 1979. After 10 years' work in industry he assumed a position at the Chair of Technical Chemistry, University of Dortmund, Germany, in 1996. One of his research interests is the chemistry of renewable resources.

Ken Irawadi earned his BSc in Agriculture Technology from Bogor Agricultural University, Indonesia and his MSc in Process Engineering at the TU Hamburg, Germany. He has been a lecturer and a researcher at Bogor Agricultural University. Since October 2006 he has been a PhD student under the supervision of Prof. Dr Arno Behr at the University of Dortmund, Germany.

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Scheme 1 Synthesis of glycerol from fats and oils.

acids (Scheme 1, Y = OH) or by transesterification with methanol yielding glycerol and fatty acid methyl esters (Scheme 1, Y = OCH₃).

The commercial production of fats and oils has increased rapidly during the last century, especially in the last three decades. Whereas in 1970 the total production of fats and oils was only in the range of 40 million tons (Mt), this value climbed to about 144 Mt in 2005. A further considerable rise to about 200 Mt can be foreseen for the year 2015. However, it must be stressed that only a small part of this material is converted within the chemical industry: about 81% of the worldwide oil production is used for the food industry, 14% in the chemical industry and 7% for feed. Today more than 20 Mt annum⁻¹ of fats and oils are processed chemically, yielding large amounts of glycerol.

A new trend has overlapped with this increasing production of natural oils and fats: for several years, renewable oils have also been used for energy applications. The so-called “biodiesel” has been implemented as automotive fuels in the US and in Europe. Biodiesel is a popular term for the fatty acid methyl esters formed according to Scheme 1, for instance from the transesterification of rapeseed oil with methanol. Biodiesel production in the EU was estimated to be about 6 Mt in 2006 and is forecasted to increase to about 12 Mt in 2010.

These trends influence remarkably the glycerol market. Before starting biodiesel production, the European glycerol market was in the range of 250 000 to 400 000 t annum⁻¹. Now, additional glycerol stemming from biodiesel production is flooding the market. One ton of biodiesel yields about 110 kg of crude glycerol or about 100 kg of pure glycerol. Therefore, by 2010 about 1.2 Mt annum⁻¹ of additional glycerol will enter the European market. Of course this influences substantially the glycerol price; while the glycerol price moved in the range of 1000 to 1300 € t⁻¹ between 2000 and 2003, from 2004 to 2006 it decreased to 500 to 700 € t⁻¹. Besides the high quality glycerol, there is a large quantity of impure glycerol on the market available for very low prices.

Obviously the question arises how this additional glycerol can be used wisely. There is already a great number of common glycerol applications; for instance, glycerol is used in pharmaceuticals, cosmetics (hair and skin care), soaps and toothpastes. Also the direct use as sweetener in candies and cakes and as a wetting agent in tobacco is widespread. Some chemical functionalisation of glycerol is also carried out in industry, especially the synthesis of some esters, polyethers and alkyd resins. There seems to be little scope to extend the uses of glycerol in these areas. So the question arises whether there are any additional fields of application, where glycerol itself or

some of its derivatives can find new handlings in the chemical industry.¹ The present article will provide a broad review regarding the areas of opportunity where it would be possible to capitalize on the surplus chemical glycerol. Well known chemistry, as for instance the formation of esters or acetals, and especially catalytic routes to new derivatives, will be considered and discussed in detail. In the following, we will first examine the production of esters, ethers, acetals and ketals of glycerol. Subsequently, the conversion of glycerol to diols and epoxides will be treated, followed by a review of the different possibilities to oxidise and to dehydrate glycerol to aldehydes, ketones or carboxylic acids. We will conclude by discussing other feasible reactions, like for instance the conversion of glycerol to synthesis gas.

2. Glycerol esters

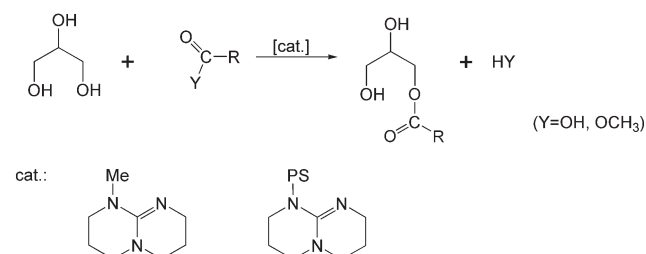
In this section we will consider mono-, di- and triesters of glycerol with carboxylic acids (section 2.1) as well as the cyclic ester of glycerol with carbonic acid, the glycerol carbonate (section 2.2).

2.1 Glycerol esters with carboxylic acids

Glycerol monoesters can be prepared by esterification of glycerol with carboxylic acids as well as by transesterification with their methyl esters (Scheme 2). They can be used as emulsifiers in the food industry, in cosmetics as well as in pharmaceuticals.

Barrault *et al.*² describe a relatively selective synthesis of monoglycerides in a “one pot” reaction by converting unprotected glycerol with different methyl esters which can vary in their chain length between 11 up to 17 carbon atoms. A guanidine catalyst is used as a homogeneous catalyst or as an immobilised catalyst fixed on crosslinked polystyrene (Scheme 2). The transesterification experiments with stoichiometric amounts of glycerol and methyl esters were performed at a temperature of 110 °C and with a relatively high catalyst concentration of 12.5 mol%. To achieve high yields between 96% and 100% a reaction time of 8 h was necessary when using the heterogeneous catalyst. With the homogeneous guanidine catalyst the reaction time increases from 2 to 3.5 h. The selectivity to monoesters reaches 65%, the selectivity to diesters 34% and the selectivity to triesters at most 5%.

The results are completely different when a heterogeneous catalyst is used. Here the selectivity to monoesters decreases from 62% for shorter methyl esters to 47% for longer methyl esters. For di- and triesters the situation is reversed: With



Scheme 2 Selective catalytic syntheses of monoglycerides (PS = crosslinked polystyrene).

Table 1 Synthesis of glycerol esters with basic oxide catalysts

Catalyst	Conversion (%)	Selectivity (%)		
		Monoesters	Diesters	Triesters
—	3	100	0	0
ZnO	18	80	20	0
MgO	80	38	50	12
CeO ₂	82	42	52	6
La ₂ O ₃	97	28	61	11

increasing chain length the selectivity also increases. This steering effect may be caused by the hydrophobicity of the esters which is rising with a longer alkyl chain. Due to the polystyrene chain the heterogeneous catalyst also has a high hydrophobicity, so that the interaction between the catalyst and the methyl ester is more intensive. In the end this leads to a higher selectivity to the di- and triesters.

The influence of solvents has also been investigated: The reaction rate is very low in solvents in which the methyl esters are only sparingly miscible. In solvents where good miscibility is achieved the reaction rate is as high as without a solvent.

Barrault *et al.* have also investigated basic oxides as possible catalysts for the synthesis of glycerides.³ All experiments have been performed at 220 °C, with an equimolar glycerol/methyl stearate mixture and a catalyst concentration of 2.7 wt.%. Experiments were performed with ZnO, MgO, CeO₂ and La₂O₃ (Table 1).

When La₂O₃ is used as catalyst the formation of the unwanted by-product acrolein is observed. Small conversions of glycerol lead to a high selectivity towards monoglycerides whereas at higher glycerol conversions the selectivity decreases dramatically. The highest conversion of glycerol could be achieved applying the catalyst with the lowest surface area.

Chang and Wu investigated the lipase-catalysed synthesis of triglycerides of phenylalkanoic acids.⁴ These esters act as pharmaceuticals which convert slowly into acids and glycerol inside the human body leading to a long residence time and a high concentration level of the active ingredient. The esterification to triglycerides could be performed in yields of 70% when the lipase Novozym 435 was used at a temperature of 60 °C. A solvent-free system leads to the best yields of triglycerides. Non-polar solvents only give very small yields whereas with increasing solvent polarity the yield to the products increases, too. By using 4-phenylbutyric acid an optimum temperature of 65 °C was found whereas higher temperatures lead to lower yields presumably because of deactivation of the enzymes. The water removal is a further very important aspect: *Via* removing the water—especially by the use of molecular sieves—the equilibrium of the reaction can be shifted towards the products. The use of saturated salt solutions or the removal of the water by pervaporation was not as effective.

Pérez-Pariente *et al.* investigated the synthesis of monoglycerides by converting glycerol with fatty acids using functionalised mesoporous materials as catalysts.⁵ The esterification of glycerol with oleic acid was performed with an equimolar ratio of the starting compounds at a temperature of 100 °C, a catalyst concentration of 5 wt.% and a reaction time of 24 h. The influence of the catalyst synthesis procedure, the effects of hydrophobicity and organosulfonic functional

groups and the impact of the catalyst structure were studied in detail. The catalyst synthesised by the so-called co-condensation method achieved a glycerol conversion of 24%, while the catalyst built by the post synthesis only led to conversions of 11%, each with a selectivity to the monoglycerides of about 69%. Hydrophobic catalysts lead to higher conversions of glycerol and to a higher selectivity of monoglycerides (75–95%). To create the acid sites of the catalyst two different sulfonation procedures were tested: The method with SO₃ proved to be more effective than the method with chlorosulfonic acid, because a higher acid content could be obtained. Concerning the catalyst structure the MCM-41 catalyst proved to be the best one, better than SBA-15, SBA-12 and SBA-2. MCM-41 led to the highest selectivity to monoglycerides (77%).

Corma *et al.*⁶ investigated Lewis basic hydrotalcites as catalysts for the conversion of methyl oleate with glycerol to esters which are valuable as surfactants and emulsifiers. In detail they compared Lewis- and Brønsted-basic materials. At a reaction temperature of 200 °C the Lewis-basic hydrotalcite led only to a yield of monoglycerides of about 60% while solid Brønsted-basic catalysts reached 80%. Water has an important influence on the catalytic performance of the hydrotalcites, because higher water amounts can block the catalytically active sites on the surface.

The conversion of glycerol with acetic acid leads to the glycerol mono-, di- and triacetins, which can be purchased for instance from Cognis.⁷ Bremus *et al.*⁸ invented a process to produce the triacetin continuously: In a first step the glycerol is converted only partly with acetic acid. In a second unit this reaction mixture is mixed with acetic acid anhydride to achieve a nearly complete conversion to triacetin. As a final step the triacetin is separated and purified by distillation. The non-toxic triacetin can be used for instance as a textile auxiliary.⁹

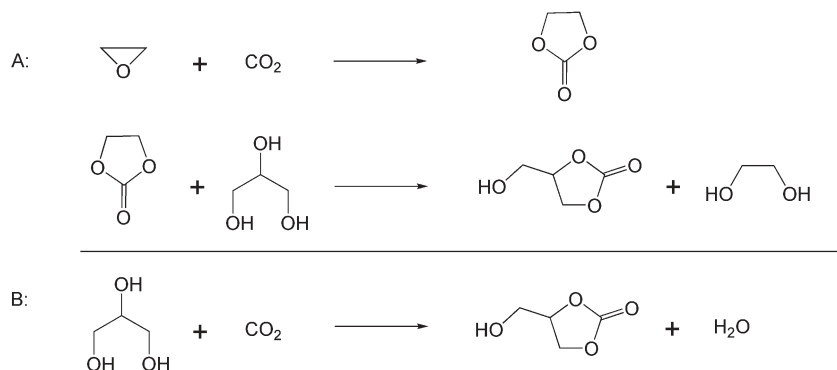
Roice *et al.* published a paper about the use of glycerol dimethacrylate as monomer. This diester can be used for the synthesis of copolymers with new interesting properties.¹⁰

2.2 Glycerol carbonate

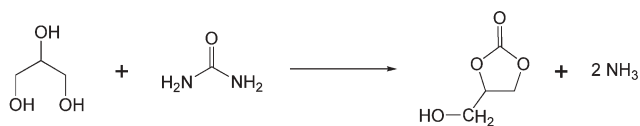
The technical synthesis of glycerol carbonate uses a multi-step reaction: First ethylene oxide reacts with carbon dioxide to yield the cyclic ethylene carbonate which then reacts further with glycerol to yield glycerol carbonate and ethylene glycol (Scheme 3, route A). Obviously, it would be more economic to convert glycerol and carbon dioxide directly into glycerol carbonate (Scheme 3, route B).

Glycerol carbonate and its esters are very interesting derivatives of glycerol, because they can be used as solvents for many applications, for instance in colours, varnishes, glues, cosmetics and pharmaceuticals.¹¹ The use as extraction medium or as monomer for the synthesis of new types of polymers may also become of interest.

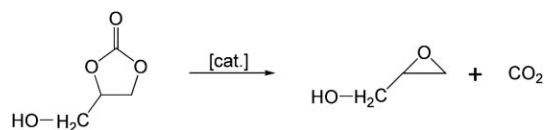
The direct synthesis of glycerol carbonate by the conversion of glycerol with carbon dioxide (route B) is therefore an interesting target of scientific research groups. Aresta *et al.*¹² have investigated this reaction using di(n-butyl)tin dimethoxide, di(n-butyl)tin oxide and tin dimethoxide as catalysts. Under the investigated reaction conditions (50 bar CO₂,



Scheme 3 Syntheses of glycerol carbonate.



Scheme 4 Synthesis of glycerol carbonate from glycerol and urea.



Scheme 5 Conversion of glycerol carbonate to glycidol.

180 °C) tin dimethoxide led only to traces of glycerol carbonate. However, di(*n*-butyl)tin dimethoxide led to a conversion of glycerol of maximum 7% depending on the reaction conditions. No solvent was used and molecular sieves were added in order to remove water from the gas phase. Using di(*n*-butyl)tin oxide as catalyst conversions of glycerol up to 2% were reported.

Similar tin catalysts were investigated successfully by Ballivet–Tkatchenko in the direct synthesis of dimethyl carbonate working in supercritical carbon dioxide.¹³ The reaction of glycerol and carbon dioxide has still to be further optimised to become a technical route to glycerol carbonate.

The catalytic conversion of glycerol with urea to glycerol carbonate has been investigated by Yoo and Mouloungui.¹⁴ Scheme 4 depicts the formal chemical equation.

Heterogeneous zinc catalysts were used to perform the reaction. At temperatures between 140–150 °C and a pressure of 40 mbar equimolar amounts of glycerol and urea react to glycerol carbonate. Table 2 shows the main results of the reaction optimisations.

In particular, the catalyst $\text{Zn}(\text{CH}_3\text{C}_6\text{H}_4\text{-SO}_3)_2$ leads to yields of more than 80% towards glycerol carbonate in a relative short reaction time of about 1 h. Similar high yields can be achieved by other catalysts, but only at longer reaction times.

Glycerol carbonate can split off carbon dioxide yielding glycidol.¹⁵ For this reaction (Scheme 5) zeolite A proved to be a very active catalyst. At a temperature of 180 °C and a

pressure of 35 mbar a yield of 86% and a purity of 99% could be attained.

Rokicki *et al.* investigated the use of glycerol carbonate as monomer to produce hyperbranched aliphatic polyethers (polyglycerols).¹⁶

3. Glycerol ethers

In the present section we will consider:

- The oligomers of glycerol in which the glycerol units are linked together *via* ether bondings to linear or cyclic compounds. When a higher number of glycerol molecules is linked together these compounds are also called polyglycerols. Both the oligoglycerols as well as their esters have already found important technical applications.

- The alkyl ethers of glycerol, for instance the glycerol tertiary butyl ethers.

- The alkenyl ethers of glycerol, for instance the telomers of glycerol with butadiene.

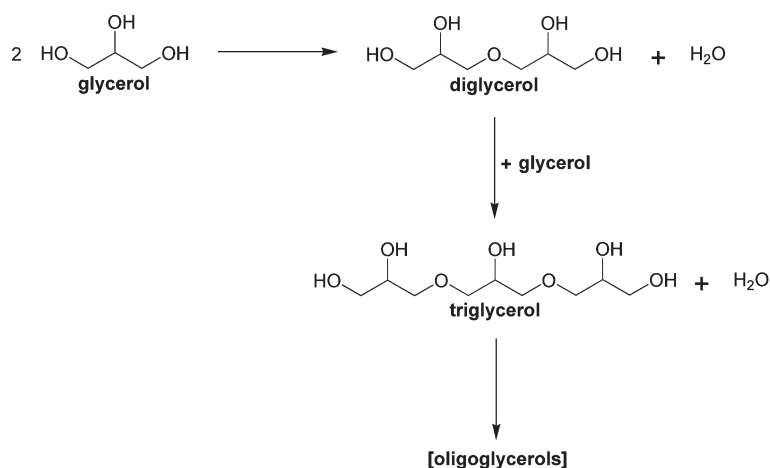
3.1 Glycerol oligomers/polymers (and their esters)

As an example Scheme 6 shows the synthesis of the linear diglycerol and triglycerol in which the glycerol units are linked together *via* their primary hydroxy groups. A great number of other linkages and of higher oligomers can be formed.

The oligoglycerols are gaining more and more interest as products used in cosmetics, food-additives or lubricants.¹⁷ Short overviews about the synthesis of glycerol oligomers from di- to pentaglycerol have been published by Rollin *et al.*¹⁸ and Pérez-Pariente *et al.*¹⁹ Generally oligoglycerols are produced using basic homogeneous catalysis, but lately increased attention has been paid towards heterogeneously catalysed processes.²⁰ Despite a lower activity heterogeneous catalysts reveal many advantages: Firstly, the separation of the catalyst does not cause any problems because the catalyst is a solid which is insoluble in the reaction medium. Secondly, a higher selectivity has been observed when heterogeneous catalysts such as

Table 2 Investigation of zinc catalysts for the synthesis of glycerol carbonate from glycerol and urea

Catalyst	Reaction time/h	Molar yield (%)
$\text{Zn}(\text{CH}_3\text{C}_6\text{H}_4\text{-SO}_3)_2$	1	81
$\text{Zn}(\text{CH}_3\text{C}_6\text{H}_4\text{-SO}_3)_2$	1.25	85
$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	2	83
ZnSO_4 (pre-treated for 3 h at 450 °C)	2	86



Scheme 6 Synthesis of oligoglycerols by intermolecular dehydration of glycerol units.

Table 3 Comparison of homogeneous and heterogeneous catalysts in glycerol oligomerisation

Catalyst	Na ₂ CO ₃	Cs-MCM-41	Amberlyst 16	Amberlyst 31
Conversion (%)	80 (8 h)	95 (24 h)	35–40	35–40
Selectivity (%)				
Diglycerol	31	59	85	75
Triglycerol	28	30	15	25
Tetraglycerol	17	11	<1	<1
Higher oligomers	24	<1	<1	<1

zeolites, ion exchangers or mesoporous molecular sieves of the type MCM-41 are used.^{17,21,22} However, it should be emphasised that so far the conversion of glycerol using heterogeneous catalysts is by far lower than using homogeneous catalysts.

A typical comparison is given in Table 3: The homogeneously catalysed oligomerisation of glycerol with the catalyst Na₂CO₃ leads to a conversion of 80% after a reaction time of 8 h, while with the heterogeneous catalyst Cs-MCM-41 the conversion reached 95% but only after 24 h. Both reactions were carried out at 260 °C under ambient pressure. The amount of catalyst used was 2 wt.%. The homogeneous catalyst yields a very broad product distribution from 31% diglycerol to 24% higher oligoglycerols. In contrast most heterogeneous catalysts yield relatively high amounts of diglycerol, for instance 59% with Cs-MCM-41, and only very low amounts of higher oligomers.¹⁷ Ion exchangers, for instance Amberlyst 16 and Amberlyst 31, are also very selective catalysts for the specific formation of the short chain oligomers and only a low reaction temperature of 140 °C is

needed. The amount of catalyst used in these reactions was in this case 5 wt.%. However, if these acidic catalysts are used, significant amounts of acrolein are formed.

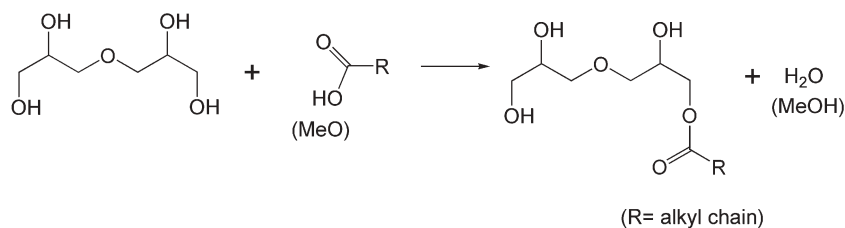
Moreover homogeneous catalysts lead to a different product distribution in contrast to heterogeneous catalysts: Homogeneous catalysts produce mostly linear oligomers whereas heterogeneous catalysts result predominantly in branched oligomers.¹⁷

Akzo Nobel reported a saponite catalyst for the synthesis of glycerol oligomers.²³ The catalyst is a Mg-rich clay which leads to a glycerol conversion of 56% after 40 h of reaction. In this case the selectivity to diglycerol is 30%.

Important derivatives of the oligoglycerols are the oligoglycerol esters. Starting from the oligomers described above, monoesters can be produced *via* esterification with carboxylic acids or transesterification with carboxylic acid methyl esters (Scheme 7). Di- or triesters of glycerol oligomers can be synthesised in a comparable way.

Plasman *et al.* discuss the applicability of these polyglycerol esters,²⁴ especially as antifogging and antistatic agents or as lubricants in the food industry. Only 0.5% of diglycerol monooleate are sufficient to achieve an antifogging effect in food packages. Polyglycerol esters are biodegradable and exhibit a high thermal stability as well as a colourless appearance even after thermal treatment in air at 250 °C.

Barrault *et al.* compared MgO and Cs-MCM-41 as heterogeneous catalysts for the selective synthesis of glycerol esters and diglycerol esters.¹⁷ Table 4 shows the results of the conversion of glycerol with methyl dodecanoate at 240 °C. At these conditions the glycerol is esterified to its mono-, di- and triesters and oligomerised to diglycerol followed by further



Scheme 7 Synthesis of monoesters of diglycerol.

Table 4 Conversion of glycerol with methyl dodecanoate using heterogeneous catalysts

Catalyst	Ester conversion (%)	Selectivity (%)					
		Glycerol			Diglycerol		
		Mono-	Di-	Tri-	Mono-	Di-	Tri-
MgO	98	10	45	34	1	5	5
Cs-MCM-41	89	7	2	38	17	18	19

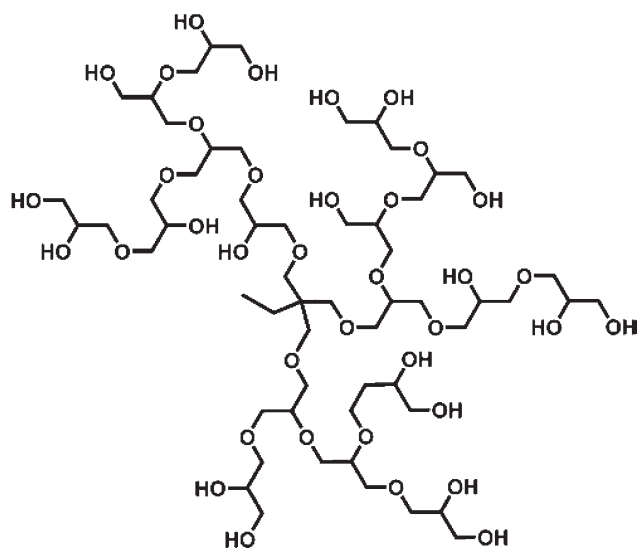
esterification. Whereas MgO leads to a high selectivity of glycerol esters (Σ 89%) the mesoporous catalyst Cs-MCM-41 leads to higher amounts of diglycerol esters (Σ 54%). The concentration of catalyst was 14 wt.% referring to glycerol and 6 wt.% referring to the ester.

Hao described polyglycerol esters which are used as stabilisation agents in water-in-gasoline microemulsions.²⁵ The addition of small amounts of water to gasoline reduces both NO_x emissions as well as soot formation. The water can be dissolved in gasoline by adding a mixture of a polyglycerol ester, a surfactant, and an alcohol thus yielding a microemulsion. The best system proved to be diglycerol diisostearate combined with sodium oleate in a ratio of 6 : 4, dissolved in 1-butanol. The highest water content in the microemulsion could be reached at a temperature of 16 °C.

Jérôme *et al.*²⁶ reported on a phosphazene catalyst for the synthesis of the mono- and diesters of glycerol derivatives. Using this catalyst, regioselective syntheses can be performed.

The last group of glycerol ethers to be presented are the hyperbranched polyglycerols. Scheme 8 depicts the general molecular structure of these compounds.

However, until now hyperbranched polyglycerols cannot be synthesised directly from glycerol as feedstock. The synthesis of such molecules, for instance *via* reaction of trimethylolpropane and glycidol, has been described in detail by Mülhaupt *et al.*^{27,28} Mecking *et al.* reported the incorporation of Pd-nanoclusters into polyglycerols to yield catalysts which are active in the hydrogenation of cyclohexene.²⁹ These palladium/polyglycerol catalysts can easily be recycled and



Scheme 8 Hyperbranched polyglycerols.

show a constant activity. Haag *et al.* presented polyglycerols able to solubilise hydrophobic drugs.³⁰

The structure of the polyglycerols and polyglycerol esters were investigated by using small-angle neutron scattering (SANS).³¹

Further investigations have been performed by Dworak *et al.*³² They investigated the polymerisation of glycidol using Lewis and protonic acids. Moreover, they elucidated the structure of the polymer by NMR-measurements and suggested a reaction mechanism.

In 2001 a company was founded which deals with hyperbranched polymers commercially.³³

Glycidol has also been mentioned for the synthesis of modified epoxy resins. Those resins are produced by Evonik.³⁴

Furthermore, hyperbranched polymers have been described which have been obtained from glycerol carbonate, which has been synthesised previously from glycerol and dimethyl carbonate.¹⁶

Glycerol as a building block for polymers has also been previously described. The Konkuk University in Seoul has made a patent application in which glycerol and fatty acids are essentials for polyurethaneamide adhesives.³⁵

3.2 Glycerol alkyl ethers

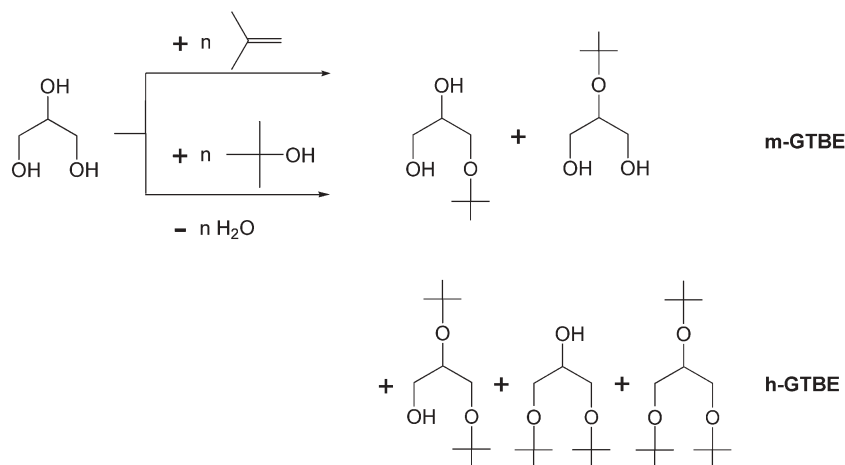
Alkyl ethers of glycerol can generally be synthesised *via* three different routes:

- The Williamson synthesis of sodium-glycerolate with an alkyl halide.
- The addition of an active alkene, especially a branched alkene, to glycerol.
- The condensation reaction between glycerol and an aliphatic alcohol under elimination of water.

Aubry *et al.* reported on the synthesis of glycerol 1-monoethers starting from 1,2-isopropylidene glycerol, potassium hydroxide and different bromoalkanes.³⁶ As these monoethers have the characteristics of solvents as well as of surfactants they are entitled “green solvo-surfactants”, which should be considered for the replacement of ethylene or propylene glycol ethers. However, their synthesis only proceeds with time-consuming protecting group chemistry and stoichiometric amounts of alkali bromides are formed as by-products.

The two other routes of ether synthesis will be demonstrated with the example of the glycerol tertiary-butyl ethers, the GTBE. They can be synthesised *via* the reaction of glycerol with isobutene or with tertiary butanol (Scheme 9).

The conversion of glycerol with isobutene yields the mono-, di- and tri-tertiary butyl ethers of glycerol. Due to the two remaining hydroxy groups the monoethers (m-GTBE) are still soluble in polar solvents, whereas a mixture of the di- and triethers, the so-called “higher ethers” (h-GTBE), are soluble in unpolar media, for instance in hydrocarbons. This property enables the application of the higher GTBE as fuel additives. Because of the glycerol content this additive can be assigned to the renewables and may help to meet the biocomponent target of the European Union. h-GTBE can be used as a diesel fuel additive, which reduces remarkably the emissions of particulate matter.^{37,38} However, because of the branched alkyl substituents the higher GTBE can also be used as potential



Scheme 9 Synthesis of GTBE *via* reaction of glycerol with isobutene or tertiary-butanol (m-GTBE = monoethers; h-GTBE = higher ethers).

components for the use in gasoline (“octane-boosters”) substituting the methyl tertiary butyl ether MTBE which is under discussion because of some environmental disadvantages.^{39,40}

The catalytic reaction of glycerol with isobutene was first investigated in 1992 by Behr and Lohr at the Henkel Company.⁴¹ They discovered some very active homogeneous and heterogeneous catalysts, for instance *p*-toluene sulfonic acid, acidic ion exchangers like Amberlyst 15 and several synthetic zeolites. In 1996 Behr and Obendorf^{42,43} continued these investigations and developed a technical process for the production of the higher GTBE. With *p*-toluene sulfonic acid (*p*-TSA) as the best catalyst the etherification of glycerol with isobutene was performed in a stirred batch reactor at 90 °C with a molar ratio of isobutene to glycerol of 2 : 1. At the beginning of the reaction the system consists of two immiscible phases, the polar glycerol and the unpolar isobutene phase. As the reaction proceeds, the mono-, di- and triethers are formed and after 40 min the reaction system becomes single-phased. After a total reaction time of about 3 h the reaction equilibrium is achieved yielding a mixture of about 45 wt.% diethers, 30 wt.% monoethers and 5 wt.% of unconverted glycerol.

Based on these laboratory investigations a continuous production process of the higher ethers was designed (Fig. 1), which enables the complete recycling of the homogeneous catalyst *p*-TSA and of the unwanted monoethers. The process consists of a reactor cascade operated at 20–30 bar followed by

an extraction at the same pressure conditions. Isobutene is fed directly to the reactor, whereas glycerol is fed to the extractor separating the catalyst and the monoethers from the reaction mixture. The polar glycerol/moethers-phase (R1) is run back to the reactor, whereas the unpolar phase is conducted to a flasher where the unreacted isobutene is stripped and then also recycled to the reaction unit. The bottom product of the flash passes a vacuum rectification column obtaining pure higher ethers overhead. The bottom product of the rectification which contains some traces of m-GTBE and the catalyst *p*-TSA is passed back to the reactor (R2). This process seems to be more economic than other processes proposed in some patents.^{44–50}

Karinen and Krause have investigated the same reaction system using Amberlyst 35WET as a heterogeneous catalyst.⁵¹ At a ratio of isobutene and glycerol of 2 : 1 the highest selectivity towards ethers of about 92% can be reached whereas a molar ratio of 4 : 1 leads to a selectivity of about 80%. 80 °C is described to be the best reaction temperature. High ratios of isobutene to glycerol lead to small fractions of monoethers, whereas small ratios lead to large amounts of monoethers, which, however, cannot be used as octane-boosters.⁴³

In 2003 Klepáčová *et al.* investigated the reaction of glycerol with *tert*-butanol in the presence of heterogeneous catalysts⁵² and compared Amberlyst 15 with the zeolites H-Y and H-Beta. By using Amberlyst 15 as catalyst the highest glycerol conversion is achieved at 90 °C after 3 h. A catalyst concentration

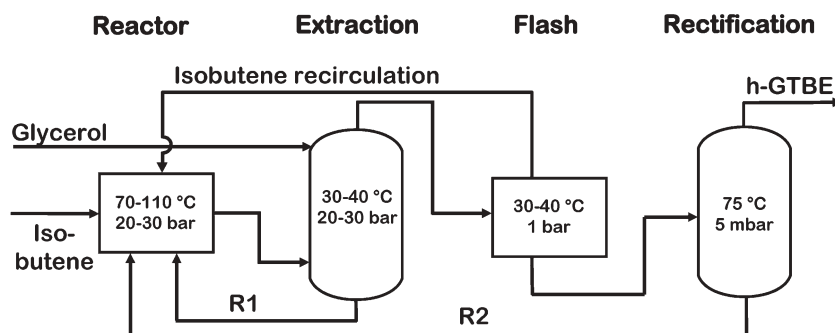


Fig. 1 Flow scheme for the technical process for the production of higher GTBE (R1 = recycle of glycerol, *p*-TSA and m-GTBE; R2 = recycle of traces of m-GTBE and *p*-TSA).

between 5 and 8 wt.% and an equimolar ratio between *tert*-butanol and glycerol gives optimum results.

In 2005 Klepáčová *et al.* published new investigations⁵³ where they compared experiments with isobutene as well as with *tert*-butanol. If the same temperature and catalyst is used isobutene always leads to higher conversions of glycerol than *tert*-butanol. This can be explained by the formation of the by-product water, which deactivates the catalyst. At 60 °C with the catalyst Amberlyst 35 in the dry form the conversion of glycerol with isobutene is almost quantitatively, whereas the conversion of glycerol with *tert*-butanol is only 86%.

3.3 Glycerol alkenyl ethers (telomers)

An atom-economic way to get unsaturated ethers of glycerol is the transition-metal catalysed telomerisation of butadiene with glycerol^{54–56} leading to the products shown in Scheme 10.

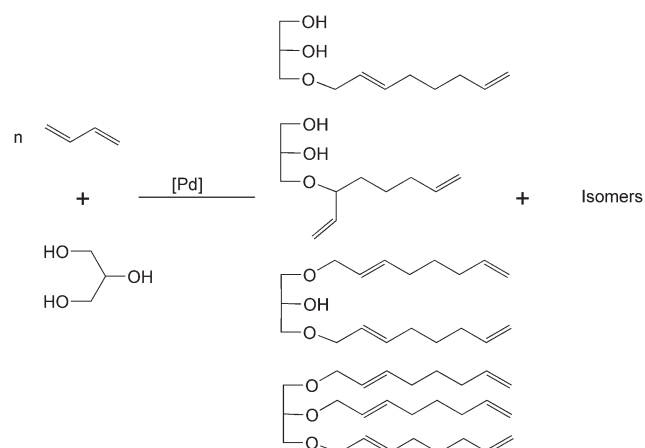
Like other ethers of glycerol they can be used as emulsifiers or surfactants due to their amphiphilic nature after hydrogenation of the remaining double bonds. Moreover, glycerol monoethers in particular have some special advantages regarding *e.g.* toxicity and biodegradability.⁵⁷

The telomerisation is catalysed homogeneously at temperatures around 80 °C by metal complexes of palladium or nickel containing suitable ligands, *e.g.* phosphines, leading to telomer selectivities > 95%.^{55,56,58,59} Because of the homogeneous catalyst, recycling of metal and ligands is necessary to make the reaction efficient. Some recycling concepts are already described in the literature.^{58,60}

4. Glycerol acetals and ketals

Various acetals and ketals can be used as ignition accelerators and antiknock additives in combustion engines either based on petrochemical fuel like diesel and Otto fuel or bio-fuels.

They can be added up to 10 vol% of the fuel used^{61,62} and one main advantage is—comparable to the GTBE—the reduction of particle emissions.⁶³ A second application of glycerol acetals is the use as scent or flavour, *e.g.* the acetalisation of phenylacetaldehyd or vanillin with glycerol leading to hyacinth or vanilla flavours.^{64,65} Glycerol acetals can also be used as the basis for surfactants.⁶⁶



Scheme 10 Telomerisation of butadiene with glycerol to glycerol alkenyl ethers.



Scheme 11 General structures of glycerol acetals and ketals (R = H, alkyl chain).

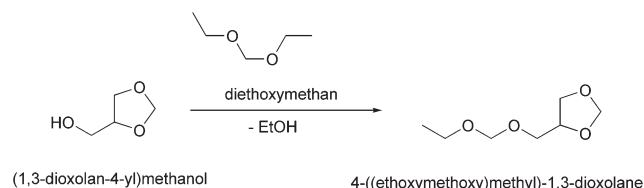
Acetals or ketals can be formed by reaction of glycerol with various aldehydes or ketones yielding five- or six-membered cycles (Scheme 11).

In the acetalisation reaction, the five- and six-ring compounds are usually formed in a ratio of 50 : 50. Some efforts have been made to change and control this ratio by varying the reaction parameters such as temperature, aldehyde or ketone to glycerol ratio and the choice of solvent. One example is the reaction of glycerol with acetone in dichloromethane at about 40 °C leading to a ratio of the five-membered to the six-membered ring as 99 : 1. In the case where the reaction is carried out with formaldehyde under the same conditions only a ratio of 22 : 78 is found.

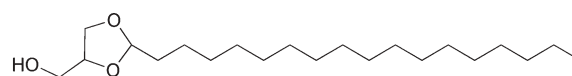
To perform an acetalisation, a catalyst is needed, which is mostly a solid acid catalyst. For example Amberlyst 15 catalyses the acetalisation of glycerol with various aldehydes or ketones *e.g.* butanal⁶¹ or acrolein⁶⁷ at temperatures below 70 °C leading to high selectivities. Also Amberlyst 36 is active in the acetalisation of glycerol, *e.g.* with formaldehyde at $T = 50\text{--}110$ °C with a yield of 77%. The glycerol formal can be used as disinfectant or solvent for medical or cosmetic applications.^{68,69} Furthermore, various zeolites catalyse the acetalisation reaction.⁶⁴ To modify the solubility and other physical properties, glycerol acetals can be varied by a further reaction of the remaining hydroxy group, which is shown in an example in Scheme 12.⁷⁰

Another standard way to change the polarity of glycerol acetals is the etherification of the remaining hydroxy group with tertiary alkenes.⁷¹

A further way to change the properties of given acetals or ketals is the transacetalisation by which *e.g.* long chained molecules (Scheme 13) can be obtained.^{72,73} Overall very polar (Scheme 12) as well as very unpolar acetals and ketals (Scheme 13) can be produced.



Scheme 12 Modification of the glycerol formal by etherification of the hydroxy group.



Scheme 13 Acetalisation of glycerol with octadecanal to 2-hepta-decyl-4-hydroxymethyl-1,3-dioxolane.

5. From glycerol to propanediols

Glycerol can be converted to 1,2-propanediol and 1,3-propanediol, which are useful final products, but also valuable starting compounds for the production of polymers. The world consumption of propylene glycols in 2003 was 1.2 million metric tons, the biggest producers being Dow and Lyondell with 35% and 25%, respectively, of the world production.⁷⁴ 1,3-Propanediol is an important diol in the production of polyesters, polycarbonates and polyurethanes. Three examples of large scale applications of 1,3-propanediol are SORONA and HYTREL made by DuPont and CORTERRA, trade mark of Shell.

While 1,3-propanediol is mainly used as a starting material for polymers, 1,2-propanediol is often used without further modification *e.g.* as an additive in nutrition products, solvent for colourings and flavours, wetting agent in tobaccos, additive in cosmetics, as component of break or hydraulic fluids, lubricants or anti-freezing agent. Furthermore, it can be used as a starting material for solvents, emulsifiers and plasticisers.

5.1 From glycerol to 1,2-propanediol

The present industrial way for manufacturing 1,2-propanediol (= propylene glycol) is the hydrolysis of propylene oxide with water at temperatures between 125 °C and 200 °C at a pressure of 20 bar (Scheme 14). After the reaction step, the mixture must be stripped and distilled to separate the product from water and the higher substituted polyols. Although there are further processes such as the acetoxidation of propene followed by hydrolysis or the direct hydroxylation catalysed by osmium compounds, the classical route based on propylene oxide is still widely used.⁷⁵

In particular, when 1,2-propanediol or its derivatives are applied in food, cosmetics or pharmaceutical products, the use of fossil raw materials is less favourable to the consumer acceptance, which leads to the demand of a renewable feedstock such as glycerol or sugars. Agribusiness companies such as Archer Daniels Midland (ADM) have developed processes based on these starting materials.⁷⁶ Glycerol can be converted to 1,2-propanediol using heterogeneous, homogeneous or biocatalysts, which are described in the following section.

(a) Heterogeneous catalysts. One possible way to obtain 1,2-propanediol from glycerol is the direct hydrogenation of glycerol by classical heterogeneous hydrogenation catalysts used in the production of fatty alcohols or in fat hardening. Moreover, catalysts containing an active copper compound such as Cu-chromite, Cu-ZnO₂ or Cu-Al₂O₃ are active in

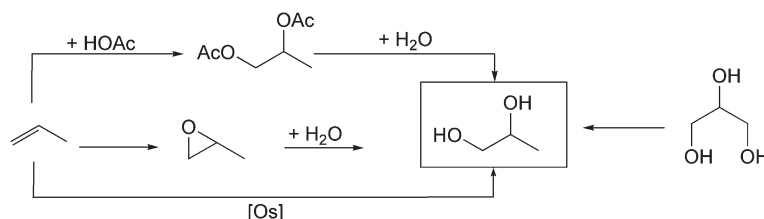
glycerol hydrogenation at temperatures between 150–320 °C and pressures between 100 and 250 bar.^{77–80} With similar reaction conditions, a catalyst system containing cobalt, copper, manganese and molybdenum as well as inorganic polyacids leads to nearly quantitative conversions with selectivities > 95%.⁸¹ Another way of converting glycerol to propylene glycol is the use of ruthenium in combination with acids or ion-exchange resins, which enables slightly milder reaction conditions, but also smaller conversions and selectivities.^{82–84}

Another approach is the use of Raney-nickel as hydrogenation catalyst. As in the case of Ru as a catalyst, reaction conditions are relatively mild.⁸⁵ The use of rhenium as catalyst metal in a multimetallic catalyst leads to conversions up to 80% with selectivities > 30% at temperatures > 120 °C and 80 bar hydrogen pressure.⁸⁶ Besides the influence of metal and support also the choice of solvent has a strong influence on the performance of the catalyst system, especially on the selectivity towards 1,2- or 1,3-propanediol.⁸⁷

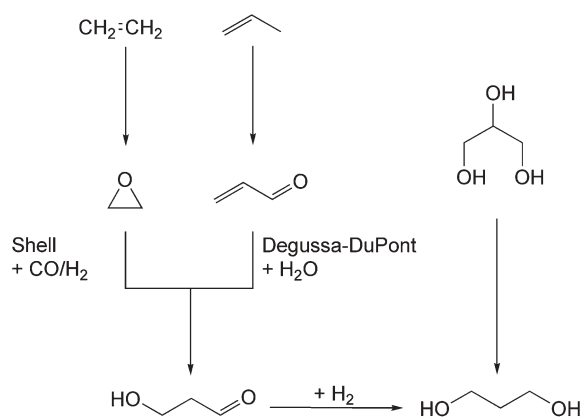
Not only the catalyst systems and solvents have been improved, but also completely new processes have been developed. One example will be described in section 5.2a.

(b) Homogeneous catalysts. In general the hydrogenolysis of glycerol by homogeneous catalysts leads to a variety of by-products such as propanol or ethers and to a mixture of 1,2- and 1,3-propanediol. The amount of different products depends on the mechanism of the product formation. Typical catalysts for this application are metals of the platinum group either in complexes with iodocarbonyl compounds⁸⁸ or phosphorous, arsenic or antimony ligands.⁸⁹ The selectivity for 1,2-propanediol of these processes is usually below 25%. These processes operate at conditions, which are comparable to the ones applied in heterogeneous systems, only the pressure range can be decreased ($T > 100$ °C, $p = 5$ –100 bar). There have also been process simulations to develop production routes leading from biomass such as glycerol or sugar to 1,2-PDO and ethylene glycol.⁹⁰

(c) Biocatalysts. A typical commercial example of a technology switch with respect to catalyst and feedstock was demonstrated by a joint venture of the chemical company Ashland Inc. and the food processor Cargill. The aim of this project was the production of propylene glycol out of glycerol from the biodiesel industry at a factory in Europe with an initial capital investment of \$80–\$100 million and a capacity of 65 000 t year⁻¹.^{91–93} Cargill has already presented a process to obtain propylene glycol out of carbohydrates with *Escherichia coli* or *Thermoanaerobacterium thermo-saccharolyticum* HG-8.^{94,95}



Scheme 14 Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol.



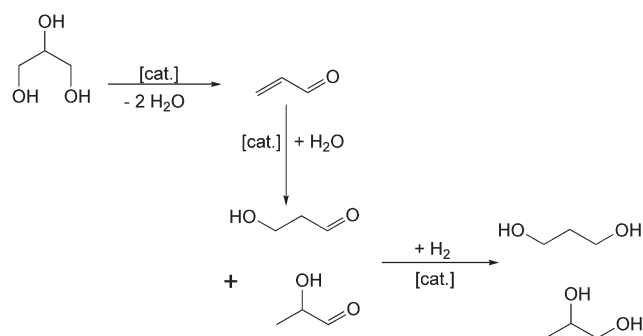
Scheme 15 Different routes to 1,3-propanediol starting from ethene, propene or glycerol.

5. 2 From glycerol to 1,3-propanediol

As mentioned above, 1,3-propanediol is an important compound in polymer production and is therefore much more valuable than 1,2-propanediol. There are two examples for the synthesis of 1,3-propanediol based on petrochemicals: the first one is the Shell process^{96–99} consisting of the hydroformylation of ethylene oxide to 3-hydroxypropanal followed by hydrogenation to 1,3-propanediol. The second is the Degussa–DuPont process^{100–103} based on the hydration of acrolein to 3-hydroxypropanal and further hydrogenation analogue to the Shell process (Scheme 15).

Problems in the conventional processes are the high pressure applied in the hydroformylation and hydrogenation steps as well as the use of aromatic solvents in the first and loss of acrolein due to extraction processes in the second example. The yields are around 80% in the first and about 40% in the second process, so besides the demand of renewable sources like glycerol, there is also a huge interest in improving yields and overall selectivity of the processes applied. Therefore, the reaction from glycerol to 1,3-propanediol *via* heterogeneous, homogeneous or biocatalytic processes may become an attractive alternative.

(a) Heterogeneous catalysts. Heterogeneous catalysts are not selective in the formation of 3-hydroxypropanal out of glycerol. That is why mainly mixtures of 1,2- and 1,3-propanediol are obtained with heterogeneous catalyst systems (*e.g.* yield, $Y(1,3\text{-PD}) = 12\%$, $Y(1,2\text{-PD}) = 6\%$ described in ref. 87. Using the present known heterogeneous catalysts an improvement of the existing production routes cannot be achieved. What can be improved, besides the catalyst, is the reaction engineering as described in ref. 104. In this process, the yield of 1,3-propanediol is 60% (1,2-propanediol 10%), which is comparable to the processes based on petrochemicals. Glycerol is dehydrated to acrolein in the first step at 250 °C–340 °C with acid catalysts such as zeolites, inorganic acids or metal oxides (Al_2O_3 or TiO_2), followed by the acid-catalysed hydration of the acrolein at 20 °C–120 °C to the hydroxypropyl aldehydes and further hydrogenation to a mixture of 1,2- and 1,3-propanediol catalysed by Raney-nickel, platinum or ruthenium on a support or nickel on Al_2O_3 ¹⁰⁴ (Scheme 16).

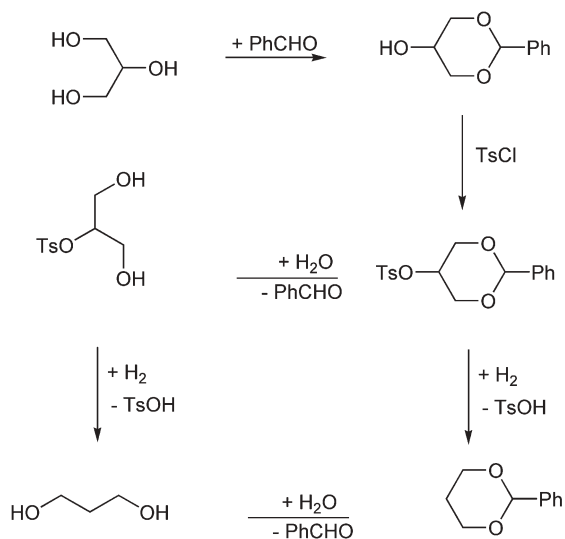


Scheme 16 Stepwise conversion of glycerol to propanediols.

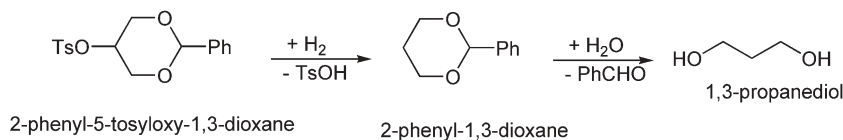
(b) Homogeneous catalysts. A typical advantage of homogeneous catalysts is their high selectivity, which can be explained by the well known mechanisms *via* organometallic species. Successful systems to convert glycerol to 1,3-propanediol are *e.g.* rhodium carbonyl catalysts such as $\text{Rh}(\text{CO})_2(\text{acac})$, which lead to a 21% selective conversion to 1,3-propanediol at room temperature and ambient pressure, which is a remarkable advantage compared to the reaction conditions used in the petrochemical routes.¹⁰⁵ Analogous to the heterogeneous systems, mixtures of different alcohols are obtained *e.g.* by using group VIII metals and/or tungsten as described in ref. 106 (yield, $Y(1,2\text{-PD}) = 26\%$; $Y(1,3\text{-PD}) = 24\%$). Moreover, process development can improve the results too, *e.g.* the process described in ref. 107 where the catalyst *p*-toluenesulfonic acid is used (Scheme 17). The process works with protection groups and consists of four steps, namely acetalisation of glycerol with benzaldehyde, tosylation of the resulting 5-hydroxy-2-phenyl-1,3-dioxane and further hydrolysis and hydrogenolysis which leads to 1,3-propanediol with an overall yield of 72%.

(c) Biocatalysts. Some enzymes and microorganisms possess a very high selectivity to convert several carbon sources to 1,3-propanediol. For instance glycerol can be converted to 3-hydroxypropanal in a one-step enzymatic reaction in an aqueous solution at room temperature and ambient pressure with yields > 85%. Six genera of bacteria are able to ferment glycerol with sufficient results, namely *Bacillus*, *Klebsiella*, *Citrobacter*, *Enterobacter*, *Clostridium* and *Lactobacillus*.^{108–114} Furthermore, some thermophilic strains have been developed to convert hot effluents from the fat industry.¹¹⁵

Besides glycerol, other polyols, like starch or glucose, can be used in the production of 1,3-propanediol by fermentation with the bacteria mentioned above. One example of a technology switch from petrochemicals to renewable sources is the fibre SORONA made by DuPont. Genencor International and DuPont have developed in conjunction a process for producing 1,3-propanediol by fermentation with recombinant *Escherichia coli*. The genome with the information about the conversion of glycerol to 1,3-propanediol has been isolated from a donor organism and transferred to *E. coli*. This modified organism is 500 times more effective than the original one.^{114,116–120} The process can convert glycerol but was afterwards switched to the cheaper glucose, now a fundamental technique for DuPont to produce 1,3-propanediol. In



or:



Scheme 17 Alternative process from glycerol to 1,3-propanediol using protection groups.

the first plant in Loudon, Tennessee, 500 t year⁻¹ of 1,3-propanediol can be produced starting from glucose obtained from corn.^{121–124} According to DuPont the process saves 40% of the energy consumed by its petrochemical counterpart.

6. From glycerol to epoxides

In the past glycerol was made out of epichlorohydrine, but—as mentioned earlier—there is no further need for a specific synthesis of glycerol nowadays. Therefore Solvay came up with the idea to reverse the classic synthesis route and to produce epichlorohydrine from glycerol (Scheme 18). This process is divided into two main steps: The first step is the chlorination of glycerol with anhydrous hydrogen chloride to 1,3-dichloropropan-2-ol at moderate temperatures of about 110 °C.^{125,126} The second step is the formation of the epoxide by addition of sodium hydroxide. Thus the desired epichlorohydrine, the so-called Epicerol, is obtained. The preparation of epichlorohydrine on the basis of glycerol shows significant advantages compared to the present process based on propene: First of all the feedstock is renewable and the water

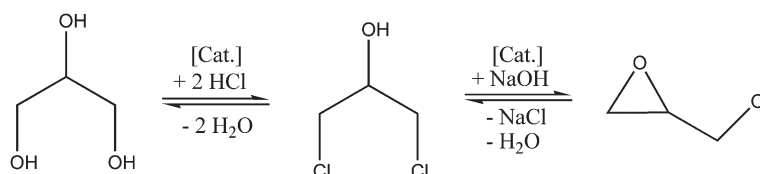
consumption is lower. In addition the chlorinated residues are reduced and the chlorination agent is hydrochloric acid instead of the more expensive chlorine.¹²⁷

Another epoxide with the glycerol structure is the glycidol whose synthesis has already been described in Scheme 5 in section 2.2.

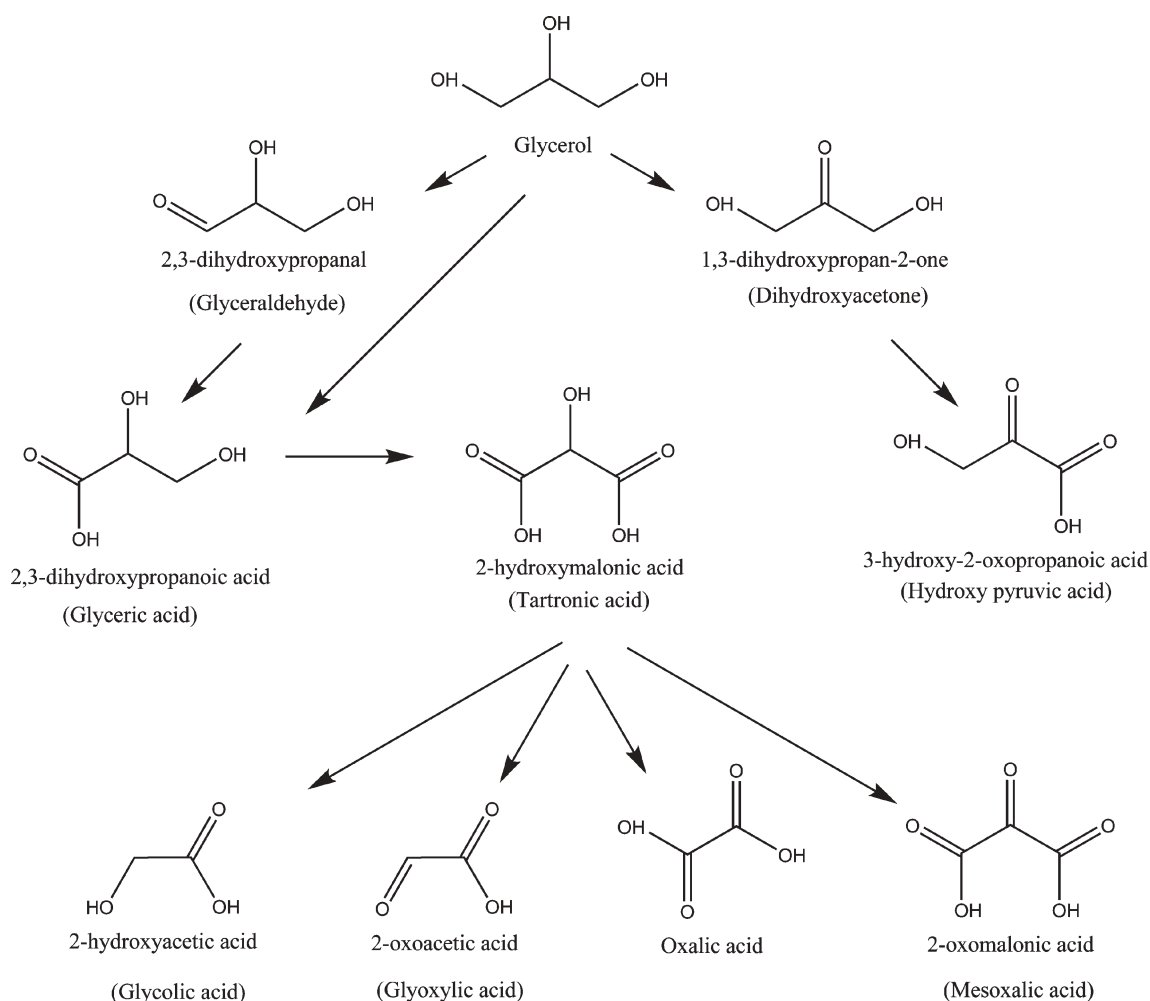
7. Glycerol oxidation and dehydration

Glycerol oxidation is a complex pathway of reactions that can lead to a large number of products (Scheme 19). Many of these products are useful intermediate substances or valuable fine chemicals. However, until now they are being produced by expensive processes and therefore their utilisation on an industrial scale is still low.

In the following section (section 7.1) some valuable glycerol oxidation products are presented together with their main application fields. Secondly, the most important catalytic oxidation processes of glycerol are discussed (section 7.2). In the last section (section 7.3) the dehydration of glycerol to acrolein is presented.



Scheme 18 Conversion of glycerol to epichlorohydrine.



Scheme 19 Oxidation products of glycerol.¹²⁸

7.1 Glycerol oxidation products

If the secondary hydroxy group of glycerol is oxidised selectively, dihydroxyacetone (DHA) is formed (Scheme 19). Conventionally, this can be done by a fermentation process, for example *via* the microorganism *Gluconobacter oxydans* in a fed batch reactor.¹²⁹ DHA has been used for years as an active substance in sunless tanning lotions. A combination of DHA incorporated in lamellar structures, *e.g.* phospholipids, and free DHA particles has resulted in a even more intensive and longer tanning effect.¹³⁰ Beside its main utilization in cosmetics, DHA has also other applications, for instance as a monomer in polymeric biomaterials.¹³¹

The oxidation of the primary hydroxy groups of glycerol produces glyceraldehyde, an intermediate in the carbohydrate metabolism. Glyceraldehyde is also used as a standard by which chiral molecules of the D- or L-series are compared. Further oxidation of glyceraldehyde produces carboxylic acids, like glyceric acid, tartronic acid and mesoxalic acid (Scheme 19). These acids are mainly converted into various market products, *e.g.* polymers or biodegradable emulsifiers. In addition to these applications, glyceric acid can be used for treatment of skin disorders,^{132,133} or as an anionic monomer of packaging material for exothermic and volatile agents.¹³⁴ In its

ester form, glyceric acid can act together with a quaternary ammonium salt as an effective and biodegradable fabric softener.¹³⁵ Tartronic acid can be used as a potentiating agent or adjuvant to increase the blood absorption of a tetracycline antibiotic.¹³⁶ Moreover, it can be used to scavenge dissolved oxygen in alkaline water.¹³⁷

7.2 Glycerol oxidation processes

Depending on the reaction conditions (pH, temperature, substrate to metal ratio) and the noble metal employed, the reaction pathway can be directed either to the oxidation of the primary or the secondary hydroxy group. Aerobic catalytic oxidations of glycerol have already been investigated with metal catalysts of platinum, palladium and recently of gold. In addition, non-aerobic electrocatalytic oxidations of glycerol using tetramethyl piperidine-1-oxyl (TEMPO) as oxidation agent and Ag/AgCl as catalyst have also been introduced.¹³⁸

Platinum metal catalysts are more selective for the oxidation of primary than for secondary alcohols. The main product of glycerol oxidation using platinum supported on active charcoal is glyceric acid (selectivity 55% at 90% conversion) with a small amount of DHA (selectivity 12%).¹³⁹ The selectivity towards the secondary alcohol can be increased by

association of the platinum with p-electron metals, especially lead and bismuth.^{140,141} These metal promoters can be added to the platinum-metals by co-impregnation, impregnation or redox surface reaction.¹⁴² In batch reactions the aerobic glycerol oxidation with Pt–Bi catalysts, prepared by means of the co-impregnation method, has a selectivity of 37% towards DHA at a 75% conversion of glycerol.¹³⁹ A still better result of the Pt–Bi catalysts could be achieved in catalytic glycerol oxidation by using a fixed-bed reactor, producing DHA with 80% selectivity at 40% conversion.^{143,144}

The utilizations of palladium catalysts for catalytic glycerol oxidations have been initiated by the group of Hutchings and the group of Kimura.^{145,146} Palladium catalysts at basic conditions have a high selectivity towards glyceric acid (77% at 90% conversion), whereas the selectivities to the other reaction products (DHA, tartronic and oxalic acids) are always lower than 10%.¹³⁹ However, palladium shows a weaker catalytic activity compared to platinum for the oxidation of the secondary hydroxy group of tartronic acid to produce mesoxalic acid.¹⁴⁷

Despite its successful application in aerobic glycerol oxidation processes, platinum suffers strongly from oxygen poisoning at high oxygen partial pressures. Therefore, this system can only be utilised at low oxygen partial pressures or by using air at atmospheric pressure, in order to limit the oxygen dissolution.¹⁴⁸ On the other hand, gold has a better resistance to oxygen poisoning compared to platinum.¹⁴⁹ Catalytic glycerol oxidation using gold catalysts have demonstrated a high selectivity to glyceric acid (more than 90% selectivity at 90% conversion), depending on the catalysts preparation methods used.¹⁴⁸

To evaluate the effect of preparation methods on glycerol oxidation, gold catalysts were prepared by different methods, e.g. by sol–gel, incipient wetness and impregnation. In the sol–gel method, the effect of protection agents, for instance polyvinyl alcohol (PVA), sodium citrate and tetrakis(hydroxypropyl)phosphonium chloride (THPC) has been investigated, and it was shown that the gold catalysts prepared by the sol–gel method have a higher activity than the catalysts prepared by the two other methods.^{148,150}

The increase in activity can also be caused by smaller catalyst particles. For gold it has been shown that the activity is highly dependent upon the particle size.^{150,151} If THPC or PVA are used to stabilise the colloid gold solutions, particles smaller than 10 nm were formed.^{148,150} However, if glyceric acid is the desired main product, the sol–gel method (Table 5, entries 3 and 4) is not the suitable method, since the selectivities are lower compared to the impregnation and incipient wetness methods (Table 5, entries 1 and 2).¹⁴⁸

Table 5 Glycerol oxidation with Au (1%) on activated carbon at 60 °C: Effect of the preparation method.¹⁴⁸

Entry	Preparation method	Glyceric acid selectivity at	
		50% conversion	90% conversion
1	Impregnation	71	70
2	Incipient wetness	80	78
3	Sol–gel (PVA)	47	35
4	Sol–gel (THPC)	52	45
5	Sol–gel (sodium citrate)	75	75

Table 6 Comparisons between monometallic and bimetallic catalysts for the glycerol oxidation at 50 °C.¹⁵³

Catalyst	Conversion (%)	Selectivity (%)				TOF/h ⁻¹ ^a
		Glyceric acid	Glycolic acid	Oxalic acid	Tartronic acid	
Pt/C	50	42	31	8	6	532
Pd/C	50	81	3	0	14	1151
	100	21	27	12	39	ns
Au/C	50	65	12	10	9	1090
	100	45	24	19	10	ns
Au–Pt/C	50	72	18	1	8	1987
	100	31	35	5	28	ns
Au–Pd/C	50	77	5	0	18	1775
	100	49	25	2	25	ns

^a Calculation of TOF/h⁻¹ after 0.25 h of reaction. TOF members were calculated on the basis of total loading of metals. ^b ns = not specified.

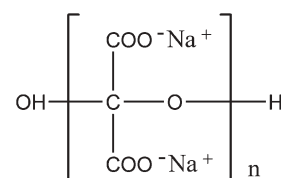
Basic reaction conditions are essential for the gold catalysis, since the initial step of the oxidation and the dehydrogenation of glycerol cannot proceed in the absence of a base. In the presence of a base, the H⁺ is readily abstracted from one of the primary hydroxy groups to form glyceric acid.^{145,152}

To improve the rate and selectivity of glycerol oxidation processes bimetallic catalysts were used. The comparisons between monometallic Au, Pd, or Pt and bimetallic Au–Pd¹⁵³ or Au–Pt^{154,155} catalysts proved that in many cases bimetallic catalysts have higher activity and resistance to deactivation (Table 6).^{141,142,153}

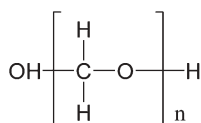
Monometallic Pd/C catalysts exhibit the highest activity with 50 °C, compared to the other metals. Under these conditions, Pd/C shows a better performance than Pt/C which cannot even reach 100% conversion because of the oxygen poisoning. However, if Pt is combined with Au, this bimetallic catalyst has the highest activity compared to all other catalyst systems. The bimetallic Au–Pd catalyst also provides an increase in activity.

The alloyed phase of the bimetallic Au–Pd system is much more active than the same system with segregated metals. The key to avoiding palladium segregation is by slowing down the reduction rate of the palladium salt. This can be achieved *via* two consecutive preparation steps: First the gold sol is immobilised on carbon using sodium boranate as reducing agent and then the palladium sol is precipitated on the Au/C surface using hydrogen as reducing agent. Applying NaBH₄ in the second step would result the unwanted palladium segregation.¹⁵⁶

One example of a three-metal catalyst in glycerol oxidation is Pd–Bi–Ce supported on charcoal. This catalyst has a multifunctional role, *i.e.* to oxidise glycerol to tartronic and mesoxalic acid and then to carry out the polymerisation of the mesoxalic acid into poly(ketomalonate) (Scheme 20).¹⁴⁷



Scheme 20 Structure of poly(ketomalonate).



Scheme 21 Structure of poly(oxymethylene).

Furthermore, in the case of excessive oxidation, a decarboxylation process takes time and results in the conversion of poly(ketomalonate) to poly(oxymethylene) (Scheme 21).¹⁵⁷ The poly(oxymethylene) is an engineering plastic which is also known as polyacetal, acetal resin, polytrioxane, polyformaldehyde, and paraformaldehyde.

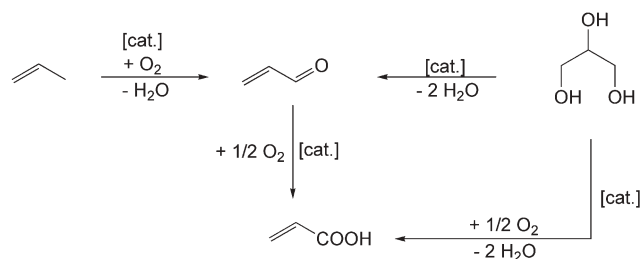
7.3 Glycerol dehydration

Acrolein is a valuable intermediate in the production of acrylic acid, glutaraldehyde and methionine. In particular, acrylic acid can be converted to water absorbing polymers, which can be used *e.g.* in diapers, as retention agents in paper production¹⁵⁸ or to remove water from hydraulic oil or fuel systems. It can also be used as an herbicide without further modification. The usual path to obtain acrolein is based on propene which is oxidised at heterogeneous catalysts containing metals such as bismuth and molybdenum at high temperatures (>300 °C) with yields $Y > 90\%$ (Scheme 22).^{159–162} Some efforts have been made to switch the feedstock from propene to the cheaper propane by using catalysts based on Mo, V and Te.¹⁶³

Additional to this petrochemical route, acrolein can also be obtained from glycerol by dehydration in the liquid or in the gas phase on heterogeneous catalysts. Typical catalysts are for instance zeolites, Nafion composites, aluminas, phosphor- or silicotungstic acids or acid salts which should all have an Hammet acidity of less than + 2 leading to a yield of greater 70% at $T = 250\text{--}350$ °C.^{164–166} A further approach is the direct reaction to acrylic acid, starting from glycerol to avoid separation problems (Scheme 22).¹⁶⁷

Heterogeneous catalysis is not the only appropriate route for the dehydration of glycerol, but also homogeneous systems or even systems without catalyst can lead to acrolein. One approach is the reaction in near supercritical or supercritical water ($T > 300$ °C, $p > 300$ bar), using either no catalyst or different additives (Table 7).

Besides using chemical pathways, acrolein can also be produced by biocatalysis. Glycerol can be fermented to 3-hydroxypropanal *e.g.* by *Lactobacillus reuteri* and subsequent thermal dehydration leads to acrolein.¹⁰⁸ The catalysts



Scheme 22 Production of acrolein and acrylic acid based on propene or glycerol.

Table 7 Yields of acrolein in supercritical water

Catalyst/additive	Yield (%)	Literature
None	12	168
Sulfuric acid (1–5 mmol l ⁻¹)	74	169,170
Zinc sulfate (0–790 ppm)	>40	171,172

and reaction systems used are the same as in the production of 1,3-propanediol with 3-hydroxypropanal as an intermediate step (section 5.2).

8. From glycerol to synthesis gas

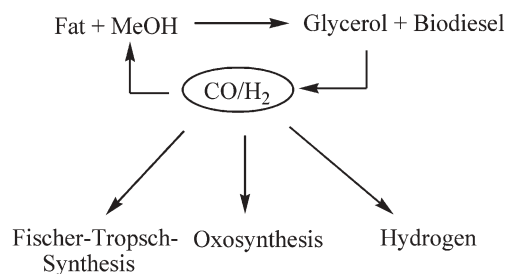
A further potential application of glycerol is its conversion to synthesis gas by enabling the production of a large variety of important chemicals: For instance methanol, a component of biodiesel, can be obtained from synthesis gas and thus a real biodiesel on the exclusive basis of renewable feedstocks can be produced (Scheme 23). In current biodiesel plants the methanol used for the transesterification step is still synthesised on the basis of petroleum.

The synthesis gas can also be utilised in Fischer–Tropsch reactions with the great advantage that the CO/H₂-mixture does not contain any oxygen impurities, making the reaction much easier to handle.

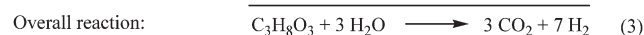
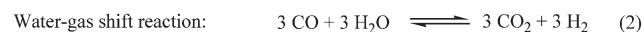
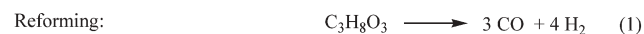
There are several processes to prepare synthesis gas from glycerol. These alternatives, the steam reforming, the aqueous phase reforming and the gasification in supercritical water, are discussed in the following sections.

8.1 Steam reforming

The steam reforming of glycerol yielding a synthesis gas of carbon monoxide and hydrogen is performed in the gas phase usually at atmospheric pressure and temperatures higher than 400 °C. The conversion of glycerol takes place according to eqn (1) in Scheme 24, resulting in a molar H₂/CO ratio of about 1.33. This ratio can be increased by the water–gas shift (WGS) reaction, shown in eqn (2), which converts carbon



Scheme 23 Production of synthesis gas from triglycerides via glycerol.



Scheme 24 Main reactions in the steam reforming of glycerol.

Table 8 Steam reforming of glycerol: Typical reaction conditions and results

Temperature/°C	Catalyst	S/C ^a	C/O ^b	Y H ₂ (%) ^c	S _{CO} (%) ^d	Lit.
1055	RhCeWc ^e	0	1.2	56	79	174
825	RhCeWc ^e	2	1.2	75	58	174
862	RhCeWc ^e	4.5	1.2	79	27	174
400	Pt/C	2.3	1	—	80	175
500–600	Ru/Y ₂ O ₃	3.3	1	82	20	173

^a Steam to carbon ratio. ^b Carbon to oxygen ratio in feed. ^c Yield H₂ according to eqn (3). ^d Selectivity from carbon to CO. ^e Rhodium–ceria washcoat. All experiments were carried out at atmospheric pressure.

monoxide into carbon dioxide. Overall, glycerol can be converted to carbon dioxide and hydrogen (eqn (3)).¹⁷³

Typical catalysts are platinum, ruthenium or rhenium applied on a carrier like carbon, yttrium oxide or ceria washcoat. Some characteristic results are listed in Table 8. Platinum is a very effective steam reforming metal because it is already active at very mild conditions (400 °C) and yields great amounts of carbon monoxide.

8.2 Aqueous phase reforming (APR)

A variation of the steam reforming described above is the aqueous phase reforming (APR). This reaction follows the same equations as shown in Scheme 24, however, in this process the glycerol is kept in the liquid phase. Much higher pressures (25–35 bar) are needed, whereas the reaction

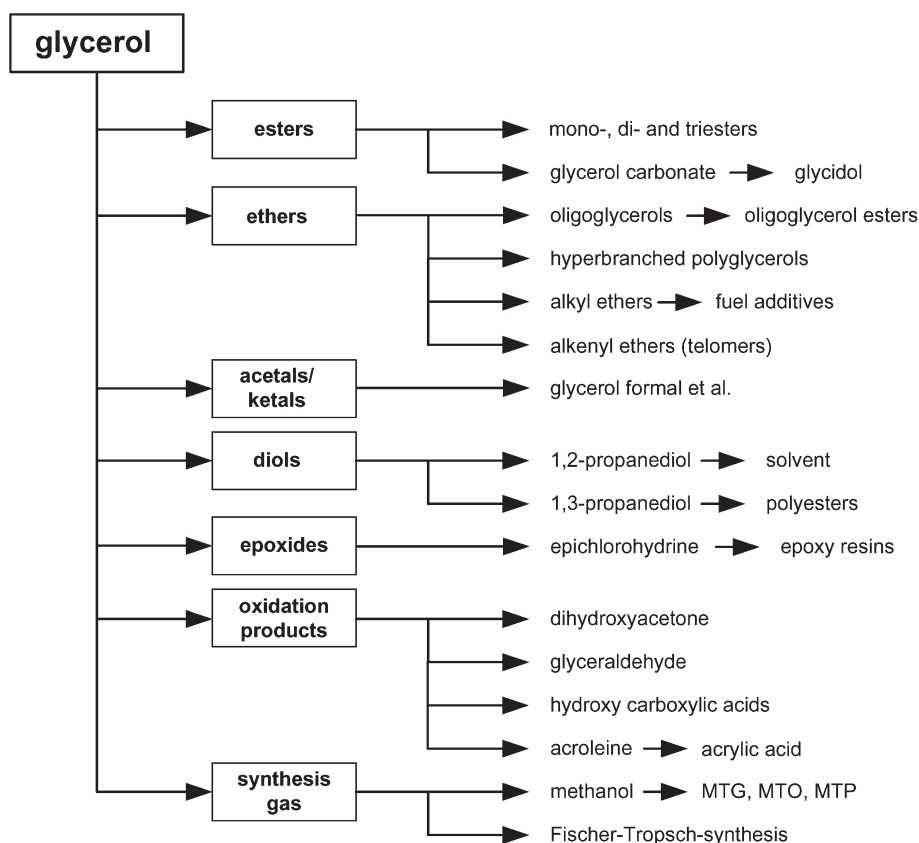
temperature can be slightly lower ($T = 125$ °C). Under these conditions the water–gas shift reaction is thermodynamically much more favourable.

The aqueous phase reforming metals such as platinum, palladium or Ni–Sn alloys show high selectivity for hydrogen production, whereas supported nickel catalysts tend to deactivation with time, which may be due to sintering of the metal particles. Also the support plays an important role in the selectivity of the APR process: Basic or neutral supports, e.g. alumina, favour the formation of hydrogen and carbon dioxide. Since the separation of H₂ and CO₂ is relatively easy, aqueous phase reforming can be used to produce pure hydrogen.¹⁷⁶

8.3 Supercritical water gasification (SCWG)

The gasification in supercritical water is a new technology to convert wet biomass to hydrogen or synthesis gas. Also glycerol can be used as feedstock in supercritical water gasification (SCWG). This reaction can already be carried out without any catalyst, whether very diluted feed solutions (<2 wt.%) are applied. However, better results are obtained if transition metal catalysts are used. A ruthenium catalyst with 3% Ru on a titanium dioxide support yields a quantitative gasification also at higher concentrated (5–17 wt.%) feed solutions.

The conversion of glycerol increases with temperatures from 20% (at 450 °C) up to 90% (at 700 °C); a further increase does not lead to higher conversions. The composition of the gas



Scheme 25 Compilation of the main glycerol derivatisation routes.

slightly changes with the temperature: at higher temperatures a larger amount of hydrogen can be obtained. Experimental results from capillary reactors showed that the pressure has no influence on the carbon efficiency and the product gas yield.¹⁷⁷

9. Conclusions

In the present review on glycerol derivatisation a great number of recently published articles and patents have been cited, thus proving the immense activity in this field. All main subjects are compiled once again in Scheme 25:

- An important aim is the selective synthesis of glycerol monoesters with both homogeneous and heterogeneous catalysts. The direct catalytic reaction of glycerol and carbon dioxide to glycerol carbonate still remains a great scientific challenge.

- The formation of glycerol ethers has been carried out via different routes using alkyl halides, alkenes and dienes as reaction partners. The application of the ethers as fuel additives would consume a great amount of the glycerol surplus formed in the biodiesel production.

- Glycerol acetals and ketals can also be considered as potential fuel additives. A great advantage of these derivatives is the broad range of polarity which can be tuned in a few reaction steps.

- The production of the two propanediols on the basis of glycerol has already been started. In particular, 1,3-propanediol seems to have become a new platform chemical in polyester chemistry.

- The two-step reaction of glycerol to epichlorohydrine, which was developed and implemented by Solvay, is a typical example for the partial change from petrochemical to renewable starting materials.

- The oxidation and dehydration chemistry of glycerol is still in its infancy and further investigations are needed to find better catalysts and reaction performance. However, the possible target molecules of glycerol oxidation may become interesting building blocks in fine and polymer chemistry.

- Finally, the conversion from glycerol to synthesis gas or pure hydrogen, respectively, has to be mentioned which may become an alternative to the traditional synthesis routes based on raw fossil materials.

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