

## Review Article

# Recent advances in the conversion of bioglycerol into value-added products

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A versatile platform chemical and energy vector, bioglycerol from biodiesel manufacturing is increasingly finding new commercial applications. We report on some of the main achievements for converting glycerol into high-value products and energy developed in the last two years, and conclude by providing an outlook on the evolving status of bioglycerol in the chemical industry.

**Keywords:** Biodiesel / Biomass / Biorefinery / Glycerol / Renewable

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## 1 Introduction

Massive production of epichlorohydrin at Solvay in Europe (10,000 t/year; and starting soon in Asia at 100,000 t/year); several thousand tons of bioglycerol used as concrete additive in 2008 at W. R. Grace; the first thousand tons of propylene glycol (PG) from crude glycerol delivered to customers in the USA by Senergy Chemical (and soon at Dow, Huntsman and other companies): These are the first three large-scale chemical processes using glycerol (or glycerin(e) when referring to commercial products of whatever degree of purity) as raw material obtained in large surplus as 10% in weight by-product from biodiesel manufacturing *via* the transesterification of triglycerides (vegetable and animal oils). Bioglycerol is also obtained from saponification reactions in the oleochemical industry. Yet, reliance on soap-making to supply co-product glycerine made it difficult to increase production to meet wartime demand. Hence, synthetic glycerin processes were national defense priorities in the days leading up to World War II and several epichlorohydrin-to-glycerol plants were built in Europe and in the USA. All that suddenly changed (and many of these plants were closed) as global production of bioglycerol from biodiesel climbed from 200,000 t in 1995 to an estimated 1,200,000 t in 2008, growing at an annual

growth rate of >50% [1]. For comparison, 2007 levels of glycerol production were about 350,000 t in the USA, and 600,000 t in Europe where a (binding) directive from the European Union requires replacement of 5.75% of petroleum fuels with biofuel across all Member States by 2010.

The bioglycerol stream typically contains a mixture of glycerol with methanol, water, inorganic salts (catalyst residues), free fatty acids, unreacted mono-, di-, and triglycerides, methyl esters, and a variety of other “matter organic non-glycerol” (MONG) in varying amounts. A look at a recent insight from an oleochemical industry’s insider available on the World Wide Web, even if it may appear not scientifically sound, helps to throw light onto the problem [2]:

“The problem with glycerine from biodiesel production is that it has heavy contamination from methanol. This makes it unsuitable to process for the glycerine consumer market. A few years ago the world glycerine market suffered a massive price slump as all of the biodiesel glycerine was coming on to the market. As it was starting to be used, it was discovered that it was unsuitable for most glycerine markets. As a consequence of this, traditional glycerine is now undergoing a massive price correction due to global shortages. It is obviously a major focus of biodiesel manufacturers to produce a pharmaceutical-grade glycerine. Unfortunately, high-temperature low-pressure distillation is the only way this can currently be done and any raw material that has been in contact with methanol is unsuitable for that type of process. Each new generation of biodiesel plant is claiming that they have developed the technology for pharmaceutical glycerine production

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to encourage enthusiastic investors. To this day though, it isn't working. For that reason, I believe that a large portion of biodiesel glycerine goes into animal feedstock."

A recent study in the USA in fact concluded that adding crude glycerol as 10% of feedlot cattle rations improves the animal's feed-to-weight-gain, as ruminants handle toxic methanol and its breakdown product, formaldehyde, better than humans [3]. Indeed, most biodiesel manufacturing processes utilize a 6 : 1 molar ratio of methanol to oil in order to drive the reaction to completion. Most of the excess alcohol (up to 60%) ends up in the bioglycerol layer. If refined to a chemically pure substance, glycerol would be a very valuable by-product. Yet, purifying it is costly and generally unfeasible for small to medium plants which recover most of the expensive MeOH from the glycerol layer, and are left with salt-grade bioglycerol.

In accordance with the industry's insider opinion reported above, the spot market price for refined glycerol has first fallen from about €1500 in 2001 to €330 per tonne in 2006 [4], but in 2007 prices recovered to eventually reach €950 per tonne in the first quarter of 2008 due to physical lack of the material, when the price of crude glycerine was €400/t [5].

Yet, despite the rapid fall of the oil price in the last quarter of 2008, the biodiesel industry will only grow in forthcoming years (see Conclusions) and so will the number of chemical processes and the new products that will use crude glycerol as raw material. The interests go well beyond the biological oils industry, with most large traditional chemical companies having launched (or announced) new products using raw glycerol as raw material.

Developing new industrial uses for glycerol in its turn will greatly increase the net energy and sustainability of biodiesel. Indeed, a recent model based on the production and sale of 80% glycerol by mass, and assigning it a value of \$0.33/kg, predicted an inverse linear relationship between the production cost of biodiesel and variations in the market price of glycerol, with an increase of \$0.0022 per liter for each \$0.022 reduction in glycerol price per kilogram [6]. Accordingly, the number of research papers dealing with glycerol's new usages published between 2000 and 2007 has doubled to >7000, and the first book on the topic appeared in mid 2008 [7].

In this context of rapid change, we have recently reported how glycerol is becoming a key raw material in the chemical industry, as chemical ingenuity is rapidly opening the route to

the creation of glycerol derivatives that are finding use in fields as diverse as fuels, chemicals, automotive, pharmaceutical, detergent and building industries [8]. Other thorough recent reviews focus on the employment of solid catalysts in heterogeneously catalyzed processes [1], on new derivatives of glycerol [9], on the chemoselective catalytic conversions of glycerol to commodity chemicals [10], and include a trade report on the first commercial applications [11]. Now, we review the most relevant advances of the last two years and report on the first industrial developments that have occurred. We conclude the article by offering insight into the economics of bioglycerol.

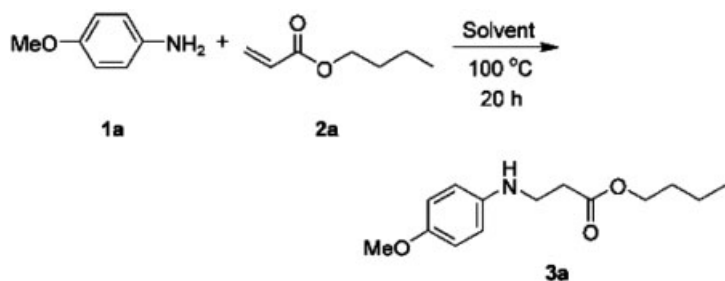
## 2 Crude glycerol as solvent

Recently, the use of crude glycerol as solvent able to considerably accelerate the reaction rate of an organic reaction has been reported [12]. In particular, glycerol and crude glycerol were found to be highly efficient for conducting many organic transformations such as aza-Michael reactions of amines or anilines, Michael reaction of indoles and ring opening of styrene oxide with *p*-anisidine without addition of any catalyst as is generally the case.

For example, the aza-Michael addition of *p*-anisidine (**1a**) to butyl acrylate (**2a**) affords 82% yield of the addition product **3a** when the reaction is performed at 100 °C in the presence of crude glycerol (Fig. 1), whereas the reaction on water proceeds at a very low reaction rate with only trace amounts of product (<5%) detected after 20 h of reaction.

In practice, glycerol and crude glycerol can be considered as "organic water" because, as solvent, they behave similarly to water in organic synthesis, promoting organic reactions without addition of any catalyst. Like water, glycerol is cheap, safe, biodegradable and reusable. Indeed, recovered glycerol was maintained under vacuum (14 mm Hg at 60 °C for 30 min) to remove all residual traces of ethyl acetate; after three cycles, yields were still comparable to that of fresh glycerol.

Yet, whereas with more hydrophobic substrates the beneficial effect of water on the reaction rate becomes limited, glycerol is able to efficiently drive the selected organic transformation. For example, association of a solid catalyst with glycerol as solvent allows the selective control of the reaction pathways



**Figure 1.** The aza-Michael reaction in glycerol under catalyst-free conditions proceeds with high yield (reproduced from [12], with permission).

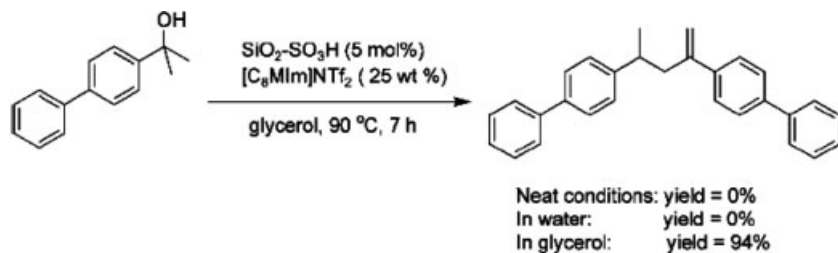
of more complex reactions, such as the tandem dehydrative/dimerization of a tertiary alcohol (Fig. 2).

### 3 Direct telomerization and etherification over CaO

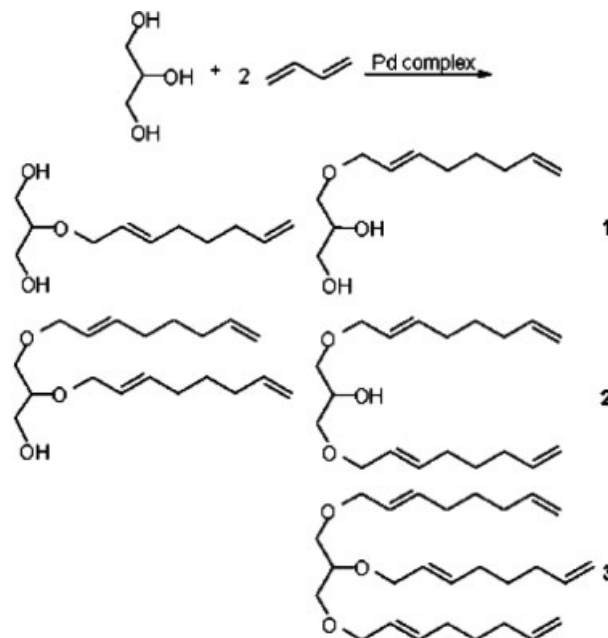
Most recently, the direct telomerization of either pure or crude glycerol with 1,3-butadiene (Fig. 3) mediated by a palladium-based molecular catalyst was described [13]. The process employs methoxy-substituted triphenylphosphine ligands and is a promising technology allowing direct access to C8-chain mono-, di-, and triethers of glycerol as useful chemical building blocks.

The resulting C8-chain ethers in fact can potentially be applied in the production of surfactant or detergent molecules. The product distribution is dependent on the butadiene/glycerol ratio and on the reaction time (rather than on pure or crude glycerol as substrate). A reaction mechanism (Fig. 4) has been proposed by studying the effects of different metal precursors and the ligand/metal ratio [14]. Formation of di- and triethers of glycerol would require the mono- and diethers to re-enter into the catalytic cycle, which is sterically very demanding, and thus not favored.

Similarly, glycerol is an attractive renewable building block for the synthesis of di- and triglycerols, which have numerous applications in the cosmetic and pharmaceutical industries. In a recent work, the selective etherification of glycerol to di- and triglycerol in the presence of alkaline earth metal oxides was compared with results obtained using  $\text{Na}_2\text{CO}_3$  as homogeneous catalyst [15]. The best selectivity values for (di- + tri-) glycerol (>90% at 60% conversion) are obtained over CaO, SrO, and BaO. Glycerol conversion increases with increasing catalyst basicity in the order:  $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$ . In each case, no substantial acrolein formation is observed. Furthermore, at the start of the reaction mainly linear diglycerol was produced, whereas at higher conversion degrees branched diglycerol started to form. In another series of experiments, different types of CaO materials were prepared to understand the relationship between the structure of Ca-based colloids and their activity. The CaO material possessing the strongest Lewis acid sites have the highest catalytic activity, comparable to that of BaO, pointing towards the important role of Lewis acidity for this etherification reaction.



**Figure 2.** Acid-catalyzed dehydrative dimerization of a hydrophobic alcohol on glycerol proceeds with 94% yield, but no reaction occurs on water (reproduced from [12], with permission).



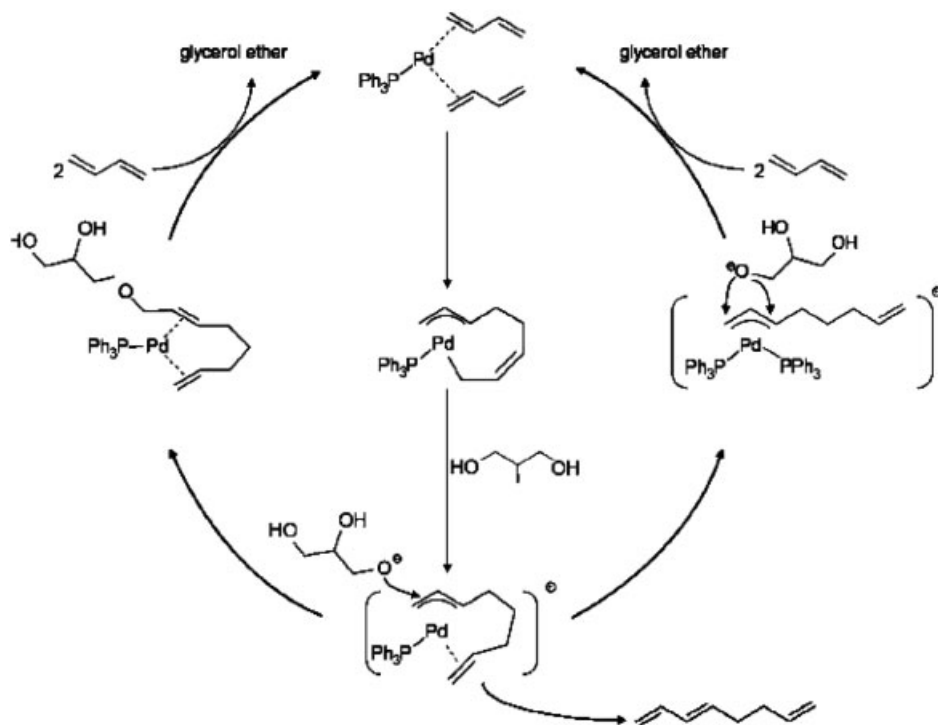
**Figure 3.** Telomerization of glycerol with butadiene to form glycerol ethers 1–3 (reproduced from [13], with permission).

Based on these observations, an alternative reaction scheme for glycerol etherification was suggested (Fig. 5), which is based on an enhanced hydroxyl leaving process. At temperatures as high as 220 °C, in the absence of a solvent, the materials defragment and form colloidal particles during the course of the reaction. Colloidal CaO particles of about 50–100 nm (Fig. 6) are then spontaneously generated during the reaction and their amount gradually increases with increasing reaction time. Catalytic testing of these CaO colloids revealed a very high etherification activity.

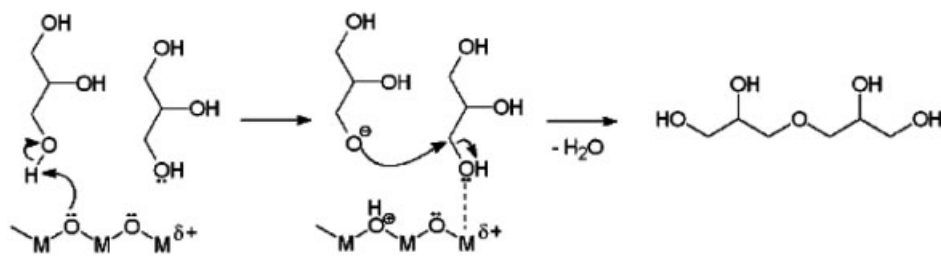
Aiming therefore at practical applications, researchers are looking for suitable ways of immobilization, since such supported colloidal systems would take advantage of both their hetero- and homogeneous nature.

### 4 New fuel bioadditives

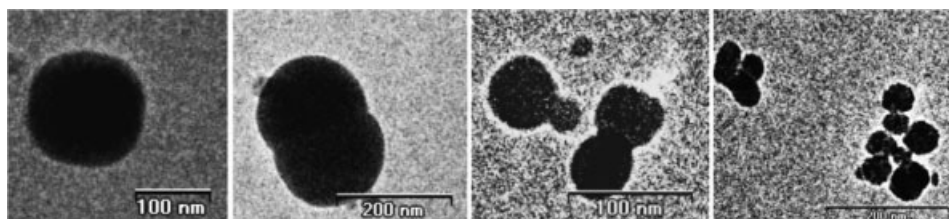
Studies on the use of glycerol di- and tri-tertiary butyl ethers as fuel additives with octane improving properties for diesel



**Figure 4.** Proposed reaction mechanism for the telomerization of 1,3-butadiene with glycerol (reproduced from [14], with permission).



**Figure 5.** Potential reaction mechanism for the base-catalyzed glycerol etherification involving Lewis acidity (reproduced from [15], with permission).

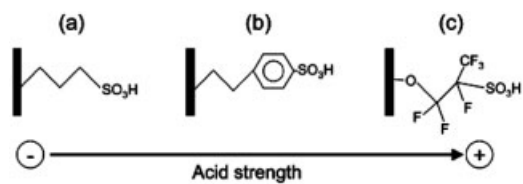


**Figure 6.** Cryo-TEM micrographs of colloidal particles formed during the glycerol etherification over CaO-C (left pair of images), and CaO-B (right pair of images) (reproduced from [15], with permission).

and biodiesel reformulation have progressed considerably. Di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) are valuable fuel additives as they also lead to decreased emissions of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes, reducing also biodiesel viscosity and thereby acting as potential cold-flow improvers. Hence, new etherification of isobutylene and glycerol with sulfonic modified mesostructured silica catalysts (Fig. 7) has been reported [16].

Under the optimized reaction conditions of Table 1, no formation of undesirable isobutylene oligomers is observed and mesostructured catalysts yield a complete glycerol conversion with a combined selectivity towards DTBG and TTBG up to ca. 90% (Fig. 8).

The acid strength of the sulfonic acid sites is the crucial factor affecting the catalytic performance of these materials. The di- and tri-ethers of glycerol are the most-desired products, and the product distribution in Table 1 shows that the



**Figure 7.** Sulfonic acid moieties in the functionalized mesostructured samples: propyl- (a), arene- (b), and perfluoro- (c) (reproduced from [16], with permission).

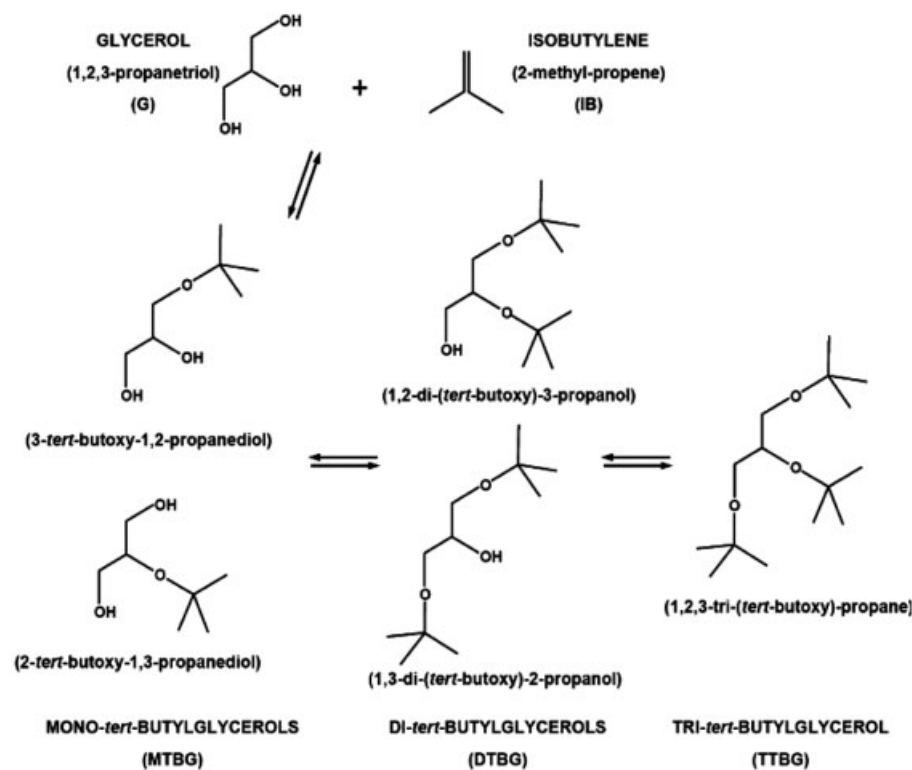
catalyst Ar-SBA-15 gives the highest productions of DTBG and TTBG. In terms of selectivity towards di- and tri-ethers, a value of 92% is obtained over Ar-SBA-15 after 4 h (77% after 1 h).

Over the Ar-SBA-15 catalyst, the amount of (non-desired) MTBG decreases up to 5 wt-% after 4 h of reaction. In contrast to macroporous commercial sulfonic acid resins used, for example, by the Dutch consortium Procédé for the *tert*-butylation of glycerol [17], no presence of oligomerization products is detected over both Ar-SBA-15 or Pr-SBA-15 catalysts, even after 4 h of reaction. Hence, the use of a silica matrix reduces the process of isobutylene oligomerization, adding an important benefit to the diesel additive final products because isobutylene oligomers must be removed from the fuel additive before use (therefore increasing costs) as they lead to the formation of clogging deposits in the motor during combustion.

Extending this approach, the same sulfonic acid-functionalized mesostructured silicas show excellent catalytic behavior in the acetylation of glycerol with acetic acid, yielding acetylated compounds (Fig. 9) with interesting properties as bioadditives for petrol fuels [18].

As in the case of butylation, in general stronger acid centers, such as those in arenesulfonic acid- and fluorosulfonic acid-modified mesostructured materials, improve performance both in glycerol conversion and selectivity. The use of high acetic acid excess to push the equilibrium toward the right simultaneously enhances (i) glycerol conversion and (ii) selectivity toward the most valuable di- and triacetylated derivatives. Optimal conditions have been found to be a temperature of 125 °C and an acetic acid-to-glycerol molar ratio of 9 : 1, when glycerol conversions over 90% and combined selectivities toward di- and triacetylglycerol of over 85% were achieved after 4 h of reaction over sulfonic acid-modified SBA-15. Such activity and selectivity values are comparable or even superior to those obtained using conventional (homogeneous and heterogeneous) acid catalysts.

Despite the high acid capacity (20.4 mmol H<sup>+</sup>/g) of H<sub>2</sub>SO<sub>4</sub> and its liquid nature allowing to avoid the mass transfer limitations, its catalytic behavior is not superior to that of Ar-SBA-15 and F-SBA-15. On the other hand, the better catalytic performance after 2 h of reaction over Ar-SBA-15 and F-SBA-15 as compared with liquid H<sub>2</sub>SO<sub>4</sub> suggests interesting *confinement* effects when a sulfonic acid group is supported



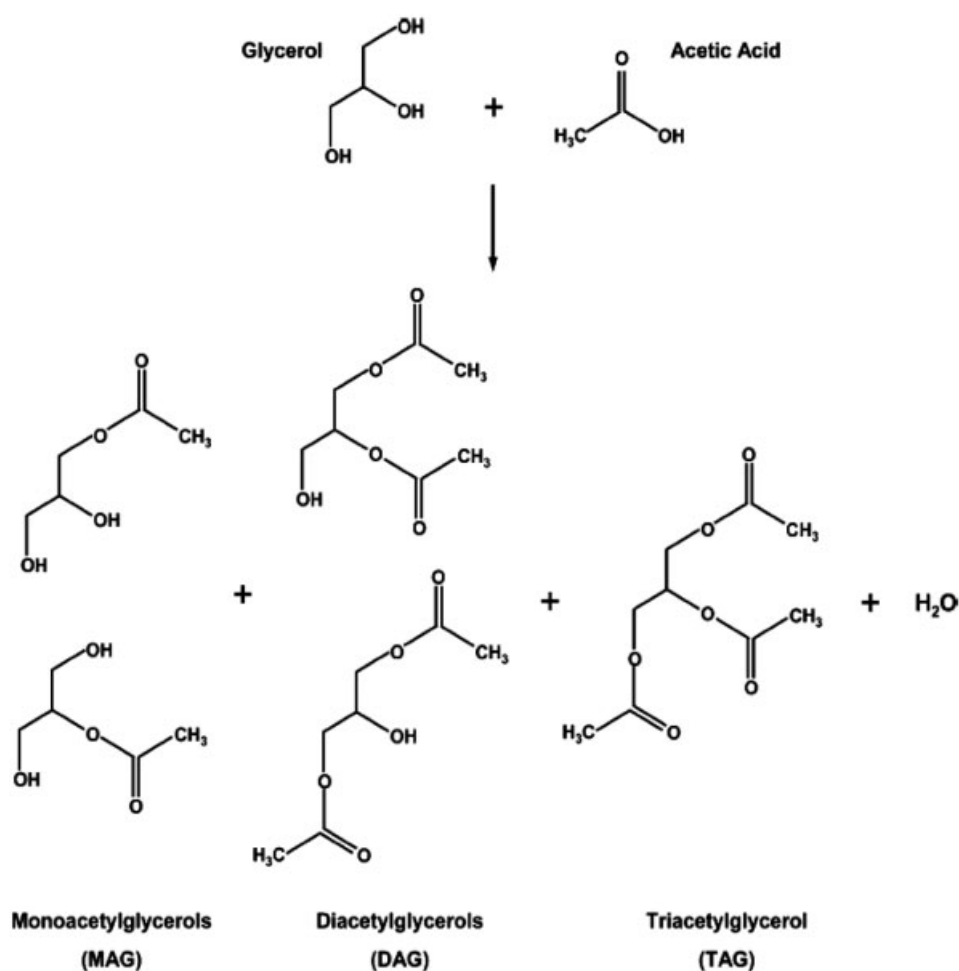
**Figure 8.** Main reaction products in the glycerol etherification with isobutylene (reproduced from [16], with permission).



**Table 1.** Comparison of sulfonic acid-functionalized mesostructured silicas for the etherification of glycerol with isobutylene (reproduced from [15], with permission).

Catalyst	Reaction time [h]	$\chi_G$ [%]	Distribution of products [wt-%]			$S_{DTBG+TTBG}$ [%]
			MTBG	DTBG	TTBG	
Pr-SBA-15	1	65	68	30	2	24
Ar-SBA-15	1	84	16	72	12	77
Pr-SBA-15	4	90	9	56	35	86
Ar-SBA-15	4	100	5	54	41	92

Reaction conditions: 5 wt-% of catalyst referred to glycerol, IB/G molar ratio = 4 : 1, temperature = 75 °C.  $\chi_G$ : glycerol conversion.  $S_{DTBG+TTBG}$ : selectivity to di- and triethers calculated as mols of glycerol reacted to form DTBG and TTBG referred to total mols of reacted glycerol.

**Figure 9.** Reaction of esterification of glycerol with acetic acid (reproduced from [18], with permission).

over a mesostructured material. The solid mesostructure does not hinder the molecular diffusion during the reaction process, leading in all the cases to approximately the same equilibrium distribution (selectivity to DAG and TAG after 4 h remains almost identical for the three catalytic systems). Yet,

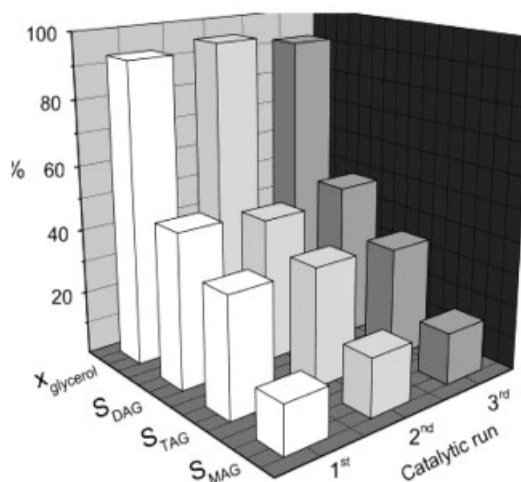
the use of heterogeneous catalysts prevents all environmental, technical and economic problems associated with catalyst recovery and reuse. The catalytic performance of these mesostructured materials in a typical conversion of glycerol with acetic acid at 125 °C (molar ratio acid/glycerol = 9 : 1)

was completely retained after a mild solvent-washing regeneration step (Fig. 10).

Currently, both esterification and etherification reactions of crude glycerol from FAME production over these solid acid catalysts are under investigation at a Repsol plant in Spain, where especially the *long*-term stability of such solid catalysts is being tested because of the high hygroscopicity of glycerol. SBA-15 and related materials in fact exhibit higher thermal stability than conventional silica-based catalysts, but they are still unstable in the presence of water or alcohols.

## 5 Glycerol as fuel or fuel precursor

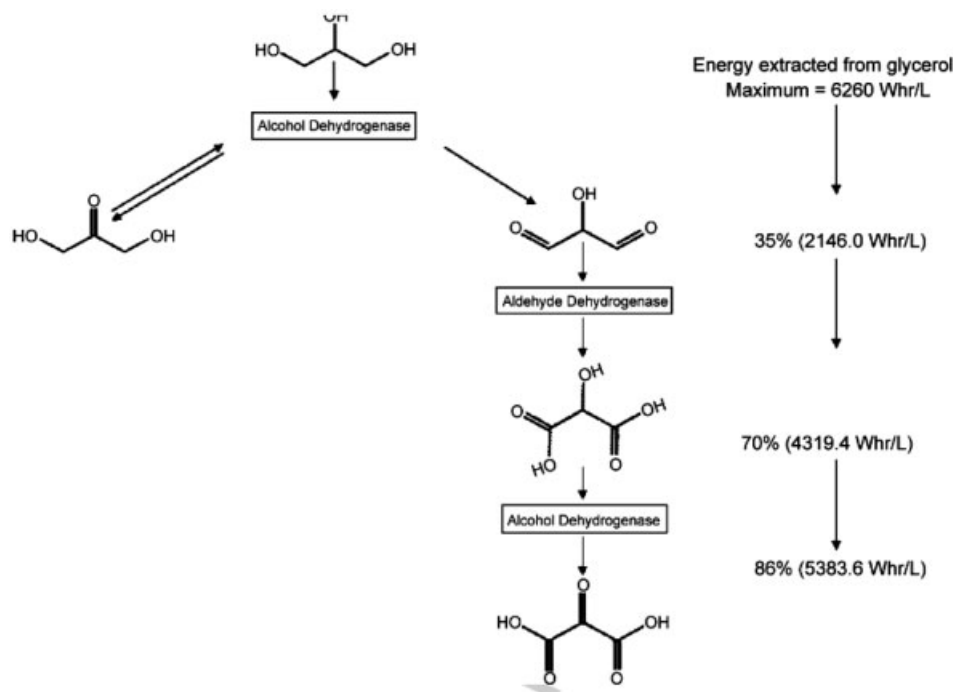
With a view to providing an outlet for the glycerol by-product of biodiesel, the most promising biological oxidation process is the recent employment of glycerol in fuel cells using membrane-immobilized enzymes [19]. Two oxido-reductase enzymes (PQQ-dependent alcohol and aldehyde dehydrogenase) are immobilized at the surface of a carbon electrode in the pores of a Nafion ion exchange copolymer membrane modified with quaternary ammonium groups, in order to expand its pores and make the environment more hydrophobic and enzyme friendly; this ensures stability of the enzymes for months or even years. These glycerol bioanodes have been incorporated into a glycerol–oxygen biofuel cell that enables multi-step oxidation of glycerol to mesoxalic acid; the overall process (Fig. 11) utilizes 86% of the energy density of the glycerol and results in power densities of up to 1.21 mW/cm<sup>2</sup> at room temperature. This is very different from metallic



**Figure 10.** Catalyst reuse: glycerol conversion and selectivity to MAG, DAG, and TAG, after 4 h, in three consecutive catalytic runs reusing catalyst Ar-SBA-15 (reproduced from [18], with permission).

electrodes, which give glycerate as the only detectable oxidation product of glycerol, and it shows that the biofuel cell can allow deeper oxidation of the glycerol fuel, increasing overall efficiency and energy density.

This technology has been licensed to the company Akermis Inc., and is progressing towards commercialization. According to the inventor, it will take about 2–4 years before glycerol clips could be used to power mobile phones [20].



**Figure 11.** Oxidation sequence for glycerol at a PQQ-ADH/PQQ-AldDH-modified bioanode (reproduced from [19], with permission).

The key to commercial development will lie in improving the lifetime and performance of enzymes over a range of temperatures. The company's technology (stabilized-enzyme biofuel cell, SEBC) immobilizes and stabilizes enzymes in a conductive polymer matrix and allows them to convert renewable organic fuels into electricity, a process that is inherently more efficient than conventional methods of portable power generation. The stability afforded by Akermin's enzyme immobilization polymers, measured in years compared to days for other biofuel cell technology, enables the first truly commercial viability for this type of power supply. Using high-energy content fuels such as glycerol (Fig. 12), such cells are more environmentally friendly and last longer than any existing fuel cell, delivering lower cost per Watt hour over their lifetime.

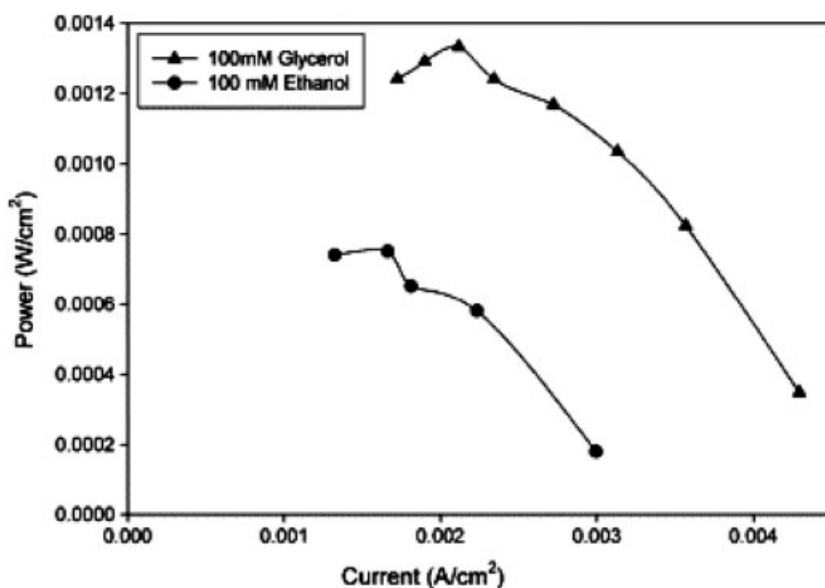
The new biofuel cell technology using a biocathode overcomes many of the traditional limitations of conventional fuel cells. Fuel cells convert the energy stored in the fuel directly into usable electrical power. One of their main drawbacks is that they are limited to simple fuels such as hydrogen or methanol, each of which gives serious safety concerns (hydrogen is explosive and methanol is flammable and highly toxic). On the other hand, glycerol is cheap, readily commercially available, safe, nontoxic, non-flammable, and contains three times more energy per gallon than liquid hydrogen.

Glycerol can also be used in a biofuel cell at 98.9% concentration without damaging the cell, whereas methanol is limited to 40% concentration. As a result, the same amount of glycerol produces almost four times as much power as methanol, and is the main alternative being currently considered for portable electronics such as cell phones and laptops. Akermin has developed several prototypes in low power ranges and has secured contracts with corporate and government entities to develop power supplies using the SEBC for commercial uses.

The aqueous phase reforming (APR) of glycerol, in which a 25% solution of glycerol is first converted to hydrogen and carbon monoxide (syngas) under relatively mild conditions using a platinum-based catalyst in a single reactor and then the mixture is turned into gasoline by the Fisher Tropsch process, has progressed further, improving yields, product composition, and reducing cost [21]. The overall process of Virent Energy Systems directly converts glycerol into gasoline, eliminating the need for specialized infrastructure and new engine designs. In early 2008, Virent thus partnered with Shell to scale up the technology for larger-volume commercial production and to accelerate commercialization of the technology [22]. The company expects to commercialize the new green gasoline, including green versions of diesel and jet fuel, at a cost lesser than ethanol, within 5 years [23].

Finally, in 2007, Gonzalez and co-workers reported that a strain of *Escherichia coli* bacterium is able to ferment glycerol anaerobically into ethanol with an estimated operational cost 39% lower than first-generation ethanol production from corn (per gallon, operating costs were estimated at 52 cents for corn and 36 cents for glycerol) [24]. Very few microorganisms are capable of digesting glycerol in an oxygen-free environment. Scientists discovered that *E. coli* is in fact able to metabolize glycerol in a purely fermentative manner, by identifying the metabolic processes and conditions that allow a known strain of *E. coli* to convert glycerol into ethanol. The co-products are formic acid and hydrogen.

The main reason for the difference in costs is that there is no preprocessing. Whereas the corn must be ground and cooked, and the sugar extracted in a process that is both capital and process intensive, glycerin does not require these steps because it comes preprocessed, avoiding the need for expensive enzymes to buy and requiring much less equipment. The



**Figure 12.** Comparison of the power curves for a single biofuel cell with two different analyte fuels (100 mM ethanol and 100 mM glycerol) at room temperature (reproduced from [19], with permission).



inventors co-founded Glycos Biotechnologies Inc. that was expected to complete a pilot plant capable of fermenting at least 10,000 L in early 2008.

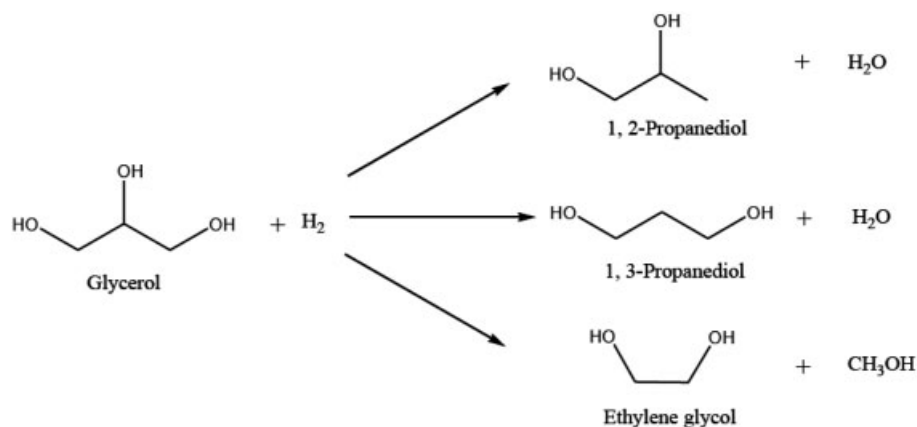
## 6 Hydrogenation: Propylene glycol

Having experienced a six times increase in the price of propylene oxide traditionally used in the manufacture of PG (= 1,2-propanediol) [25], it is perhaps not surprising that major chemical manufacturers have announced plans to produce PG from selective hydrogenation of glycerol. With a 2 million tons market annually, PG is the preferred glycol for manufacturing high-performance unsaturated polyester resins, polyurethane foam systems, and as a safer replacement for ethylene glycol-based products such as antifreeze, and aircraft deicers. Similar plans to get PG from bioglycerol were reported by leading biodiesel producers such as Cargill and Archer Daniels Midland.

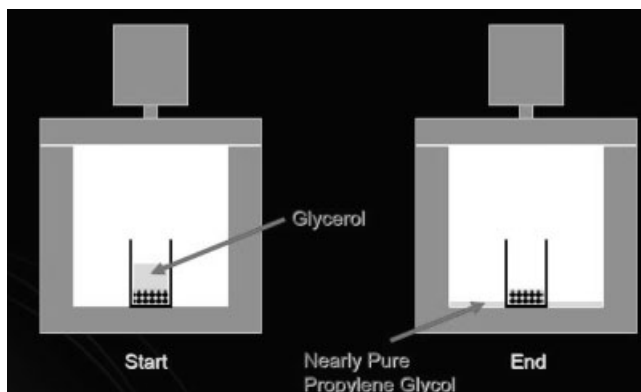
Fig. 13 shows that in older, non-selective hydrogenation processes, the by-products ethylene glycol and 1,3-propanediol were usually obtained lowering the process productivity and requiring costly product purification.

A suitable selective process, on the other hand, is based on hydrogenolysis (*i.e.* in the dehydration + hydrogenation) of crude glycerol to PG. The method is a reactive distillation (Fig. 14) carried out over a copper-chromite catalyst ( $\text{CuO} \cdot \text{Cr}_2\text{O}_3$ ) at 200 °C and less than 10 bar coupled with a reactive distillation, eventually affording PG of >73% yield at significantly lower cost than PG made from petroleum [26]. Overall, the process results in an antifreeze product (70% PG + 30% glycerol) that can be produced, easily refined and marketed directly by the existing biodiesel facilities [27].

The technology, which affords a near-USP-quality grade of PG, was licensed to the Senergy Chemical start-up business and developed into a projected \$200 million plus revenue in less than 2 years. In the southeast USA, Senergy Chemical built the first commercial facility to use this technology with a capacity of 25,000 t/year.



**Figure 13.** Summary of the overall reaction of converting glycerol to propylene and ethylene glycols.



**Figure 14.** Early observation of the outcomes of glycerol hydrogenolysis over CuCr catalyst showed that the process is actually a reactive distillation (reproduced from Prof. G. J. Suppes, with permission).

Other recent reports show that PG can be obtained selectively under more moderate conditions using Raney nickel at relatively low pressure (10 bar). No solvents or additives were required, and the product could be distilled out of the reaction mixture [28]. Finally, Davy Process Technology has developed its own process in which the vapor phase hydrogenation of glycerol over a heterogeneous copper catalyst affords 99.5% PG and less than 0.2% water, as required by the customer polymer industry [29]. Conducting the process in the vapor phase (*versus* existing liquid-phase processes) accounts for the high selectivity and the high purity of the product. Previously, the vapor phase hydrogenation had been considered impossible because, due to the high boiling point of glycerol (290 °C), its volatilization would require high temperatures causing coking problems. However, using temperatures of 195–200 °C at a pressure of 20 bar made it possible to achieve vapor phase conditions if a high  $\text{H}_2$ /glycerin feed ratio of 500 : 1 was used with low residence times of <1 s. In 2007, Ashland and Cargill created a joint venture which has licensed Davy's technology for manufacturing and marketing of bio-based PG, starting with a 65,000 t/year plant based in Europe.

## 7 Dehydration: Acrolein and acrylonitrile

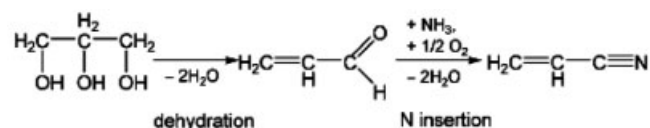
Acrolein is an important and versatile intermediate for the chemical industry that can be obtained by glycerol dehydration. A highly toxic, explosive chemical, acrolein is widely employed in the production of acrylic acid esters, polyester resins, polyurethanes, PG and acrylic acid. Older processes to convert glycerol into acrolein were not commercialized due to high cost and low catalyst stability. Most recently, however, Corma and co-workers have developed a dehydration process resulting in full glycerol conversion to acrolein which makes use of the solid acid catalyst ZSM-5 zeolite [30]. The catalyst and the reaction products are separated, and the catalyst is continuously regenerated. The method has a number of advantages because (i) it can process glycerol solution in whatever concentration; (ii) it does not need any co-solvent to carry out the reaction; and (iii) it continuously regenerates the catalyst so that catalyst activity can be maintained over large periods of time, even with contaminated feeds. Furthermore, the less valuable heavy by-products of the reaction can be burned inside the process, thus generating the heat that is necessary to carry out the process, as water vaporization requires large heat input.

Most recently, a highly selective process for reacting glycerol with ammonia to form acrylonitrile in gas phase at 400 °C has been reported [31]. The proposed reaction scheme involves a combination of the glycerol dehydration mechanism followed by a C–N bond formation (Fig. 15).

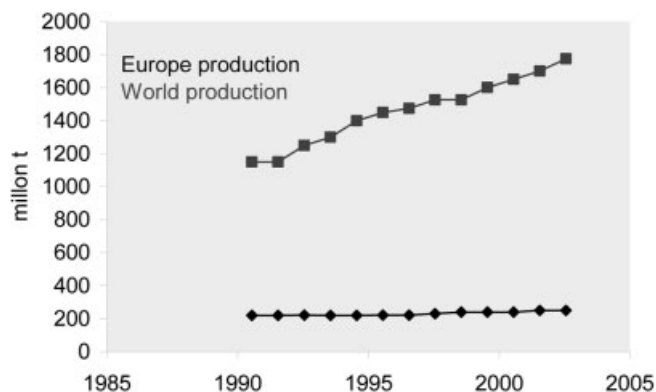
Among the supported oxides, vanadium-containing catalysts afford significantly higher conversions of glycerol. Doping the supported vanadium oxide with Sb and Nb modulates selectivity. The glycerol conversions are high, and the catalysts are more selective to acrolein and acrylonitrile, with acrylonitrile obtained as the main product. Thus, VSb/Al is slightly less active than alumina-supported vanadium oxide, but it produces acrylonitrile with 56% selectivity at 71.6% conversion. When the catalyst is further promoted with the acidic dopant Nb (VSbNb/Al), both the conversion of glycerol and selectivity to acrylonitrile increase. The process is very promising as it affords good selectivities at high conversions. A systematic study is currently underway to assess the molecular structure–activity relationships and reaction mechanism, and to optimize the catalyst formulation and reaction conditions.

## 8 Crude glycerol as additive for concrete

Crude glycerol from biodiesel production is an excellent additive for concrete, enhancing its resistance to compression and grinding and lowering its setting time [32]. Concrete additives composed of organic molecules and of a minor inorganic part (blends or formulations) are added to the 60% of the world cement production (Fig. 16), with the main commercial additives being obtained from ethylene oxide, and thus from petroleum.



**Figure 15.** The glycerol-to-acrylonitrile reaction (reproduced from [31], with permission).



**Figure 16.** World consumption of cement is constantly rising, whereas in Europe it is constant at about 200 million tons per annum (source: Grace Construction Products).

Comparative mechanical tests carried out on pure and crude glycerol using three “clinkers” (the cement precursor which is mixed with gypsum to yield the concrete) show, in all cases, that crude glycerol – a 95 wt-% glycerol mixture containing 5% NaCl with a pale brown color due to dissolved natural dyes – yields better mechanical and chemical properties compared to those afforded by the use of pure glycerol as well as compared to several other commercial additives. Production cost of cement is mainly due to the cost of electricity for grinding; hence, even modest improvements that improve grinding efficiency have a large impact on reducing the cost of production. Following preliminary tests carried out on industrial scale with crude glycerol originating from Europe’s biodiesel manufacturer confirmed the results on laboratory scale and in 2008 large-scale commercialization of cement added with biodiesel glycerol started at W. R. Grace & Co.

## 9 Outlook and conclusion

The technology to make biodiesel is simple and it is evolving to reach a high degree of efficiency with new heterogeneous processes that only afford pure glycerol as by-product [33] and use oil from high-yield seeds from non-edible crops such as the *Jatropha* trees that are being planted in Africa and Latin America by BP [34]. The raw materials are not localized in a few countries, but instead their production is increasingly determined by land availability. All this makes the production

of biofuel an inevitable reality, even beyond the provision of governmental subsidies. The overall consequence is that glycerol will become a central raw material for the chemical industry, along with interesting novelties that, we argue, will originate in Latin America, South-East Asia and also in Africa. Well-regarded experts in the industry estimate that biodiesel production could rise to 9 million tons by 2010 in Europe alone, translating into 900,000 t of glycerol. This gives a clear indication of the developing status of glycerol as a key raw material.

Indeed, the scope and pace of the innovation in the last two years is impressive. Progress is not limited to the reactions mentioned in this account. For example, new catalytic aerobic oxidations over gold catalysts afford either 32% dihydroxyacetone [35] or valued ketomalonic acid derivatives [36]. However, beyond such processes suitable for small-scale consumption of glycerol, new processes capable to absorb the large global glycerine surplus are of primary industrial interest. This is the case, for example, for a new and highly selective process to produce methanol directly from bioglycerol over an undisclosed, supported metal catalyst at temperatures of just 100 °C and a 20 bar pressure of hydrogen gas [37].

Experts realistically predict the end of cheap oil by 2040 at the latest, since increased consumption will irrevocably diminish fossil raw materials and build up environmental pressure [38]. It follows that a progressive move by the chemical industry towards renewable feedstocks will become a necessity; and the transition to a more bio-based production system in which biomass is catalytically converted to chemicals and transportation fuels is now underway [39]. In 3–5 years, glycerol will be seen as an environmentally friendly way of replacing other competing petroleum products. In conclusion, to paraphrase a biodiesel industry practitioner, glycerol stands up to become “the next biodiesel” [40].

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## Conflict of interest statement

*The authors have declared no conflict of interest.*

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