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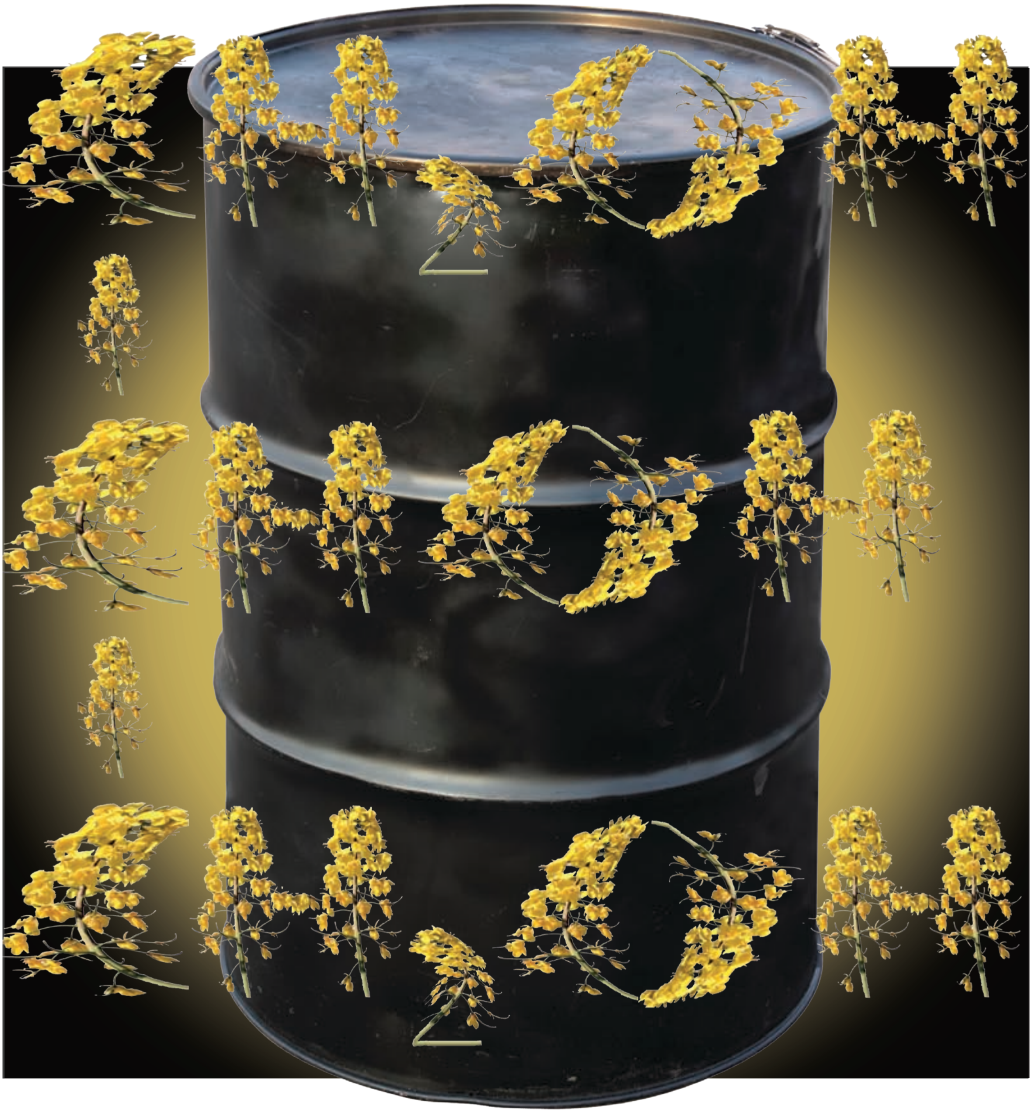
Mario Pagliaro and Michele Rossi

The Future of Glycerol



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The Future of Glycerol

2nd Edition

RSC Green Chemistry

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The Future of Glycerol

2nd Edition

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Preface to the 2nd Edition

Massive production of epichlorohydrin at Solvay in France (10 000 tonnes per year); several thousand tonnes of bioglycerol used as a concrete additive since 2008 by W R Grace; the first thousand tonnes of propylene glycol delivered to customers in the US by Senergy Chemical; a 20 000-tonne production plant for methanol in the Netherlands opened by BioMCN in 2008—these are examples of the first wave of plants employing crude glycerol for large-scale production. This raw material is now available in large quantities as a 10% by-product of biodiesel manufacture.

The preface to the first edition of this book contained this intriguing prophesy:

> *It is obvious that the greatest contributions are going to be brought about by today's students, whose creativity will produce spectacular advances.*

In the past two years the major advances arising from chemical ingenuity have been striking, and amply justify this second edition.

In common with other sections of the economy the 2008–09 global recession had a devastating effect on the global chemical industry. Indeed, many of the plans for new plants in Asia, Europe and the USA for the catalytic conversion of glycerol to important chemical building blocks remained unfulfilled. In the USA alone the production of biodiesel in 2009 was 50% lower than in 2008, along with a long list of bankruptcies (J. Jobe, *Biodiesel Magazine*, December 2009). But despite

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this, over the same period the annual global output of biodiesel reached 40 million tonnes, with a number of newer entrants playing their part such as Argentina, India, the Philippines, Brazil and the African continent.

It is now recognized that manufacture of biodiesel using a heterogeneous acid-catalyzed process offers in excess of 50% return on capital and has relatively low start-up costs. Newer plants are sustainable without government subsidy (B. Smith *et al.*, *Ener. Environ. Sci.* 2009, **2**, 262). With oil priced at more than $70 a barrel, despite the economic crisis, it comes as no surprise that the number of countries manufacturing biodiesel is now approaching 100.

The social and economic advantages of independent fuel manufacture are obvious, as is the ability to provide a solution which is adaptable to a variety of feedstocks. Countries producing their own biodiesel are less dependent on non-renewable fuels and at the same time they provide substantial benefits to rural communities.

The enormous potential of the biodiesel by-product glycerol as a versatile feedstock for a whole catalogue of chemicals, polymers and fuels is rapidly becoming appreciated. Many of the new chemical outlets for glycerol developed during the past five years are already in use. In some instances start-up enterprises have been quicker off the mark than traditional large chemical companies.

The second edition of this monograph has been thoroughly revised and updated. New sections have been added to cover such topics as the use of crude glycerol as an antioxidant, as reaction solvent, as lubricant, as a feedstock for methanol and as a fuel additive. We are confident that this new edition will be found valuable by professionals in the chemical and energy industries, including both managers and technologists, and no less by back-room chemists and renewable energy researchers.

Mario Pagliaro, Michele Rossi
Palermo and Milan

Preface to 1st Edition

Whoever is right—Tad Patzek in pointing out that massive biofuel production will cause ecological devastation, or Shell in claiming that its new fields of Jathropa trees will not impact food production—it is impossible to ignore the immense quantities of glycerol resulting from biodiesel manufacture. The volumes of glycerol remaining unsold up to mid-2005 certainly paint a tragic picture of wasted energy and material resources, to say nothing of human intelligence and effort, brought about by the lack of suitable conversion processes for what is the oldest organic molecule known to man. We have even witnessed biodiesel producers experimenting by adding glycerol to animal feed, or spraying it on dirt roads to keep the dust down—and even using it as landfill, as though glycerol were spent nuclear fuel!

Following three or four years of intense research activity, chemical ingenuity worldwide has opened up a number of practical avenues for converting glycerol into value-added products. Many of these are potentially large volume outlets, and may incidentally go some way towards improving the tarnished public image of chemistry. In reviewing and commenting on these achievements this book aims to remind chemical industry professionals, both managers and technologists, of the enormous potential of glycerol as a versatile feedstock for the production of a whole range of chemicals, polymers and fuels. In the ten chapters which follow, readers will find a thorough discussion of new uses for glycerol as a raw material, many of which are already having their impact worldwide.

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For example, during the devastation brought about by hurricane Katrina in 2005 the New Orleans petrochemical refineries were shut down, interrupting the supply of a variety of chemicals, including ethylene and propylene glycols. This led a global manufacturer of cement additives to replace these glycols with crude glycerol from biodiesel refineries (Chapter 3). Again, in 2007 Solvay started its retrofitted plant in Tauvaux, France, where instead of making glycerol from epichlorohydrin as had been done for decades, it began to produce this epoxy resin precursor using glycerol supplied by a French biodiesel producer (Chapter 4). Thirdly, by the time this book is published the world's first plant for the manufacture of propylene glycol from glycerol will be in full production in Atlanta, USA (Chapter 5).

This monograph tells a chemical success story, the conversion of glycerol into value-added products, and it identifies the factors which have brought this about. Whether as a solvent, antifreeze or detergent, or as a monomer for textiles or drugs, new catalytic conversions have been developed for glycerol in the synthesis of products with applications ranging from everyday household items to the manufacture of fine chemicals.

Readers will see the ways in which a number of practical limitations posed by the chemistry of glycerol, such as the low selectivity of traditional catalytic conversions, have been solved by a better understanding of its fundamental chemistry and the application of catalysis technology. In addition they will find in Chapter 10 a discussion of the sustainability issues associated with bioglycerol production. The authors are convinced that chemists and chemical engineers must be in a position to present the "triple bottom line" dimensions—societal, environmental and economic—to the community, the media and to the business world. Indeed, it is an undue emphasis on sustainability on its own which has often led to controversy such as that mentioned above. It has to be accepted that both politicians and ordinary citizens are interested in the arguments for biodiesel and glycerol production, and in turn they want to be reassured that refineries are necessary and environmentally sound. To paraphrase Ozin, emerging biomass-based companies and research centers need young, wise, educated scientists capable of crossing the boundaries between fields and who can explain simply the advantages and problems.

Chemical research on glycerol has shown that, given a strong economic incentive, chemists can rapidly devise a whole set of upgraded processes for biorefineries, and that the integration of these in producing energy and chemicals is not just a romantic dream promoted by green-minded scientists, but an inescapable reality.

Will the biorefinery of the future make use of other platform chemicals apart from glycerol? We have no doubt about it. In 2007, one of us had the good fortune to review University of Peking's Yuan Kou's paper on direct production of fuels from wood lignin. As we write, this seminal work is undergoing further peer-review after in-depth evaluation by editors and referees of *Science* and *Angewandte Chemie*. Yet, besides known problems with scientific publishing, enormous volumes of lignin, a by-product of cellulose manufacture, are burned in power stations, a low quality outlet parallel to that sought for many years for surplus glycerol. In one sense it could be claimed that the low price of oil in the 1990s ($10 to $20 a barrel) applied a dampener on chemical ingenuity for the whole decade, since many developments were put on the shelf until a day in the future when their use would become ‘‘economically viable’’. Today, not only has the price of oil multiplied by a factor of 10, but the concept of energy return on energy invested (EROI) shows that in the USA domestic petroleum now returns as little as 15 Joules for every Joule invested—whereas in the 1930s the figure was 100 Joules (C. Cleveland *et al.*, *Science*, 2006, **312**, 1746). It is exactly this decreasing trend that is forcing society globally to switch from fossil to renewable fuels, until the day when cheap and abundant solar energy becomes a reality. In this evolutionary period biofuels—and biodiesel in particular—will certainly play a role, and it inevitably follows that glycerol will remain a key raw material for many years to come. For example, following the Dumesic findings (Chapter 2) we can readily envisage a time when syngas obtained in high yield from glycerol will be used to synthesize both fuels and methanol by the Fisher–Tropsch process.

Finally, it is obvious that the greatest contributions are going to be brought about by today's students, whose creativity will produce spectacular advances. To avoid this monograph rapidly becoming out of date it is our intention that it must remain a ‘‘living’’ book, and that readers will have access to periodic updates posted online on the RSC website.

Mario Pagliaro, Michele Rossi
Palermo and Milan

Dedication

This book is dedicated to Francesco and Davide Pagliaro: May they one day enjoy the pleasure of writing

Contents

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About the Authors

Mario Pagliaro (b. Palermo, 1969) is a research chemist and management thinker based in Palermo at Italy's CNR, where he leads a research group and Sicily's Photovoltaics Research Pole. His research focuses on the development of functional materials for a variety of uses and operates at the boundaries of chemistry and materials science. Between 1998 and 2003 he led the management educational center, Quality College del CNR, using the resulting income to equip his laboratories and establish a research group which currently collaborates with researchers in 11 countries.

Mario holds a PhD in chemistry from Palermo University (1998), the topic of his thesis being the selective oxidation of carbohydrates; mentors were David Avnir in Jerusalem and Arjan de Nooy in the Netherlands. He has also studied and worked in France and Germany. In 2005 he was appointed *Maître de conférences associé* at the Montpellier Ecole Nationale Supérieure de Chimie. Between 1993 and 1994 he worked in the Netherlands, initially at the Rijks Universiteit, Leiden, and then at the TNO Food Research Institute in Zeist. In 1998 he was with Michel Vignon at the Grenoble's CNRS, and in 2001 he joined Carsten Bolm's research group at Aachen Polytechnic. Mario has co-invented a number of novel technologies, some of which have been commercialized. He is author or co-autoher of the books *Flexible Solar Cells, Silica-Based Materials for Advanced Chemical Applications, Nano-Age, The Future of Glycerol, BIPV* and *Il Nuovo Fotovoltaico*; as well of the management books *Scenario: Qualità* and *Lean Banking*. He is the author of five international patents and a large number of scientific papers. In 2008 he gave the "John van Geuns" Lecture at the University of Amsterdam, and in 2009 he chaired the 10th FIGIPAS Meeting in Inorganic Chemistry held in Palermo July 1 through 4. Since 2004 he has organized the prestigious Seminar "Marcello Carapezza". His website is qualitas1998.net.

Michele Rossi (b. Milan, 1939) is full professor of inorganic chemistry at Milan University, where he has taught in the Faculty of Science until early 2009. He graduated in industrial chemistry at the University of Milan in 1963. In 1974 he became Professor of Inorganic Chemistry at the University of Bari and since 1988 he holds a similar position at the University of Milan. Professor Rossi's current research is in the fascinating world of nanoscience, particularly metal-based catalysis for the activation of small molecules. His research group has discovered the surprising catalytic activity of gold nanoparticles in liquid-phase oxidation of organic compounds. Professor Rossi has been engaged by the World Gold Council for the preparation of gold on carbon catalysts as the reference standard for liquid-phase oxidation. This standard catalyst is in use throughout the world among scientific and industrial researchers.

His scientific activity, the subject of over 150 scientific papers and a number of patents, began at the prestigious school of Lamberto Malatesta and Adriano Sacco, specializing in organometallic chemistry. In one remarkable study, Sacco and Rossi discovered the first example of reversible coordination of molecular nitrogen, at room temperature and pressure, which opened the route to "nitrogen fixation", the front-line inorganic chemistry of the period 1968–1978. From this research arose the now famous compound $CoHN_2(PPh_3)_3$, which has since become a standard feature of chemistry textbooks. During this period he joined Sei Otsuka's group in Osaka, where he spent one year working on low-valency metal complexes. Later he moved into research on the catalysis of fine chemicals synthesis. Application of catalytic hydrogenation and oxidation have been the source of several scientific contributions and patents in the technology of clean processes. Professor Rossi's research group collaborates with a number of other research groups in Italy and abroad, and is a partner in the EU Auricat research project aimed at developing the industrial application of gold catalysis.

Acknowledgements

We wish to express our sincere appreciation to our academic and industrial colleagues who have provided expertise in reviewing a number of the chapters of this book. In many cases they are the leading researchers in the areas covered in the book, and the book itself owes much of its relevance to their admirable scientific efforts.

We acknowledge particularly the assistance of Professors Maria Jerzykiewicz (Wroclaw University), François Jerome (Université de Poitiers), Gadi Rothenberg (University of Amsterdam), Shelley D Minteer (Saint Louis University), Elio Santacesaria (University of Naples), and John Whittall (University of Manchester). Our thanks are also offered to industry researchers Christian Hulteberg (Biofuel–Solution), Katarina Klepacova (Procede Group), Paolo Forni (formerly of Grace Construction Products), Jean-Luc Dubois (Arkema) and Roger Lawrence (Davy Process Technology).

Once again, we would like to thank our research collaborators, especially Rosaria Ciriminna, Cristina Della Pina and Giovanni Palmisano, for their creative input leading to the introduction of alternative uses for glycerol.

Thanks are also due to Don Sanders for his formidable editing of the original manuscript. In addition Merlin Fox of RSC Publishing has been instrumental in producing the second edition of this book.

Mario Pagliaro, Michele Rossi

CHAPTER 1

Glycerol: Properties and Production

1.1 Properties of Glycerol

Glycerol (1,2,3-propanetriol, Figure 1.1) is a colorless, odorless, viscous liquid with a sweet taste, derived from both natural and petrochemical feedstocks. The name glycerol originates from the Greek word for ''sweet'', *glykys*, and the terms glycerin, glycerine, and glycerol tend to be used interchangeably in the literature. On the other hand, the expressions glycerin and glycerine generally refer to a commercial solution of glycerol in water, of which the principal component is glycerol. Crude glycerol is 70–80% pure and is often concentrated and purified prior to commercial sale to 95.5–99% purity.

Glycerol is one of the most versatile and valuable chemical substances known, with more than a thousand uses and applications.[1] It is used in a wide range of products on account of its distinctive characteristics. Its physical and chemical properties make it a versatile organic compound. Food products, cosmetics, toiletries, and drugs are just a few of the products in which glycerol is employed either as a constituent or forming part of the processing. It serves as a humectant, sweetener, solvent or preservative. Its hygroscopic properties are of particular value in the food and beverage industries. In prepared or manufactured foods containing low amounts of fat, glycerol is used as a filler.

In the modern era, glycerol was identified in 1779 by Swedish chemist Carl W. Scheele, who obtained a novel transparent, syrupy liquid by

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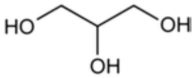


Figure 1.1 Structure of glycerol.

Table 1.1 Physicochemical properties of glycerol at 20 °C. (Reproduced from Ref. 2, with permission)

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 g/mol
Density	1.261 g/cm^3
Viscosity	1.5 Pa.s
Melting point	18.2 °C
Boiling point	290 °C
Food energy	4.32 kcal/g
Flash Point	160 °C (closed cup)
Surface tension	64.00 mN/m
Temperature coefficient	–0.0598 mN/(mK)

heating olive oil with litharge (PbO, used in lead glazes for ceramics). It is completely soluble in water and alcohols, slightly soluble in many common solvents such as ether and dioxane, but is insoluble in hydrocarbons.

In its pure anhydrous condition glycerol has a specific gravity of 1.261, a melting point of 18.2 °C and a boiling point of 290 °C under normal atmospheric pressure, accompanied by decomposition. At low temperatures glycerol may form crystals which melt at 17.9 °C. Overall it possesses a unique combination of physical and chemical properties (Table 1.1), which are utilized in many thousands of commercial products.[2] Indeed, glycerol has over 1500 known end uses, including many applications as an ingredient or processing aid in cosmetics, toiletries, personal care products, pharmaceutical formulations and foodstuffs.[3] In addition, glycerol is highly stable under normal storage conditions, compatible with many other chemical materials, virtually non-irritating in its various uses, and has no known adverse environmental effects.

Glycerol contains three hydrophilic alcoholic hydroxyl groups, which are responsible for its solubility in water and its hygroscopic nature. It is a highly flexible molecule, forming both intra- and intermolecular hydrogen bonds. There are 126 possible conformers of glycerol, all of which have been characterized in a study using density functional theory (DFT) methods.[4] In particular, a systematic series of *ab initio* molecular

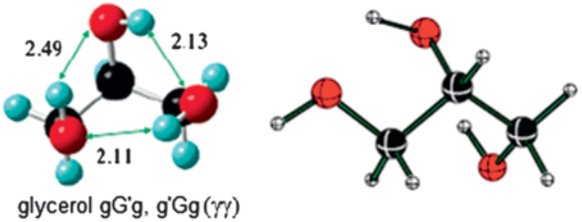


Figure 1.2 Selected bond lengths in Å for glycerol in its lowest energy conformer in the gas (*left*) and liquid (*right*) phase as determined by DFT methods (reproduced from ref. 4, with permission).

orbital and density functional theory optimizations of all the possible staggered conformers of glycerol (including calculation of the Boltzmann distributions in the gas and aqueous phases) has indicated that the enthalpic and entropic contributions to the Gibbs free energy are important for an accurate determination of the conformational and energetic preferences of glycerol. In the lowest energy conformer at the CCSD–(T)/6–31 + G(d,p)//HF/6–31G(d) and CBS–QB3 levels, the hydroxyl groups form a cyclic structure with three internal hydrogen bonds. This conformer, termed gG′g,g′Gg (γγ), has the structure with the internal hydrogen bond lengths displayed in Figure 1.2 and provides the starting geometry for the mechanism of many reactions with practical applications. This conformer (*left* in Figure 1.2) is the only form of glycerol which possesses three intramolecular hydrogen bonds, a structure offering considerable energetic benefit.

In the aqueous phase glycerol is stabilized by a combination of intramolecular hydrogen bonds and intermolecular solvation of the hydroxyl groups. Indeed, taking into account solvation, the conformer with two intramolecular hydrogen bonds shown on the right in Figure 1.2 is the most energetically stable. This is due to the fact that in aqueous solution the left conformation is now of higher relative energy, because all three hydroxyl groups are involved in intramolecular hydrogen bonding and are therefore unavailable to interact with the solvent. Many structures that possess intramolecular hydrogen bonding arrays still provide low energy conformations in aqueous solution, even when compared with structures without intramolecular hydrogen bonds.

In condensed phases, glycerol is characterized by a high degree of association due to hydrogen bonding. A first molecular dynamics simulation suggests that on average 95% of molecules in the liquid are connected.[5] This network is very stable and only rarely, especially at high temperature, releases a few short-living (less than 0.5 ps) monomers, dimers or trimers. In the glassy state a single hydrogen-bonded network is observed, involving 100% of the molecules present.

A highly branched network of molecules connected by hydrogen bonds exists in all phases and at all temperatures. The average number of hydrogen bonds per molecule ranges from about 2.1 in the glassy state to 1.2 in the liquid state at high temperature, with an average activation energy of 6.3 kJ mol^{-1} being required to break the hydrogen bond. Crystallization, which occurs at 291 K, cannot be directly achieved from the liquid state but requires special procedures. Due to the existence of such an extended hydrogen-bonded network, the viscosity and the boiling point of glycerol are unusually high. Glycerol readily forms a supercooled liquid which by lowering the temperature undergoes transition at about 187 K to a glassy state, whose nature has been the object of a number of investigations. Remarkably, a recent single-molecule analysis has revealed a foam-like structure for glycerol at temperatures above the glass transition point (T_g, 190 K) comprizing pockets of fluid isolated from one another by glass-like regions, which retain their distinct dynamics over surprisingly long timescales.[6]

The intramolecular energy is the prevailing factor in determining the average molecular structure in the condensed phases. The intermolecular hydrogen bonds, however, do not significantly stabilize energetically unfavored gas phase structures. In the gas phase within the range 300–400 K glycerol in practice exhibits only three backbone conformations, namely αα, αγ and γγ (Figure 1.3).

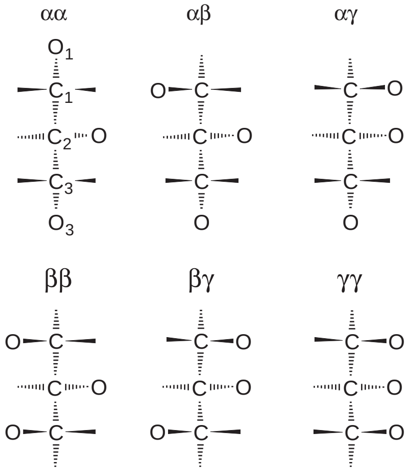


Figure 1.3 Backbone conformers of the glycerol molecule (reproduced from Ref. 5, with permission).

Table 1.2 Percentage probability distribution of the glycerol backbone conformations in the liquid and gas phase.[a] (reproduced from Ref. 5, with permission).

	400 K		*300 K*	
Conformer	*Liquid*	*Gas*	*Liquid*	*Gas*
αα	44 (3)	39.9 (5)	48 (1)	43.0 (8)
αγ + γα	45 (2)	47.0 (3)	46.0 (6)	46.9 (5)
γγ	6 (1)	11.0 (2)	4.4 (6)	9.8 (4)
αβ + βα	3.8 (9)	1.40 (1)	1.4 (4)	0.22 (1)
βγ + γβ	1.2 (5)	0.67 (1)	0.2 (1)	0.11 (1)
ββ	0.01 (1)	0.03 (1)	0	0.002 (1)

[a] Errors in the last digit are given in parenthesis.

Intermolecular interactions slightly stabilize the αα conformation and destabilize the γγ conformation as the temperature decreases (Table 1.2). As the liquid approaches freezing point, about half of the molecules are present in the αα conformation.

The activation energy for a conformational transition is around 20 kJ mol^{-1}, which means that it is much higher at room temperature than at freezing temperature. The high activation energy, and the fact that nearly half of the molecules must undergo at least one conformational transition to reach the αα structure typical of the crystalline state, is responsible for the remarkable stability of supercooled glycerol. The network dynamics involved spans three distinct and increasingly longer timescales, due to vibrational motion, to neighbor exchange and to translational diffusion, respectively.

In biochemistry glycerol plays a major role in stabilizing enzymes due to the effect of its polyhydric alcohol functionality,[7] a fact which is generally attributed to the enhancement of the structural stability of the entire protein by a large alteration in the hydrophilic–lipophilic balance (HLB) upon clustering around the protein.[8] This results in practical implications of dramatic importance, as glycerol also protects biologicals during sol–gel entrapment in a silica-based matrix, either by formation of poly(glyceryl silicate) as sol–gel precursors,[9] or by direct addition to bacteria prior to the sol–gel polycondensation.[10] This enables reproducible and efficient confinement of proteins, cells and bacteria inside hybrid bio-doped glasses. These materials display activity approaching or even exceeding those of the free biologicals, together with the high stability and robustness that characterizes sol–gel bioceramics, and accordingly are finding application over a wide field, ranging from biocatalysis to biosensing and biodiagnostics. Finally, it is worth recalling at this point that theoretical physicist David Bohm

Figure 1.4 Glycerol with a high concentration of dye is inserted into the space between two concentric transparent plastic cylinders with the space between them filled with clear glycerol. The inner cylinder is then slowly and steadily rotated. As the cylinder is rotated, the dye smears and appears to be diffused. Since the flow of the viscous glycerol is laminar, there is little actual diffusion. When the inner cylinder is rotated in the opposite direction, the dye regains the initial profile (reproduced from Ref. 12, with permission.)

formulated the implicate order theory,[11] inspired by a simple experiment in which a drop of dye was squeezed on to a cylinder of glycerol. When the cylinder rotated (Figure 1.4), the dye diffused through the glycerol in an apparently irreversible fashion; its order seemed to have disintegrated. When the inner cylinder was rotated in the opposite direction, the dye regained its initial profile.[12]

1.2 Traditional Commercial Applications

Traditional applications of glycerol, either directly as an additive or as a raw material, range from its use as a food, tobacco and drugs additive to the synthesis of trinitroglycerine, alkyd resins and polyurethanes (Figure 1.5).[13]

Currently, the amount of glycerol going annually into technical applications is around 160 000 tonnes, and is expected to grow at an annual rate of 2.8%.[1] Of the glycerol market, pharmaceuticals, toothpaste and cosmetics account for around 28%, tobacco 15%, foodstuffs 13% and the manufacture of urethanes 11%, the remainder being used in the manufacture of lacquers, varnishes, inks, adhesives, synthetic plastics, regenerated cellulose, explosives and other miscellaneous industrial uses. Glycerol is also increasingly used as a substitute for propylene glycol.

As one of the major raw materials for the manufacture of polyols for flexible foams, and to a lesser extent rigid polyurethane foams, glycerol is the initiator to which propylene oxide and ethylene oxide are added. Glycerol is widely used in alkyd resins and regenerated cellulose as a

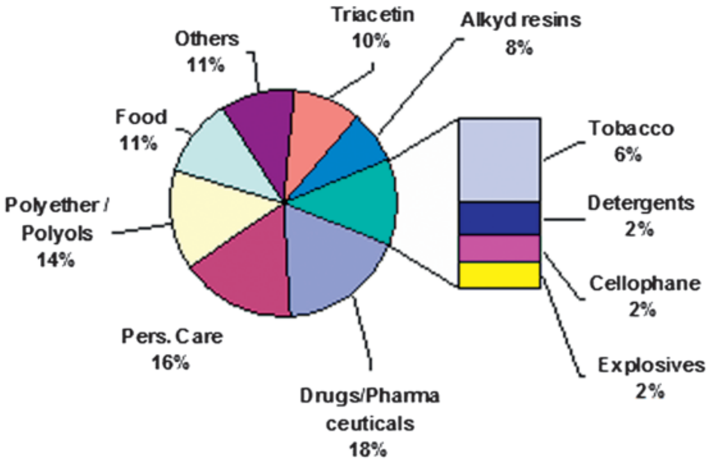


Figure 1.5 Market for glycerol (volumes and industrial uses; source: Novaol, May 2002).

softener and plasticizer to impart flexibility, pliability and toughness in surface coatings and paints.

Most of the glycerol marketed today meets the stringent requirements of the United States Pharmacopeia (USP) and the Food Chemicals Codex (FCC). Also available is Food Grade Kosher glycerol, which has been prepared and maintained in compliance with the customs of the Jewish religion.[14] However, technical grades of glycerol that are not certified as USP or FCC quality are also available.

The primary function of glycerol in many cases is as a humectant, a substance for retaining moisture and in turn giving softness. Glycerol draws water from its surroundings and the heat produced by the absorption makes it feel warm. Due to this property, glycerol is added to adhesives and glues to keep them from drying too rapidly. Many specialized lubrication problems have been solved by using glycerol or glycerol mixtures. Many thousand tonnes of glycerol are used each year to plasticize various materials, such as sheets and gaskets. The flexibility and toughness of regenerated cellulose films, meat casings and special quality papers can be attributed to the presence of glycerol. It also acts as a solvent, sweetener and preservative in food and beverages, and as a carrier and emollient in cosmetics. The effectiveness of glycerol as a plasticizer and lubricant gives it wide applicability, particularly in food processing, because it is nontoxic. Glycerol is also used in alkyd resin manufacture to impart flexibility. Alkyd resins are used as binders in products such as paints and inks, where brittleness is undesirable.

Glycerol is used in specialist lubricants where oxidation stability is required, for example in air compressors. In all applications, whether as a reactant or as an additive, the non-toxicity and overall safety of glycerol is of paramount benefit.

Due to the rapid decline in its price, glycerol is rapidly substituting other polyols which are used on a large scale as sugar-free sweeteners. Polyols are used mostly in confectionery, food, oral care, and pharmaceutical and industrial applications. Characteristics of polyols are a reduction in calories, a pleasant sweetness, the ability to retain moisture, and improved processing. The most widely used polyols are sorbitol, mannitol, and maltitol. Sorbitol is facing particularly stiff competition from glycerol. Glycerol contains approximately 27 calories per teaspoonful and is 60% as sweet as sucrose; it has about the same food energy as table sugar. However, it does not raise blood sugar levels, nor does it feed the bacteria that cause plaque and dental cavities. As a food additive glycerol is coded E422. Baked goods lose their appeal when they become dry and hard during storage. Being hygroscopic, glycerol reduces water loss and prolongs shelf life.

Glycerol is used in medical and pharmaceutical preparations, mainly as a means of improving smoothness and providing lubrication, and also acts as a humectant, a hygroscopic substance which keeps the preparation moist. Glycerol also helps to maintain texture, it controls water activity and prolongs shelf life in a host of applications. It is also widely used as a laxative and, based on the same induced hyperosmotic effect, in cough syrups (elixirs) and expectorants.

In personal care products glycerol serves as an emollient, humectant, solvent, and lubricant in an enormous variety of products, including toothpaste, where its good solubility and taste give it the edge over sorbitol. Toothpastes are estimated to make up almost one-third of the personal care market for glycerol. Related applications include mouthwashes, skin care products, shaving cream, hair care products and soaps. It is for example a component of "glycerin soap" (Figure 1.6), which is used by people with sensitive, easily irritated skin because its moisturizing properties prevent skin dryness. In general, however, very low concentrations (0.05–1%) are employed, which are unable to absorb the large surplus of biodiesel-generated glycerol on the market.

Glycerol is similar in appearance, smell and taste to diethylene glycol (DEG), which has often been used as a fraudulent replacement for glycerol. In the USA, for example, the Food, Drug, and Cosmetic Act was passed in 1938 following the "elixir sulfanilamide" incident, which caused more than 100 deaths due to the contamination of medicines with DEG. The revamped 1938 law provided food standards, addressed

Figure 1.6 Glycerin soap (photo courtesy of A. K. A. Saunders, Inc).

Figure 1.7 Early FDA laboratory (photo courtesy of FDA History Office).

the safety of cosmetics, and required that drugs were checked for safety before sale, reinforcing the role of the Food and Drugs Administration (Figure 1.7).[15] As late as 2007 the Food and Drug Administration blocked all shipments of toothpaste from China to the US following reports of contaminated toothpaste entering *via* Panama. The toothpaste contained DEG, killing at least 100 people. The poison, falsely labeled as glycerol, had in 2006 been mistakenly mixed into medicines in

Panama, resulting in the fatal poisonings. The DEG had originated from a Chinese factory which had deliberately falsified records in order to export DEG in place of the more expensive glycerol.[16] Eventually, a large batch of toothpaste contaminated with DEG also reached the EU market, a number of poisoning cases being reported in Italy and southern Europe.

The glycerol market has undergone radical changes, driven by very large supplies of glycerol arising from booming biodiesel production, the intrinsic volatility of which, due to changing taxation regulations in the richest European countries and in the USA, is adding to the historic volatility of the glycerol market. In any case, researchers and industry have been investigating new outlets for glycerol to replace petrochemicals as a source of chemical raw materials, and in a relatively few years there have been an impressive series of achievements. After the lengthy period of increasing oil prices from the early 2000s, glycerol is establishing itself as a major platform for the production of chemicals and fuels. These topics are discussed in the chapters which follow.

1.3 Production of Bioglycerol and Commercial Trends

Glycerol provides the molecular skeleton of all animal and vegetable fats (triglycerides, the energy reservoir for materials in nature). It is also the oldest organic molecule isolated by man, obtained by heating fats in the presence of ash to produce soap as early as 2800 BC.[17] It constitutes on average about 10% by weight of fatty matter. When the body uses stored fat as a source of energy, glycerol and fatty acids are released into the bloodstream. The glycerol component is converted to glucose by the liver and provides energy for cellular metabolism. Natural glycerol is obtained hydrolytically from fats and oils during manufacture of soap and fatty acids, and by transesterification (an interchange of fatty acid groups with another alcohol) during production of biodiesel fuel (Figure 1.8). It should not come as a surprise, therefore, that in these energy intensive days glycerol has become a hot topic throughout industry.

In a certain sense glycerol was already a national defense priority in the days leading up to World War II, as the supply of glycerol originating from soap manufacture was insufficient to meet the wartime demand for nitroglycerine, *i.e.,* for dynamite, the smokeless gunpowder for all types of munitions, discovered by Swedish industrialist Alfred Nobel. Nobel built bridges and buildings in Stockholm, and while researching new methods for blasting rock he invented in 1863 the

FOOD VS. FUEL: WHERE DOES VEGETABLE OIL FIT?

September 2006

BIODIESEL

MAGAZINE

Combating the Glycerin Glut

Researchers Identify Unique Uses, Producers Address Quality Concerns

BBI

Figure 1.8 Cover of the September 2006 issue of *Biodiesel Magazine* (photo courtesy of the publisher).

detonator for igniting nitroglycerine by means of a strong shock rather than by heat combustion. Nitroglycerine, invented by Italian chemist Ascanio Sobrero in 1846, in its natural liquid state is very volatile; in 1866 Nobel discovered that mixing nitroglycerine with silica (kieselguhr) could turn the liquid into a malleable paste, known as dynamite, which could be kneaded and shaped into rods suitable for insertion into drilling holes.

Clearly, the supply of glycerol became a strategic war priority for industrial nations worldwide. For example, when World War I began in 1914, DuPont was the only company in the USA which manufactured smokeless powder and was the nation's leading producer of dynamite.[18] Soon after the end of World War I the US Government therefore decided to make production of dynamite independent of soap manufacture, and instead based it on high yield reactions using petroleum feedstock. Since that time glycerol has been produced from epichlorohydrin obtained from propylene, and thus from fossil oil. Today, however, glycerol plants of this type are being replaced by other plants which use glycerol as a raw material, even for the production of epichlorohydrin itself (see Chapter 4).[19] This is the result of the large surplus of glycerol (1,5 million tonnes produced in 2008 compared with about 600 000 tonnes in 1992) created as a by-product in the manufacture of biodiesel fuel by transesterification of seed oils with methanol using NaOH as a base catalyst, or from batch esterification of fatty acids catalyzed by sulfuric acid (Figure 1.9).[20]

In the traditional manufacturing process biodiesel is produced by a transesterification reaction between the vegetable oil and methanol, catalyzed by KOH. It is an equilibrium reaction with the following stoichiometry (Figure 1.10):

100 kg of oil + 10.5 kg MeOH = 100 kg methyl esters (biodiesel) + 10.5 kg glycerol

Figure 1.9 A batch of home-made canola oil biodiesel sitting on top of its glycerol layer (photo courtesy of Biodieselcommunity.org).

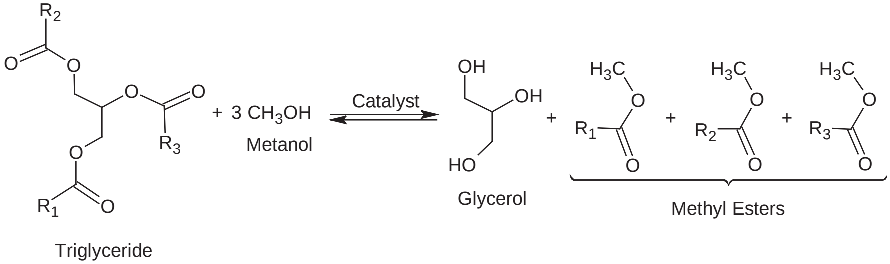


Figure 1.10 Transesterification of a triglyceride with methanol.

Colza, soybean and palmitic oils have the most suitable physicochemical charateristics for transformation into biodiesel. Raw vegetable oil is first refined by degumming (elimination of lecithins and phosphorus) and deacidification (elimination of free fatty acids). The latter comprise some 2% of the original product, and the distilled fatty acids are recovered and sold as by-products. The oil is charged into large batch reactors and heated at 55 °C with a 30% excess of a mixture of methanol and KOH. After reaction for 2 h, the mixture is left to stand. The glycerol–methanol solution is heavier than methanol and the esters, and is run off from the bottom of the reactor (Figure 1.9). Methanol is expensive, and is recovered and reused in a further reaction run. The remaining mixture, comprizing biodiesel, glycerol–methanol solution and methanol, is distilled to complete the recovery of methanol and washed and centrifuged to eliminate traces of glycerol. The resulting product, a mixture of biodiesel and water, is dried under vacuum and put into stock pending analytical tests. Fundamental analysis parameters are the ester content (minimum 96.5%) and the free glycerol content (maximum 200 ppm).

The glycerol side-stream typically contains a mixture of glycerol, methanol, water, inorganic salts (catalyst residue), free fatty acids, unreacted mono-, di-, and triglycerides, methyl esters, and a variety of other "matter organic non-glycerol" (MONG) in varying proportions. The methanol is typically stripped from this stream and reused, leaving crude glycerol after neutralization. In its raw state crude glycerol has a high salt and free fatty acid content and a substantial color (yellow to dark brown). Consequently, crude glycerine has few direct uses, and its fuel value is also marginal. An economic solution for the purification of crude glycerol streams combines electrodialysis and nanofiltration, affording a colorless liquid with low salt content, equivalent to technical grade purity (Figure 1.11).[21]

The recovered glycerol, after polishing if necessary using ion exchange and removal of water–methanol solution by evaporation, easily meets US Pharmacopeia (USP) glycerol standards. This membrane-based technique avoids expensive evaporation and distillation, and such problems as foaming, carry-over of contaminants, and limited recovery. A recent insight provided by an oleochemical industry insider is available online and sheds light on the problem, even if not entirely accurate scientifically:[22]

> *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*

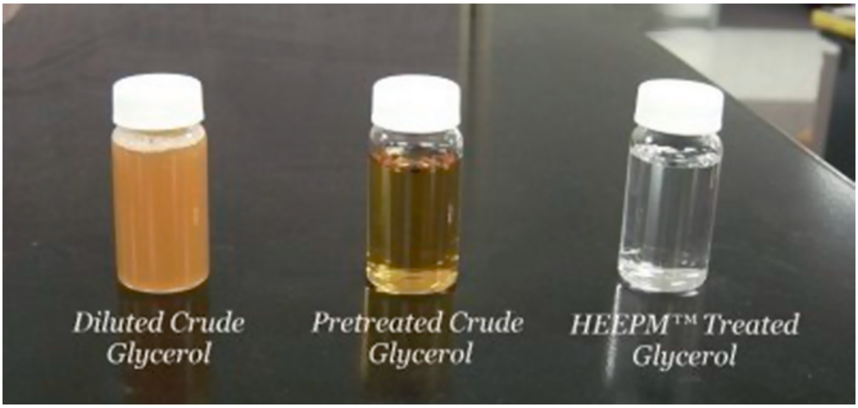


Figure 1.11 Glycerol purified by membranes combining electrodialysis and nanofiltration (photo courtesy of the EET Corporation).

> *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 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 feed stock.*

A recent study has in fact concluded that adding crude 10% glycerol to cattle rations improves the animal's feed to weight-gain ratio, as ruminants can handle toxic methanol and its breakdown product, formaldehyde, more effectively than can humans.[23] Indeed, most biodiesel manufacturing processes utilize a 6 to 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 condition, glycerol would be a very valuable by-product. However, purifying it is costly and generally not feasible for small- to medium-scale plants, which recover most of the expensive methanol from the glycerol layer, and are left with salt-grade bioglycerol.

In general, the traditional biodiesel manufacturing processes have a number of disadvantages, including:

- soap formation (from the NaOH catalyst);
- use of an excess of alcohol (to shift the equilibrium to fatty esters), which has to be separated and recycled;
- homogeneous catalysts, which require neutralization, causing salt-laden waste streams;
- the expensive separation of products from the reaction mixture; and
- relatively high investment and operating costs.

In 2005 the Institut Français du Pétrole (IFP) disclosed a novel biodiesel process, called Esterfif. Starting from triglycerides, the transesterification step is conducted using a solid catalyst, a mixed Zn–Al oxide.[24] The process runs at higher temperature and pressure than the homogeneous method, and uses an excess of methanol, which is vaporized and recycled. It has two reactors and two separators, needed for shifting the methanolysis equilibrium (Figure 1.12). At each stage the excess methanol is removed by partial evaporation, and the esters and glycerol are separated in a settler.[25]

A second alternative, developed in 2006 by Gadi Rothenberg's research group at the University of Amsterdam, and licensed to the

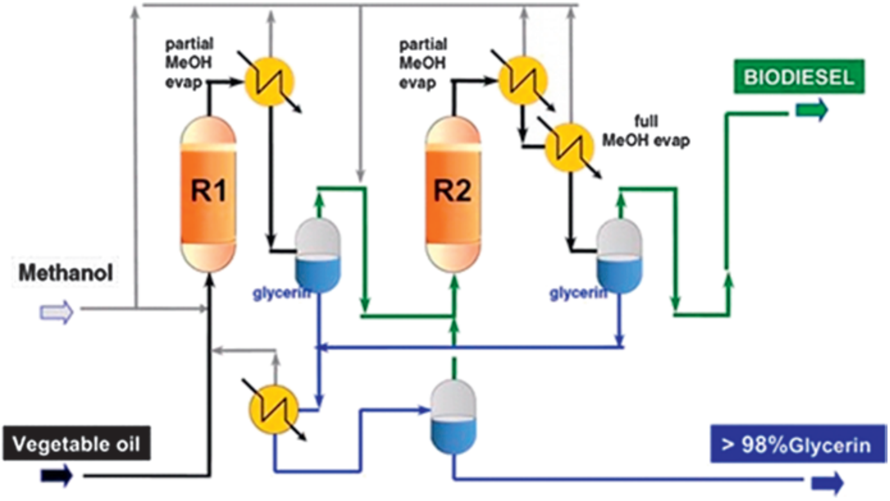


Figure 1.12 Simplified schematic of the IFP Esterfif biodiesel process, based on two consecutive reactor–separator stages (reproduced from Ref. 24, with permission).

company Yellow Diesel BV, is especially suited to mixed feedstocks with high free fatty acid (FFA) content, such as used cooking oil and low-grade grease.[26] The process combines the reaction and the separation in a single step, using reactive distillation (also known as catalytic distillation, Figure 1.13).[27]

This intensifies mass transfer, allows *in situ* energy integration, reduces equipment costs, and simplifies the process flow sheet and operation. A number of processes based on heterogeneous alcoholysis of triglycerides, using classical acid or base catalysts in addition to biocatalysts, have been developed during the past five years, many of which result in significant savings.[28] For example, thanks to novel catalyst and integrated process design, the heterogeneous process saves up to 40% of capital costs and 30% of operating costs compared to a conventional plant.

Importantly, this process can be adapted to various types of feedstock, including low-quality oils, waste oils and fats, an example being the Austrian city of Graz, in which the buses run on biodiesel derived from waste cooking oil (Figure 1.14).[29]

In October 2009 Yellow Diesel succeeded in producing high-quality biodiesel in a continuous fixed-bed micro-plant using heterogeneous catalysis, and is now scaling up the process. This gives pure biodiesel plus cosmetics and food-grade glycerol, with practically no waste streams. The biodiesel specifications are in advance of those required by the European standard, EN 14214 (Table 1.3).[30]

In accordance with the industry insider opinion reported above, the spot market price for refined glycerol first fell from around €1500 per tonne in 2001 to €330 in 2006;[31] but then in 2007 prices recovered due to lack of material and eventually rose to €950 per tonne in the first quarter of 2008, at which time the price of crude glycerol was €400 per tonne.[32] By 2009, with the world facing serious economic recession, the spot market price for *refined* glycerol had reached $400–600 per tonne.[33]

Nonetheless, despite the fall in biodiesel production in the USA (where production was 50% lower in 2009 than in 2008), worldwide biodiesel capacity will have grown to 39.8 million tonnes by 2010 (9% above 2009), even though many plants worldwide have been running at extremely low rates following the global economic downturn;[34] increases are most notable in Asia and South America. Asia is the largest producer and consumer of refined glycerol, accounting for 44% and 35% of world production and consumption, respectively, in 2007; it is expected to remain the largest market in 2012, with increased demand in all applications including new markets for refined glycerol, such as epichlorohydrin. Western Europe is the second largest producer and consumer of refined glycerol, accounting for almost 35% and 28% of world

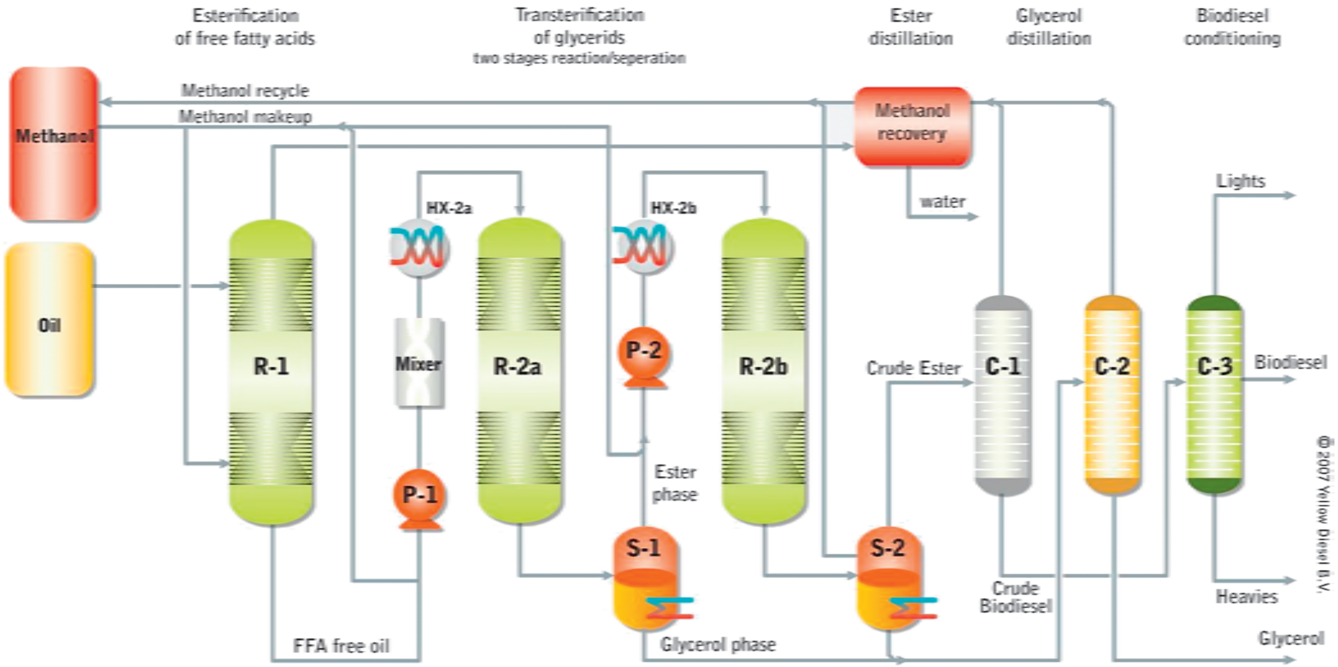


Figure 1.13 Schematic of the Yellow Diesel catalytic distillation process for making biodiesel from high-FFA oils, by integrating the reaction and separation within one reactive distillation column using a solid acid catalyst (reproduced from Ref. 23, with permission).

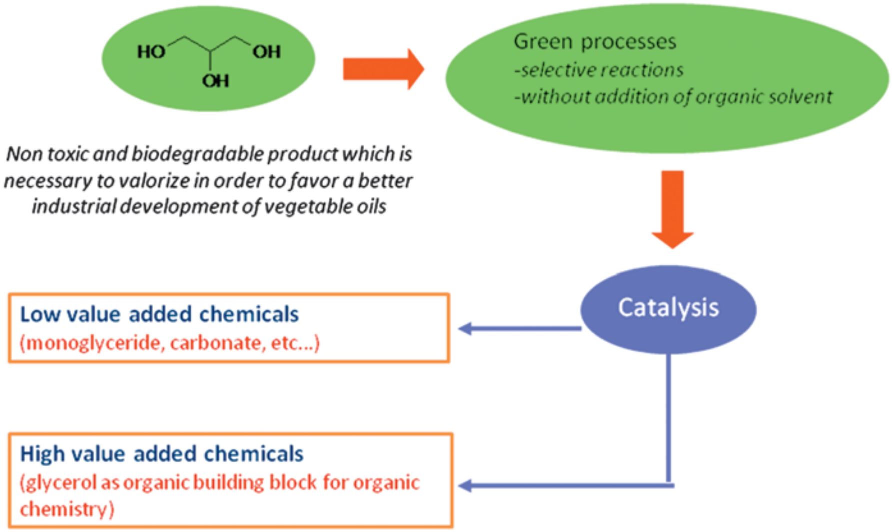
Figure 1.14 The entire bus fleet of the Graz public transport company runs on 100% biodiesel, most of which stems from reprocessed used cooking oil (reproduced from Ref. 23, with permission).

Table 1.3 Quality specifications of biodiesel made from industrial-grade rapeseed oil using the Yellow Diesel heterogeneous process (data from independent laboratory, NofaLab).

Analysis results	*Yellow Diesel*	*EN14214*
Ester content	99.5%	>96.5%
Density at 15 °C	0.8740	0.860–0.900
Flash point	>120 °C	>120 °C
Methanol content	0.02%	<0.2%
Monoglyceride	0.57%	<0.8%
Diglyceride	0.19%	<0.2%
Triglyceride	0.15%	<0.2%

production and consumption, respectively, in 2007. North America was the third largest market during that year.[35]

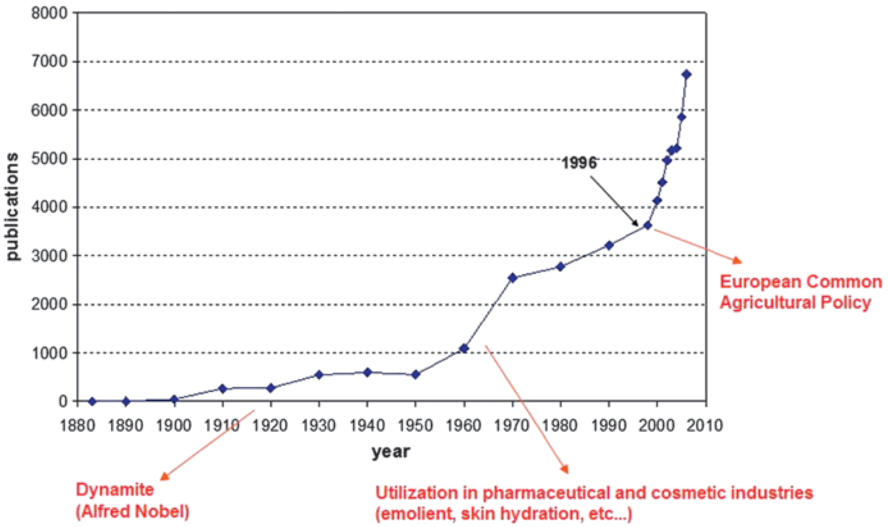
In this context, the range of chemical processes and new products based on crude glycerol as starting material will continue to grow. For example, in 2009 the US has become a net importer of crude glycerol, due to increased demand for vegetable-based glycerol for conversion to propylene glycol which is outstripping domestic availability.[33] Developing new industrial uses for glycerol (Scheme 1.1) will continue to increase the net energy content and sustainability of biodiesel.



Scheme 1.1 Logics behind the use of catalysis to convert glycerol into value-added products (image courtesy of Professor François Jerome).

A model based on the production and sale of 80% glycerol by weight, and assigning it a value of \$0.33 per kg, predicts 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 litre for each \$0.022 reduction in glycerol price per kg.[36] Accordingly, the number of research papers dealing with new usages for glycerol published between 2000 and 2007 has doubled to more than 7000 annually (Figure 1.15); and the interest generated by the first edition of *The Future of Glycerol*, published in mid-2008, has confirmed this high level of activity.

At that time we showed how glycerol was becoming a key raw material for the chemical industry, and that chemical ingenuity was rapidly opening the route to glycerol derivatives for use in fields as diverse as fuels, chemicals, pharmaceuticals, detergents, and the automotive and building industries. Current reviews focus on the employment of solid catalysts in heterogeneously catalyzed processes,[37] on novel glycerol derivatives,[38] on the chemo-selective catalytic conversion of glycerol to commodity chemicals,[39] and include a trade report on new commercial applications.[40] In the paragraphs and chapters which follow we review the most important scientific and industrial developments which have taken place during the past two years, including the remarkable findings on the use of glycerol as reaction solvent.



European Common Agricultural Policy

Dynamite (Alfred Nobel)

Utilization in pharmaceutical and cosmetic industries (emolient, skin hydration, etc...)

Figure 1.15 Trend of publications on glycerol (data from SciFinder database; image courtesy of Professor François Jerome).

1.4 Glycerol as Solvent in Organic Reactions

It has been recently been reported that use of crude glycerol as a solvent can considerably accelerate the reaction rate of an organic reaction.[41] The production of solvents from glycerol is an interesting possibility from two points of view. Firstly, solvents are used in huge amounts in a wide variety of applications and are therefore good candidates for absorbing surplus glycerol production. Secondly, solvents derived from petroleum are often harmful VOCs (volatile organic compounds), so their substitution by less hazardous solvents derived from renewable resources is a clearly an interesting environmental possibility.

In particular, glycerol and crude glycerol are found to be highly efficient solvents 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. Unusually, these reactions can be conducted in glycerol without the presence of a catalyst. For example, the aza-Michael addition of *p*-anisidine (**1a**) to butyl acrylate (**2a**) yields 82% of the addition product **3a** when the reaction is performed at 100 °C in crude glycerol (Figure 1.16), whereas in water the reaction proceeds at a very low rate with only trace amounts of the addition product (< 5%) detectable after 20 h.

Pure and crude glycerol can in practice be regarded as "organic water", since as a solvent they behave in a similar manner to water in

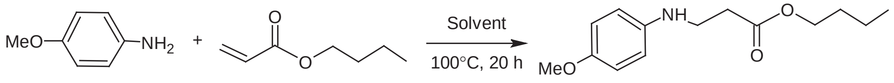
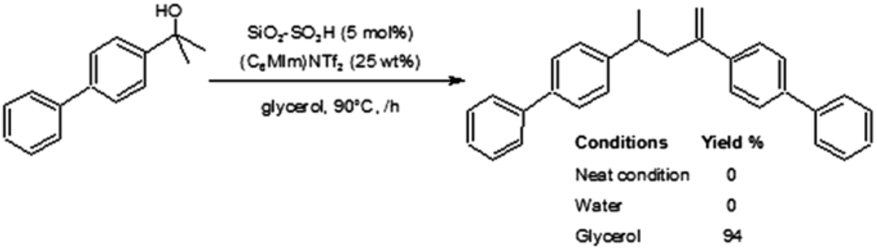


Figure 1.16 The aza-Michael reaction in glycerol under catalyst-free conditions proceeds with high yield (Reproduced from ref. 41, with permission).



Conditions	Yield %
Neat condition	0
Water	0
Glycerol	94

Figure 1.17 Acid-catalysed dehydrative dimerization of an hydrophobic alcohol on glycerol proceeds with 94% yield, but no reaction occurs on water. (Reproduced from ref. 12, with permission).

organic synthesis, promoting organic reactions without the presence of catalyst. Like water, glycerol is abundant, cheap, safe, biodegradable and reusable. Moreover, compared with water glycerol has a higher boiling point (290 °C) and a lower vapor pressure (< 1 mm Hg at 50 °C), which makes the development of catalytic processes at temperatures around 100 °C technically simpler. Indeed, recovered glycerol maintained under vacuum (14 mm Hg at 60 °C for 30 min) to remove residual traces of ethyl acetate, after three cycles still gives yields comparable to that with fresh or crude glycerol. In addition, whereas with more hydrophobic substrates the beneficial effect of water on reaction rate becomes limited, glycerol is found to continue to drive the reaction. For example, association of a solid catalyst with glycerol as solvent allows selective control of the reaction pathway of more complex reactions such as the tandem dehydrative dimerization of a tertiary alcohol (Figure 1.17).

Researchers from the same group led by François Jerome, have also demonstrated that the use of surfactant combined catalysts (SCCs) overcomes all drawbacks to the use of glycerol as a solvent by permitting better diffusion of organic substrates in the glycerol phase, creating a hydrophobic environment within which it is possible to inhibit the reactivity of glycerol.[42] The catalytic ring opening of 1,2-epoxydodecane with dodecanoic acid was investigated using different aminopolysaccharides

(APs) as basic catalysts. The idea was that the APs form hydrophobic environments in glycerol, and that due to hydrophobic–hydrophilic interactions, diffusion of glycerol inside these hydrophobic pockets should be difficult. This makes the development of selective catalytic processes possible, and the reaction proceeded smoothly with high selectivity.

Moreover, micellar catalysis in glycerol offers a remarkable advantage compared with water because the emulsions formed in glycerol are unstable. As a result two phases rapidly form at the end of the reaction, permitting easy extraction of the reaction products without the involvement of organic solvents, as is generally the case in water (Figure 1.18).

Similarly, a family of glycerol-based solvents (Figure 1.19), consisting of eighteen 1,3-dialkoxy-2-propanols and 1,2,3-trialkoxypropanes either symmetrically or asymmetrically substituted in the terminal positions, has recently been tested as new solvents in the epoxidation of cyclooctene with hydrogen peroxide, either using a diselenide catalyst or no catalyst at all.[43] The results were in some cases comparable to those in standard organic solvents, but in others even better results were achieved.

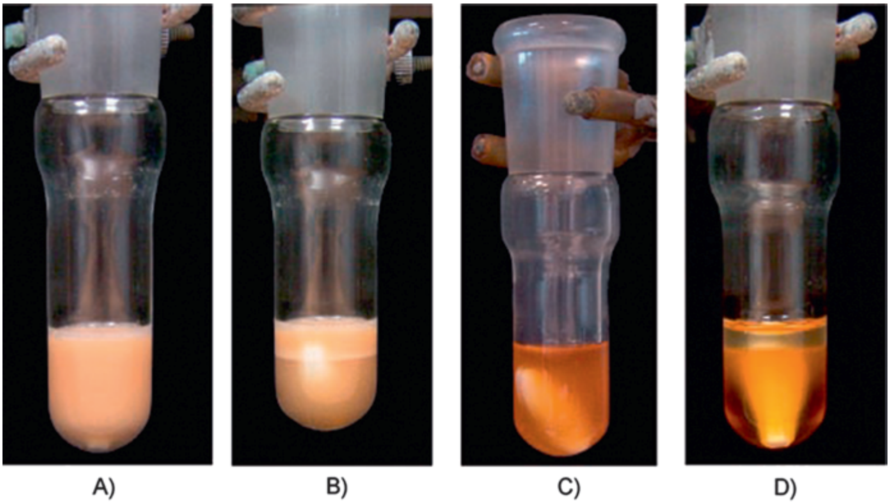


Figure 1.18 Emulsion behaviour of APs in A) water during the reaction (70% yield after 8 h at 908C), B) in water after centrifugation at the end of the reaction, C) in glycerol during the reaction and D) in glycerol after centrifugation at the end of the reaction. (Reproduced from ref. 42, with permission).

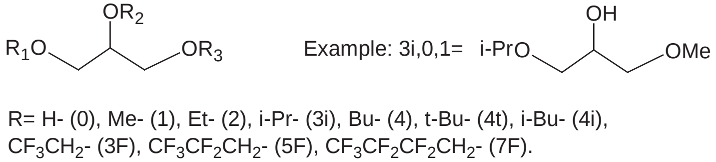


Figure 1.19 Structures of glycerol-based solvents. (Reproduced from ref. 43, with permission).

Furthermore the researchers established a quantitative relationship between solvent polarity and rate of epoxidation, leading to the conclusion that the best solvents for this transformation should have good hydrogen bond donor capability, but low hydrogen bond acceptance (Lewis basicity). The robustness of the regression model has been tested and can successfully predict the behavior of new glycerol-derived solvents in this epoxidation reaction. Finally, the solvents employed under oxidation conditions showed remarkable stability, even in the case of secondary alcohols. In no case were by-products caused by solvent oxidation found, nor were peroxide compounds or decomposition by-products observed when the solvent was subjected to 50 bar O_2 (8%) at 100 °C for 4 hours.

1.5 Bioglycerol Purification

In general, almost all today's biodiesel production is based on homogeneous catalysis and involves alkaline catalysts (*i.e.* NaOH) with impurities such as catalyst, soap, methanol and water being concentrated in the glycerin phase. The glycerol phase is typically neutralized with hydrochloric acid and the cationic component of the catalyst is incorporated as sodium chloride. The salt content in crude glycerol, stemming from the use of homogeneous alkaline catalysts, often ranges from 5 percent to 7 percent. Conventional distillation, the most commonly practiced method for purifying glycerin in high yield, is an energy-intensive process, and thus very costly. New low-cost purification strategy have thus been developed in the last 3 years, which are based on ion-exchange techniques tailored to the high salt content of glycerin issued from biodiesel production.

Along with the process commercialized by EET Corporation mentioned above, another such process is the Ambersep BD50 high productivity process jointly developed by Rohm and Haas and Novasep Process which consumes small quantities of water for the separation of

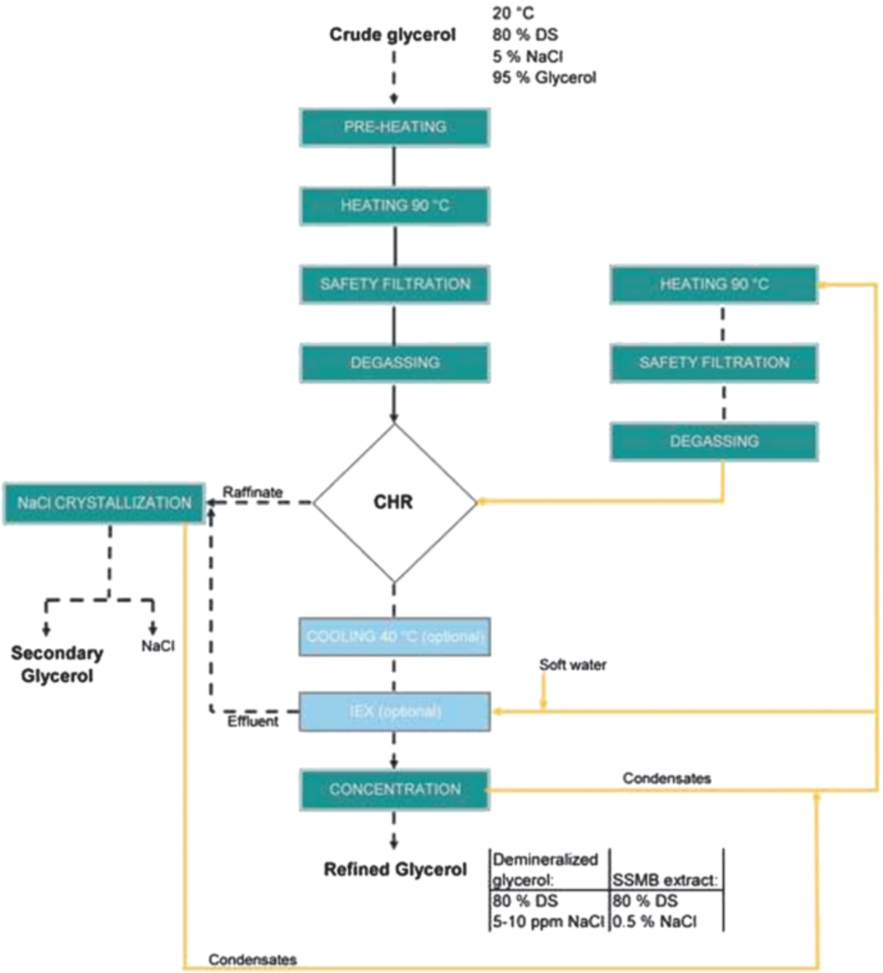


Figure 1.20 The process steps for the purification of crude glycerin from biodiesel developed by Novasep Process with Rohm and Haas. (Reproduced from ref. 44, with permission).

the salt fraction from glycerin and does *not* require the vaporization of glycerol. (Figure 1.20).[44]

Crude glycerol from storage is first heated to 90 °C on a heat exchanger, using energy recovered from the purified glycerol stream, plus steam. After a safety filtration (to protect the downstream processing steps from fouling by suspended materials) the hot and clean crude glycerin is degassed before entering a chromatographic separator using a chromatographic separation resin (Ambersep BD50) to purify crude glycerin with a high salt composition. Due to the systematic recycling of the condensates produced during the reconcentration of the purified glycerin fraction, no source of fresh water is necessary for the operation of the chromatographic separator during normal operations.

Depending on the required purity of the final glycerin, it is possible to produce a purified glycerin product with 99.5 percent purity or to add a polishing step employing an ion-exchange demineralization unit which enables the end user to produce a high quality glycerin product with 5 parts per million to 10 parts per million salt content.

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12. We thank Prof. A. Helman, University of California, Santa Cruz, for allowing reproduction of this figure from the Physics Lecture Demonstration Catalog: http://physics.ucsc.edu/lecturedemonstrations.
13. See the recent report from Frost & Sullivan: ‘‘R&D Creating New Avenues for Glycerol’’ (4 August 2006). Available online at the URL: https://www.frost.com/prod/servlet/market-insight-top.pag?docid=77264824.
14. The term kosher refers to food recognized as such by the Torah. The laws of kosher detail the permitted and forbidden animals, fish, and fowl, and describe the separation of dairy and meat. Jewish Rabbis certify food products, including glycerol for cough syrups, accordingly. To be Kashrut endorsed, glycerol must be from vegetable sources instead of from animal tallow.
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CHAPTER 2

Reforming

2.1 Glycerol as a Platform for Green Fuels

As pointed out by Huber and Dumesic, biomass has the potential to serve as a sustainable source of energy and organic carbon for our industrialized society.[1] For this, however, we need to develop catalytic transformation of biomass-derived oxygenated feedstocks (primarily sugars and sugar alcohols) in the liquid phase to value-added chemicals and fuels. From both industrial and innovation viewpoints, one of the major achievements of the new glycerol chemistry is the aqueous phase reforming process (APR), in which glycerol is converted to hydrogen and carbon monoxide (the synthesis gas, or "syngas") under relatively mild conditions (temperatures between 225 and 300 °C) using a Pt–Re catalyst in a single reactor in the aqueous phase.[2] Such formation of synthesis gas is crucial to the biorefinery, because the gas can be used as a source of fuels and chemicals using the Fischer–Tropsch (or methanol) synthesis, offering an energy-efficient alternative to liquid transportation fuels derived from petroleum (Figure 2.1).

Similarly, an equally mild APR process using a Pt catalyst offers the rapid production of high yields of hydrogen fuel from glycerol at very low CO concentrations, due to more favorable water–gas shift (WGS) thermodyamics, and with considerably lower energy consumption than traditional methane reforming (Figure 2.2).[3]

Hydrogen from renewable sources with low CO content is urgently needed for fuelling the highly efficient fuel cells that will soon find widespread use for the heating of buildings, hospitals and factories, and probably also for cars and other vehicles. Petroleum currently provides a

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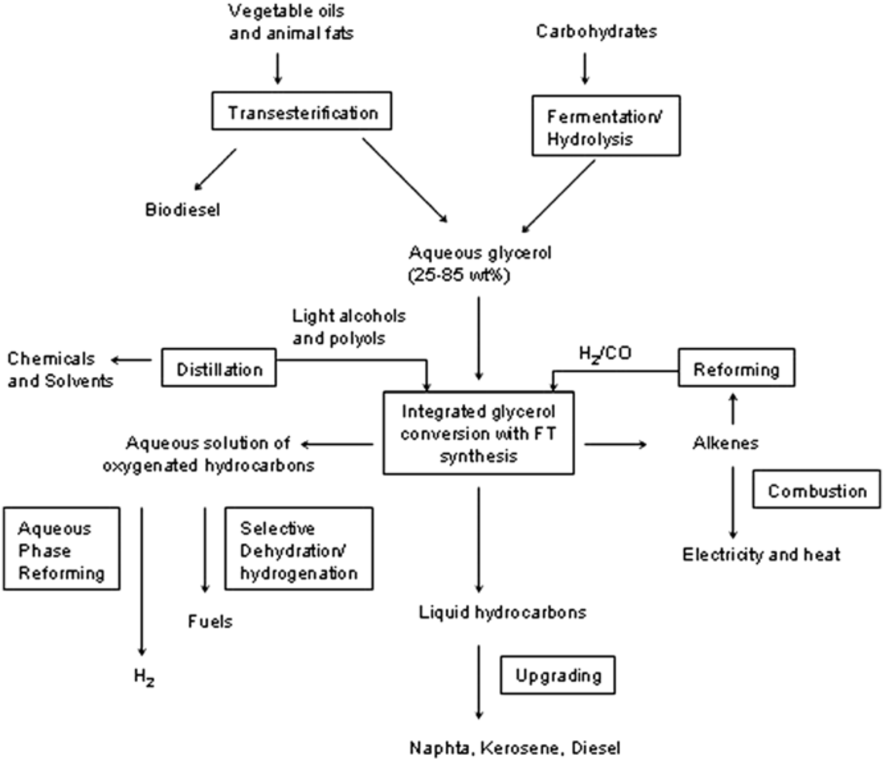
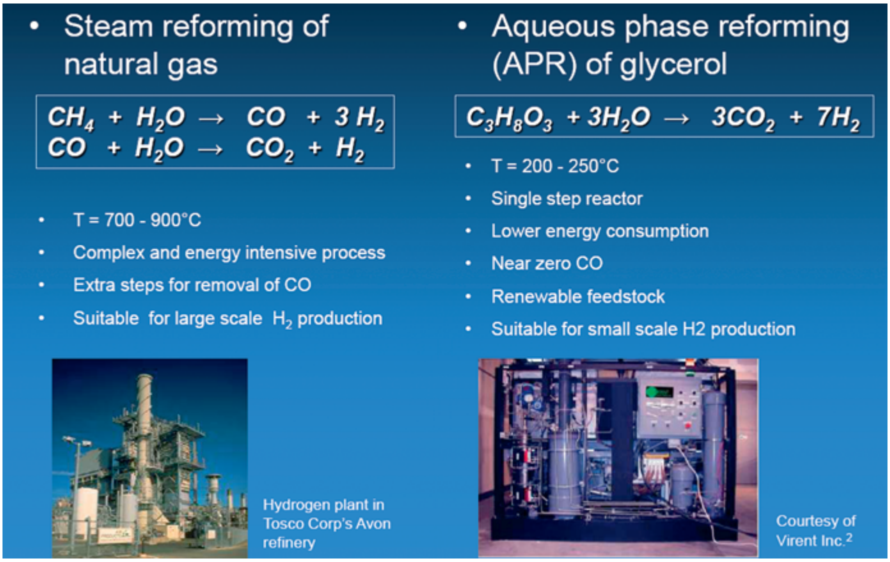


Figure 2.1 Process pathway for production of liquid fuels from biomass by integrated glycerol conversion to synthesis gas and Fischer–Tropsch synthesis (reproduced from Ref. 1, with permission).

significant fraction (37%) of the world's energy.[4] Almost 70% of this is consumed by the transportation sector, which relies entirely on petroleum for its energy needs.[5] Biomass is the main candidate as an alternative source of transportation fuel, since it is renewable and CO_2 neutral (Figure 2.3).[6] The quantity of biomass grown annually is sufficient to provide energy for approximately 70% of the transportation sector, provided that it can be converted to clean-burning fuels having high energy density, as is currently available from petroleum.[7]

Biomass is comprised primarily of lignin and carbohydrates (*e.g.*, starch and cellulose),[3] and one method of converting these to liquid fuels is by fermentation to liquid alcohols such as ethanol and butanol. However, the overall energy balance for production of bioethanol from grain-derived starches by a combination of hydrolysis, fermentation, and distillation is not favorable,[5] in fact it has been estimated that the amount of energy required to produce bioethanol is slightly greater than



- Steam reforming of natural gas

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

- T = 700 - 900°C
- Complex and energy intensive process
- Extra steps for removal of CO
- Suitable for large scale H_2 production

Hydrogen plant in Tosco Corp's Avon refinery

- Aqueous phase reforming (APR) of glycerol

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$$

- T = 200 - 250°C
- Single step reactor
- Lower energy consumption
- Near zero CO
- Renewable feedstock
- Suitable for small scale H2 production

Courtesy of Virent Inc.[2]

Figure 2.2 Production of hydrogen by aqueous phase reforming of glycerol is more convenient than steam reforming of natural gas (reproduced from Ref. 2, with permission).

the energy content of the ethanol produced (energy return on investment (EROI) = 1.15).[8]

On the other hand, the energy balance for the coupled APR and FT reactions (Figure 2.4) is favorable. Formation of synthesis gas from glycerol is highly endothermic, with an enthalpy change of about 80 kcal/mol, but the conversion of synthesis gas to alkanes (along with CO_2 and water) is highly exothermic (–110 kcal/mol). This means that the conversion of glycerol to alkanes by a combination of reforming and Fischer–Tropsch synthesis is mildly exothermic overall, with an enthalpy change and an overall gain in energy of about –30 kcal/mol of glycerol. This process therefore provides the opportunity for improving the economic viability of biomass-based Fischer–Tropsch synthesis by reducing the cost of synthesis gas production and by improving its thermal efficiency. Glycerol can in fact be obtained by the fermentation of glucose,[9] giving a 25% solution of glycerol; this offers an energy-efficient alternative to ethanol-based production, since higher product concentrations can be obtained. On the other hand the fermentation process used to produce bioethanol from carbohydrates leads to an aqueous solution containing only 5–10 wt% ethanol, and significant expenditure of energy is required to produce fuel grade ethanol by distillation of such a dilute solution.[10]

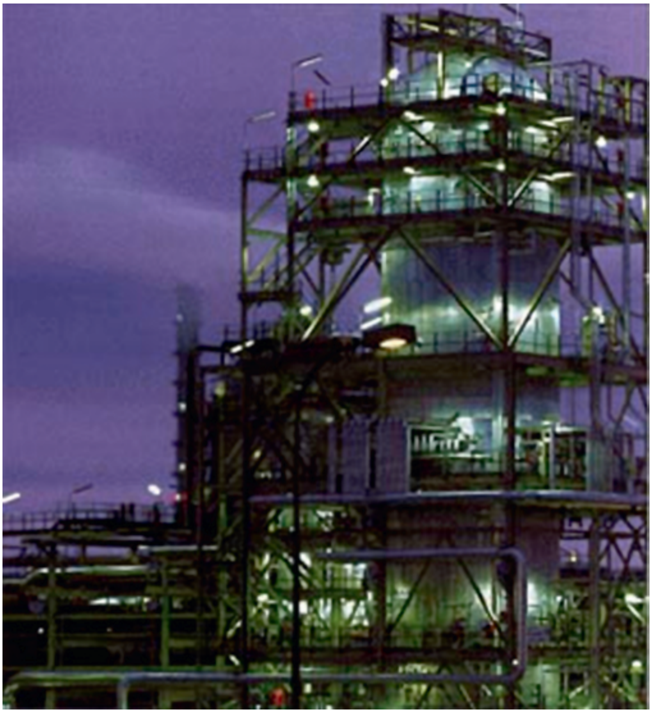


Figure 2.3 The Fischer–Tropsch process (here showing a plant reactor at Sasol) can produce a high quality diesel fuel from biomass. The fuel is competitive if oil is above $40 a barrel. Currently, at least three projects (Ohio River Clean Fuels, Illinois Clean Fuels, and Rentech Natchez) are combining coal and biomass feedstocks, creating hybrid-feedstock synthetic fuels. (Reproduced with the permission of Sasol Corporation, South Africa).

Such improvements in synthesis gas generation and thermal efficiency to improve the economics of the Fischer–Tropsch synthesis are crucial. The low thermal efficiency and high operating costs of this process, of which more than 50% stem from synthesis gas generation,[11] has traditionally made liquid alkane production by this synthesis economically viable only on the large scale. And this holds true equally for both conventional Fischer–Tropsch synthesis (*i.e.*, using coal or natural gas), and also for the "green" Fischer–Tropsch synthesis involving advance gasification of biomass to form the synthesis gas.[12]

Finally, a major recent advancement in the conversion of glycerol to synthesis gas (selectivity higher than 80%) with small amounts of water, or no water at all, uses plasmas at low temperature and atmospheric pressure without external heating (Figure 2.5).[13]

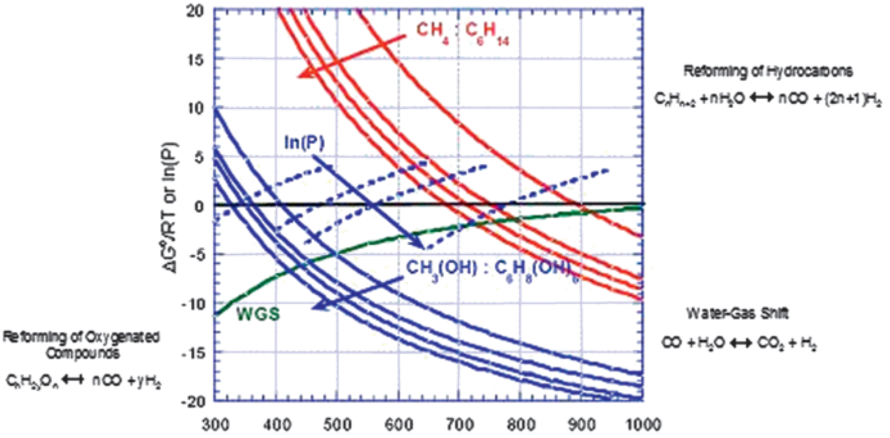


Figure 2.4 APR of polyols is thermodynamically favorable at significantly lower temperature than steam reforming of methane (reproduced from Ref. 2, with permission).

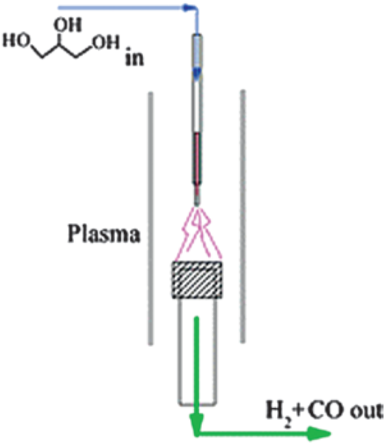


Figure 2.5 Glycerol can be effectively converted to synthesis gas (selectivity higher than 80%) with small amounts of water, or no water, using plasmas at low temperature and atmospheric pressure, without external heating (reproduced from Ref. 13, with permission).

2.2 Production of Hydrogen *via* Aqueous Phase Reforming

The APR process efficiently generates easily purified hydrogen by the reaction of glycerol with water to form carbon dioxide and hydrogen

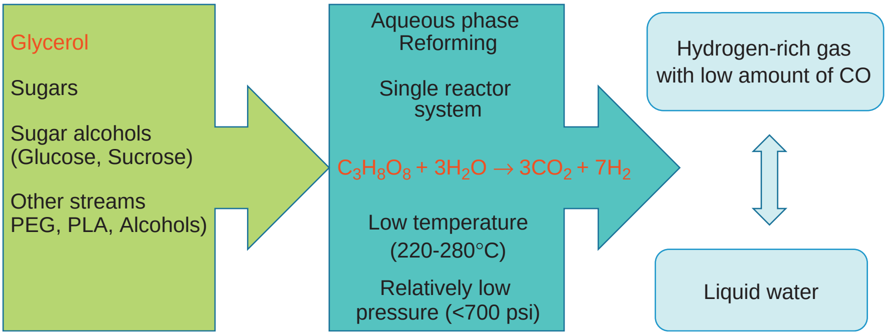


Figure 2.6 The APR process efficiently generates hydrogen from biomass polyols. Carbon released as carbon dioxide in this case derives from plants and thus from photosynthetic CO_2 fixation.

(Equation 1):

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \tag{1}$$

This reforming reaction takes place over a catalyst in a single reactor at temperatures between 200 and 250 °C and at pressures above the bubble point of water (16 and 40 bar, respectively). The gas stream leaving the APR can be utilized directly as a high energy fuel for internal combustion engines, gas-fired turbines, and solid oxide fuel cells (Figure 2.6).

The annual worldwide market for hydrogen is estimated to be approximately 45 million tonnes. In addition to its use as an energy provider in transportation applications, hydrogen is a key building block for many chemical processes. This is particularly the case in ammonia fertilizer production, and also in oil refineries for upgrading lower quality oil fractions into gasoline and diesel and to remove sulfur contaminants. It is additionally important in the manufacture of glass, vitamins, personal care products, lubricants, refined metals and food products.

The APR process for the production of hydrogen from glycerol is cost effective since:

- it generates hydrogen without the need to volatilize water, representing a major energy saving;
- it takes place at temperatures and pressures where the water–gas shift reaction is favorable, making it possible to generate hydrogen with low quantities of CO in a single chemical reactor;

- it occurs at pressures, typically 15 to 50 bar, at which the hydrogen-rich effluent can be purified effectively using pressure-swing adsorption (PSA) technology; and
- it takes place at low temperatures, which minimizes the undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures.

The choice as a starting point for hydrogen production decreases in the order: glycerol > sorbitol > glucose. The raw water-soluble glycerol waste from biodiesel manufacture is an ideal feedstock for the APR process. At the reaction temperatures investigated, CO concentrations were below 300 ppm, and this method is particularly well suited for generating hydrogen on demand in a compact and highly efficient single-step reactor (Figure 2.7).

Operating temperatures are one-third of those in other processes, with the generation of 10 times more hydrogen per g of catalyst. In the original study,[2] the reaction of glycerol was conducted over a precious metal catalyst supported on γ-alumina. Subsequent investigations have shown that a range of catalyst compositions are active for the generation of hydrogen by aqueous phase reforming of oxygenated compounds, in particular inexpensive nickel-based materials and selective APR catalysts.[14]

The non-condensable gas stream leaving the APR contains predominately carbon dioxide and hydrogen. Hydrogen is readily purified from this gas stream utilizing PSA technology. Importantly, the gas stream leaving the APR is within the required feed pressure range for the PSA unit (between 16 and 40 bar). Accordingly, the PSA unit does not need an expensive and energy-consuming compressor to provide the necessary feed pressure. This results in lower capital costs and increased energy efficiency.

Due to the pressure swing and purging cycles the PSA technology generates a waste hydrogen stream (typically 10–20% of the feed), which also contains the alkanes generated in the APR process. Combustion of

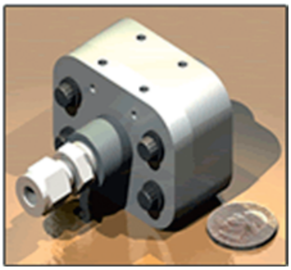


Figure 2.7 An aqueous phase reforming reactor is small and generates hydrogen locally on demand (photo courtesy of Virent Inc).

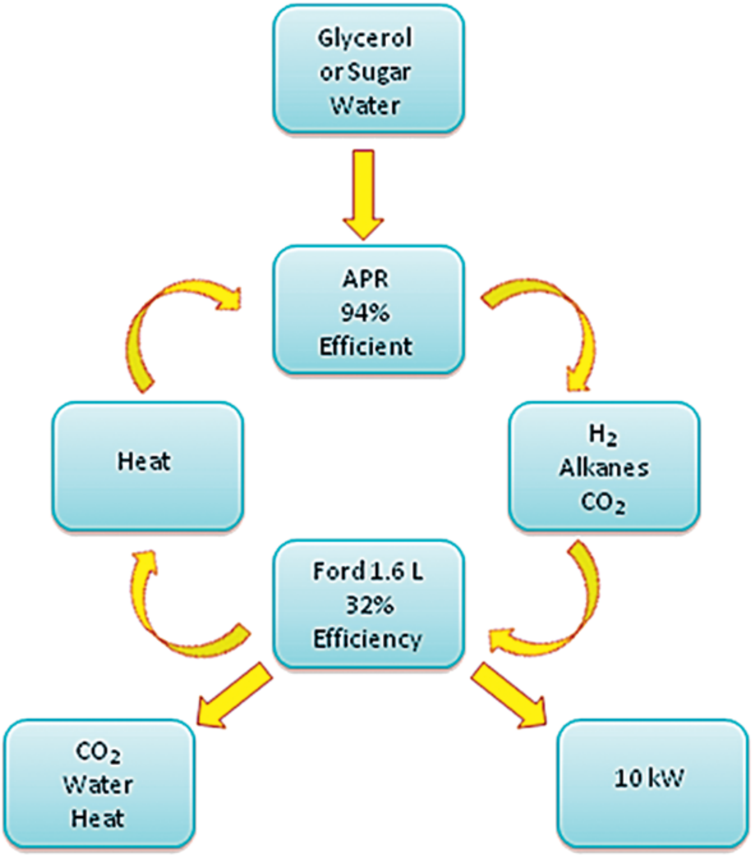


Figure 2.8 The APR reactor at the MGE plant uses heat generated by the combustion of hydrogen and methane to generate electricity (adapted from Ref. 16, with permission).

the waste hydrogen and alkanes can provide much of the process heat necessary for the reactor, because the reforming reaction is endothermic and requires heat input. Since the APR process runs at low temperature, an alternative method of providing this process energy is to recycle the high temperature waste heat, as shown in Figure 2.8.

2.3 Production of Hydrocarbon Fuels *via* Aqueous Phase Reforming

Liquid alkanes can be produced directly from glycerol in a two-bed reactor system using an integrated process consisting of APR followed in a single reactor by Fisher–Tropsch conversion.[15] Glycerol can be converted in this way to synthesis gas at high rates and selectivity at temperatures between 225 °C and 335 °C, according to Equation 2.

$$C_3O_3H_8 \rightarrow 3CO + 4H_2 \tag{2}$$

Operation at low temperatures provides the opportunity to couple this endothermic glycerol conversion with the exothermic Fischer–Tropsch synthesis to produce liquid transportation fuel from aqueous glycerol solutions *via* an integrated process (Equation 3):[1]

$$C_3O_3H_8 \rightarrow {}^{7}\!/_{25}C_8H_{18} + {}^{19}\!/_{25}CO_2 + {}^{37}\!/_{25}H_2O \tag{3}$$

In particular, either glycerol conversion or Fischer–Tropsch synthesis can be carried out effectively under the same conditions in a two-bed reactor system (Figure 2.9).

This integrated glycerol-based process improves the economics of "green" Fischer–Tropsch synthesis by reducing costs, by eliminating the need for an a biomass gasifier, by reducing the size of the synthesis

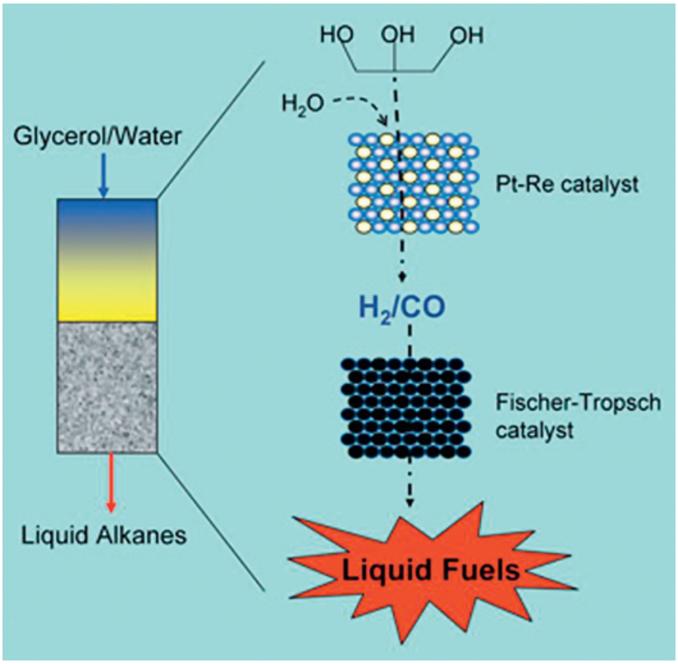


Figure 2.9 The integrated process for making fuels from glycerol is a simple two-step catalytic process that can be carried out at low temperature and moderate pressure, and can effectively harness the energy from a renewable resource (reproduced from the RSC website, with permission).

reactor, by producing an undiluted synthesis gas stream and by eliminating subsequent cleaning steps. In addition, the process can produce synthesis gas of varying $H_2:CO$ composition, thus eliminating the need for a water–gas shift reactor and allowing for the use of Fischer–Trospch catalysts that operate at different H_2 : CO ratios. Synthesis gas production and clean-up are indeed the critical steps in producing liquid alkanes from biomass and account for more than 50% of the total cost of producing these by "green" Fischer–Tropsch synthesis.

Hence, for example, conversion of glycerol over a 10 wt% Pt–Re/C catalyst with a Pt : Re ratio of 1:1 produces a synthesis gas stream that is suitable for Fischer–Tropsch synthesis (H_2 : CO between 1.0 and 1.6) from concentrated glycerol feed solutions at low temperatures (275 °C) and pressures up to 17 bar, where incomplete vaporization of the glycerol feed occurs (Figure 2.10). The synthesis gas produced in the first process is fed directly into the second reactor consisting of a 2.9 wt% $Ru–TiO_2$ catalyst bed whose intermediate value of χ ($50\times10^{16}\,m^{-1}$) leads to optimum C_{5+} selectivity.

This combined process produces liquid alkanes, with S_{C5+} between 0.63 and 0.75 at 275 °C and pressures between 5 and 17 bar, with more than 40% of the carbon in the products contained in the organic liquid phase at 17 bar. The aqueous liquid effluent from the integrated process contains between 5 and 15 wt% methanol, ethanol and acetone, which can be separated from the water by distillation and reused, or recycled for conversion to gaseous products. Importantly, the coupling of

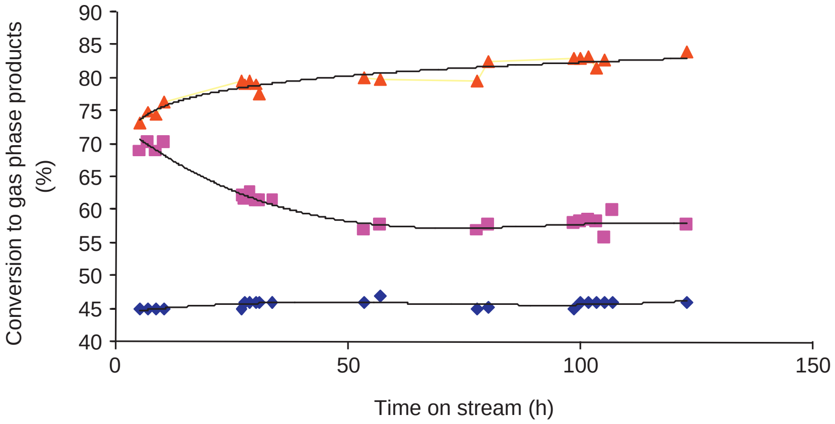


Figure 2.10 Conversion to gas phase products (▲), CO/CO_2 molar ratio (■), and H_2/CO molar ratio (◆) for gas phase processing of 30 wt% aqueous glycerol feedstock at 548 K and 8.3 bar (adapted from Ref. 14, with permission).

glycerol conversion to synthesis gas and Fischer–Tropsch synthesis leads to synergies in the operations of these processes, such as:

- avoiding the highly endothermic and exothermic steps that would result from the separate operation of these processes;
- eliminating the need to condense water and oxygenated hydrocarbon by-products between the catalyst beds;
- allowing operation at higher pressures (*i.e.*, 17 bar), at which synthesis gas production over Pt–Re/C is decreased and the production of liquid by-products increased; and
- causing an increase in selectivity to C_{5+} hydrocarbons.

The primary oxygenated hydrocarbon intermediates formed during conversion of glycerol to synthesis gas are ethanol, acetone, and acetol; all have positive effects on the Fischer–Tropsch synthesis step. In particular, water, ethanol and acetone have a slightly positive effect, such as increasing the selectivity to C_{5+} hydrocarbons (S_{C5+}) by a factor of 2 (from 0.30 to 0.60). Acetol can participate in Fischer–Tropsch chain growth, forming pentanones, hexanones and heptanones in the liquid organic effluent stream.

Figure 2.11 shows the product molecular weight distributions for experiments that combined glycerol conversion with Fischer–Tropsch

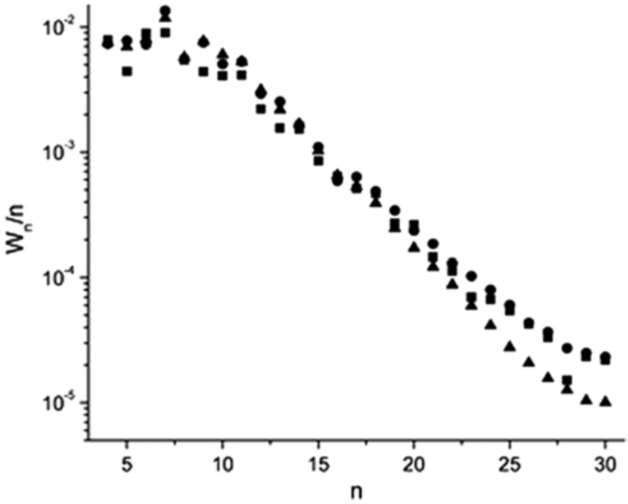


Figure 2.11 Molecular weight distribution for combined glycerol conversion with Fischer–Tropsch synthesis experiments at 548 K, and 5 bar (■), 11 bar (•), and 17 bar (▲) (reproduced from Ref. 14, with permission).

synthesis, and these distributions exhibit deviations from the kinetics of the Anderson–Schulz–Flory (ASF) chain growth model similar to the Fischer–Tropsch experiments, indicating α-olefin readsorption effects. The oxygenated hydrocarbon by-products from glycerol react over the Ru–TiO_2 bed, most probably by entering into chain growth. The C_{5+} selectivity, selectivity to pentanones, hexanones and heptanones in the organic liquid, and the conversion of CO for combined glycerol conversion with Fischer–Tropsch synthesis at 11 and 17 bar, are all higher than those at 5 bar, despite the fact that synthesis gas production from glycerol is decreased at these elevated pressures. The more favorable Fischer–Tropsch conditions (*i.e.*, higher pressure) are more important to the integrated process than the synthesis gas production rate.

2.4 Industrial Applications

Methanol is a widely employed industrial chemical. Today around 90% of methanol is produced from fossil natural gas *via* the synthesis gas. An alternative production method relying on bioglycerol would be an excellent economic opportunity and environmentally sound. In the Netherlands, BioMethanol Chemie Nederland uses crude glycerol to produce synthesis gas (and CO_2), which is then reformed at high pressure and temperature to make biomethanol.[16] In 2006 the company, a consortium, reopened the Methanor production facilities in Delfzijl after the plant was taken over from the previous owners. The feasibility of the glycerol-to-methanol process was demonstrated on the pilot plant scale in March 2008, and the company is currently building a larger unit with a capacity of 200 000 tonnes per year, expected to come on stream by late 2009. The site can accommodate a further three such units, with an eventual capacity of 800 000 tonnes/year of biomethanol.

Similarly, in 2008 the research group of Edman Tsang at Oxford University announced the discovery of a new supported metal catalyst capable of directly and cleanly converting glycerol to methanol. The process involves a hydrogenation step and is claimed to be mild, proceeding at low temperature and pressure, without formation of by-products (Figure 2.12).

Towards the end of 2009 the UK company DT Chemicals was in the process of purchasing the exclusive rights to the process *via* Oxford University and was seeking investment to scale up the process. The company aimed to have the commercial process completed by early 2010.[17]

The APR technology has a large commercial potential, and this has been reinforced by coupling with Fisher–Tropsch fuel production. The different product streams of the integrated APR–FT process each have

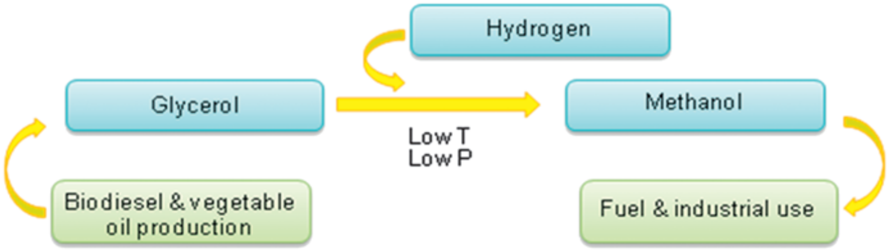


Figure 2.12 Discovered in Oxford in 2008, the new mild catalytic process to convert glycerol into methanol involves hydrogenation over a supported (undisclosed) metal catalyst.

potential end-uses (see Figure 2.1). The most likely use for the gas alkanes would be combustion to produce process heat and electricity, with some of the unconverted hydrogen and carbon monoxide being recycled to the Fischer–Tropsch bed.

The aqueous liquid product stream containing oxygenated hydrocarbons (*e.g.*, ethanol, methanol and acetone) at concentrations between 5 and 15 wt% is suitable for distillation to isolate the oxygenated hydrocarbons, which are used as intermediates and solvents in the chemical industry. Indeed, the process has spawned the company Virent Energy Systems Inc., created in 2002 to commercialize the APR process. Having labeled as "BioForming" the process which enables the production of renewable fuels and chemicals from glycerol and carbohydrates, in 2005 Virent contracted with a local utility, Madison Gas and Electricity (MGE), to build an integrated BioForming reactor that converts glycerol into hydrogen and methane and burns the mixture to drive a 10 kW generator for electricity production. The system (Figure 2.8) has delivered a minimum of 10 kW of power to the MGE grid since its start-up at the beginning of 2006. It also utilizes the waste heat from the internal combustion engine to provide the limited amount of process heat required for the reactor. As a result, the system thermal efficiency for this initial unit is excellent. The APR reactor initially used pure glycerol, but it was also designed to run on glycerol in crude form.

The success of the system encouraged large companies such as Cargill, Shell and Honda to invest in the company, since they were interested to see how the technology could be adapted to supply renewable hydrogen for fuel cells. Collaboration with Shell Hydrogen is expected to speed the time of the technology to market. The production of gasoline *via* APR in June 2006 confirmed that the technology was a viable pathway to the production of liquid fuels and chemicals currently derived from fossil

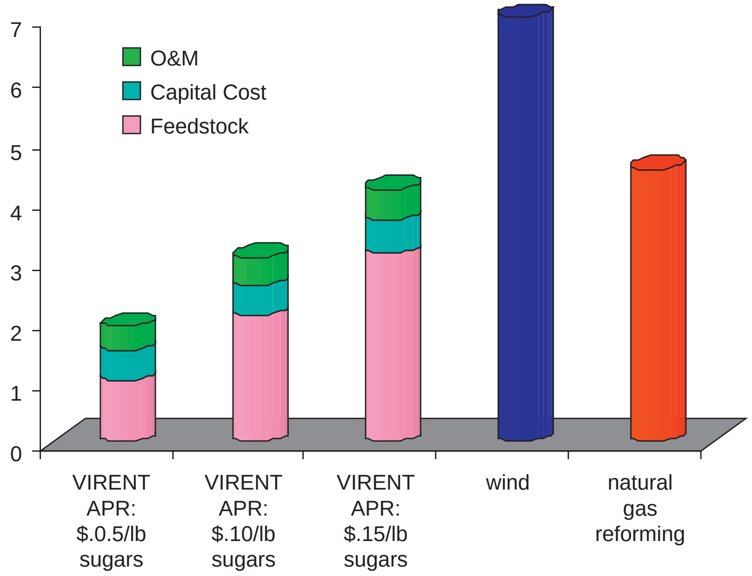


Figure 2.13 Since cost of the feedstock is the primary driver of the overall cost of hydrogen generated from biomass-derived hydrocarbons, increasing biodiesel production will make its production from glycerol a commercial reality (adapted from Ref. 16, with permission).

fuels. Biodiesel-generated glycerol is a cost-effective feedstock and positions the APR process to compete effectively with conventional fuels, even before consideration of renewable tax incentives. As can be seen in Figure 2.13, the primary economic driver for the APR process is the feedstock.[18] A comparable steam reformer utilizing non-renewable natural gas is expected to be 56% efficient, and could generate hydrogen at a cost of $4.50 per kg in a distributed system.

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CHAPTER 3

Selective Reduction

3.1 Reduction of Glycerol

From a commercial viewpoint, the production of 1,2-propanediol by reduction of glycerol is the most relevant achievement of the new glycerol chemistry.[1] 1,2-Propanediol (or propylene glycol, PG) is an important commodity chemical traditionally derived from propylene oxide. The dependence on crude petroleum oil as a source of propylene and propylene glycol has caused instability in both price and supply, but the availability of abundant and cheap bioglycerol overcomes this problem. Provided long-term contracts for glycerol are in place with biodiesel (vegetable glycerol) manufacturers, both profitability and market stability are assured. For example, bio-routes enable the reduction of glycerol to 1,3-propanediol, an important monomer which can be polymerized with terephthalic acid to produce polyester fibers known as Sorona (DuPont) or Corterra (Shell).

3.2 Hydrogenolysis to Propylene Glycol

Figure 3.1 summarizes the conversion of glycerol to glycols. In the presence of metallic catalysts and hydrogen, glycerol can be hydrogenated to 1,2-propanediol (propylene glycol), 1,3-propanediol (PDO), or ethylene glycol.

The production of 1,2-propylene glycol by glycerol hydrogenolysis is a process now adopted commercially in the USA for manufacture of both industrial grade (99.0%) and US Pharmacopeia grade (>99.5%)

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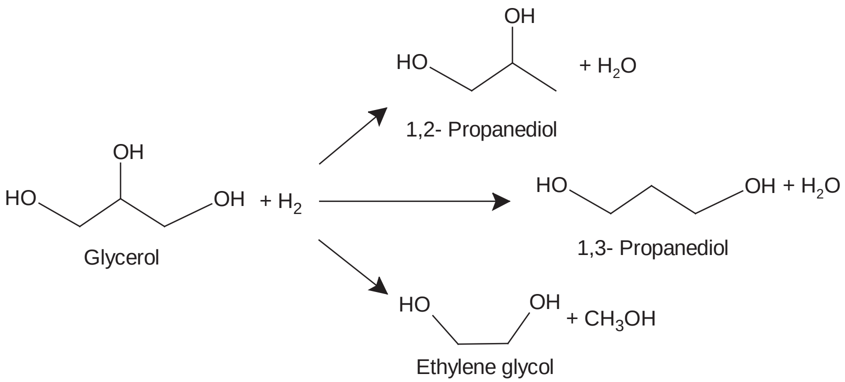

Figure 3.1 The conversion of glycerol to propylene and ethylene glycols.

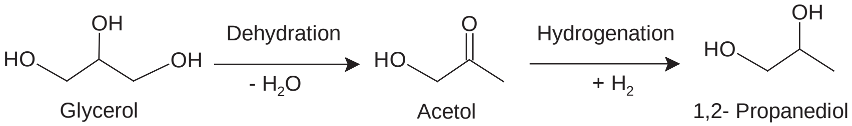

Figure 3.2 Reaction mechanism for conversion of glycerol to propylene glycol (reproduced from Ref 3, with permission).

propylene glycol from glycerol of vegetable origin.[2,3] The reaction pathway proceeds *via* an acetol (hydroxyacetone) intermediate, by means a two-step reaction process under mild conditions (Figure 3.2). In the first step glycerol is converted at 200 °C and 0.65 bar pressure in the presence of a copper chromite catalyst ($CuO.Cr_2O_3$) to relatively pure acetol. In the second step, the acetol is further hydrogenated to 1,2-propanediol at 200 °C and 13.8 bar hydrogen pressure using a similar catalyst.

The reaction has been shown to be a true reactive distillation (Figure 3.3).

Propylene glycol is obtained in >90% yield and at a significantly lower cost than by starting from petroleum.[4]

A screening study of catalysts (Figure 3.4, with $T = 200\,^\circ C$ and $P = 13.8$ bar) has shown that good selectivity for propylene glycol and high conversion is readily achieved using a copper chromite catalyst. Virtually pure propylene glycol is obtained from the autoclave. At temperatures above 200 °C the selectivity to propylene glycol decreases, due to excessive hydrogenolysis of the 1,2-propanediol.

Major problems were encountered when the reaction was conducted in a single step, for example the catalyst became coated with oligomers

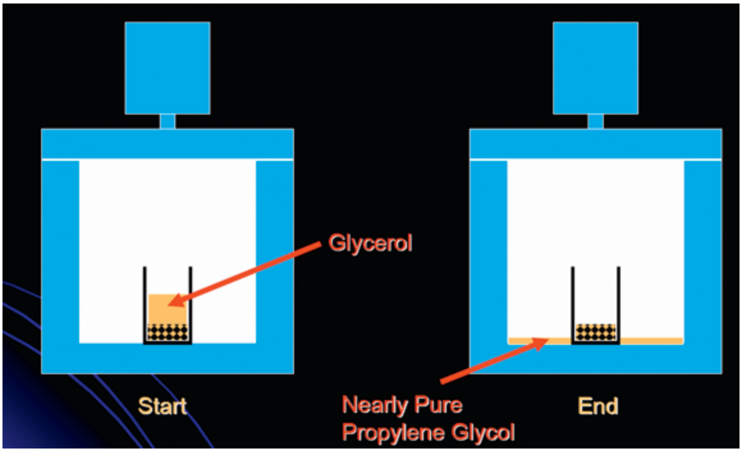

Figure 3.3 Early observation of the outcomes of glycerol hydrogenolysis over Cu–Cr catalyst showed that the process was actually a reactive distillation (reproduced from Ref. 4, with permission.)

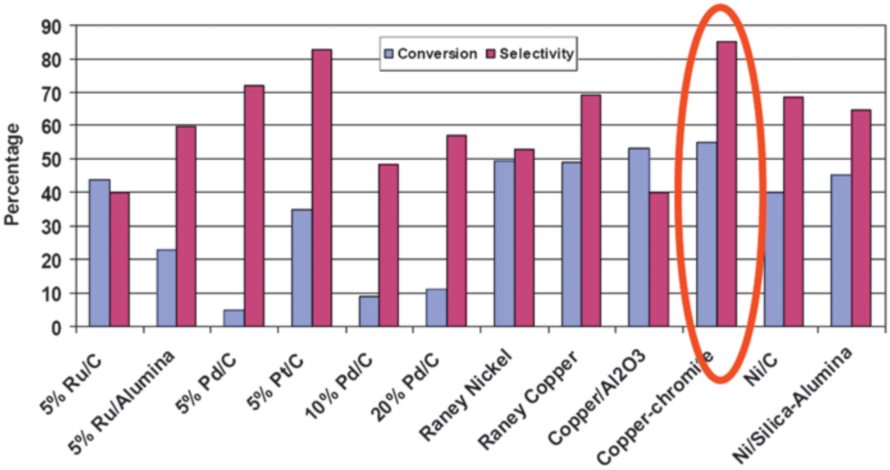

Figure 3.4 Commercial catalysts screened for use in glycerol hydrogenolysis (reproduced from Ref. 4, with permission).

and selectivity for propylene glycol greater than 80% was difficult to achieve. It was found, however, that if the reaction and separation steps were separated, *ca.* 99% yield of propylene glycol could be achieved. A feature of the process is that acetol and water are removed from the reaction mixture as they are formed (glycerol boils at 290 °C and acetol at 140 °C). In addition, the use of lower pressure during the first step prolongs the life of the catalyst. Further reduction of the acetol–water distillate (50 wt%) with hydrogen over a similar copper chromite catalyst at 185 °C and 13.8 bar gives 1,2-propylene glycol at >95% selectivity and 99% conversion.

There are two main advantages to the new process. Firstly, the copper chromite catalyst can be used to convert crude glycerol without further purification, whereas supported noble metal catalysts are readily poisoned by contaminants such as chlorides.[5] Secondly, the acetol formed as an intermediate is itself an important monomer, used industrially in the manufacture of polyols. When produced from petroleum acetol costs *ca.* $10 per kg, whereas by hydrogenolysis of glycerol it costs as little as $1 per kg, opening up yet further potential applications and markets for glycerol.

In addition, Davy Process Technology has developed a proprietary process in which the vapor-phase hydrogenation of glycerol over a heterogeneous copper catalyst yields 1,2-propanediol (Figure 3.5).[6]

Plant development is expected to proceed once 70 000 tonnes per annum of glycerol of reliable quality becomes available for processing at the right economics. Impressive selectivity for this product (>96%) has been reported using this catalyst system. Finally, BASF has patented a similar process for the preparation of 1,2-propanediol by hydrogenation of crude glycerol with high selectivity and low energy consumption, including that required, for example, for separating off the water. The process makes use of a copper-containing heterogeneous catalyst at a temperature between 100 °C and 320 °C and a pressure of 100–325 bar.[7] BASF intends to construct an initial industrial unit at Ludwigshafen with an annual capacity of 100 000 tonnes.

Bioglycerol can be converted to propylene oxide using an alkali-loaded silica catalyst at 44% conversion and 70% selectivity.[8] A propylene glycol molecule adsorbed on the surface of the catalyst is converted to an effective nucleophile by abstraction of the primary hydroxyl proton. This is followed by attack of the C^2 atom by the nucleophilic C^1–O^-, accompanied by dehydroxylation of the secondary OH group, to produce propylene oxide and water (Figure 3.6).

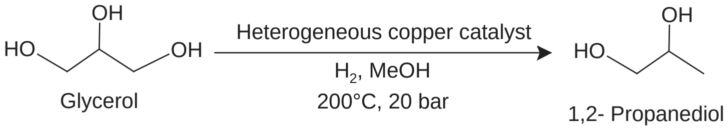

Figure 3.5 Davy method for production of propylene glycol by glycerol hydrogenation using a copper catalyst at 200 °C and hydrogen at 20 bar.

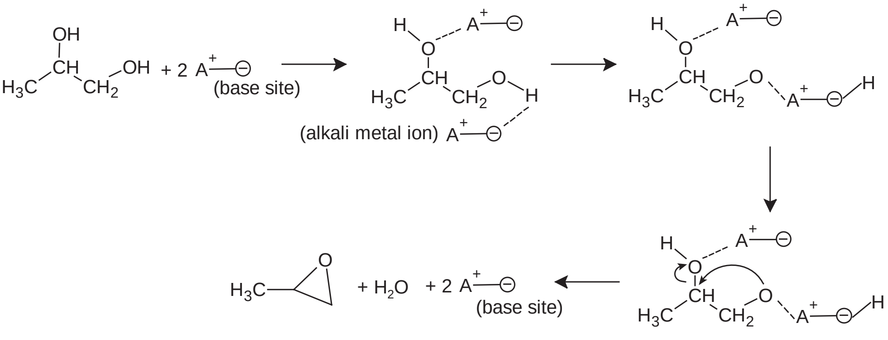

Figure 3.6 Plausible mechanism of PG intramolecular dehydration to PO over alkali-loaded silica catalysts (reproduced from Ref. 8, with permission).

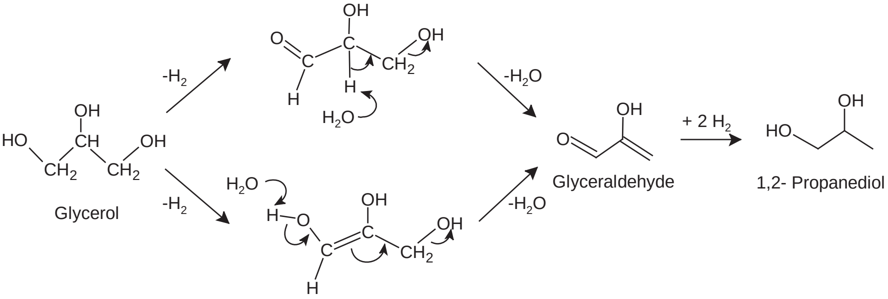

Figure 3.7 Reaction mechanism for conversion of glycerol to 1,2-propanediol over Raney copper (reproduced from Ref. 7, with permission).

A number of routes to propylene glycol are available from other renewable feedstocks. The most common of these is by hydrogenolysis of sugars or sugar alcohols at high temperature and pressure in the presence of a metal catalyst, producing propylene glycol and lower polyols. In spite of much research effort this potentially important reaction is so far limited to the laboratory scale. One drawback is the use of high temperatures and pressures, which necessitate expensive high pressure equipment and increased capital cost. Typically, hydrogen pressures between 100 and 325 bar and temperatures in the range 200–350 °C are used, and the selectivity towards propylene glycol is in general low. For example, the hydrogenolysis of glycerol under hydrogen at 300 bar and 260 °C in the presence of Raney nickel or Ru, Rh or Ir catalysts yields mainly methane, but in the presence of Raney copper, 1,2-propanediol is the primary product (Figure 3.7).

Similarly, poor yields are obtained by hydrogenolysis of glycerol using heterogeneous metal (Cu, Pd, Rh) catalysts in a range of solvents (*e.g.*, water, sulfolane or dioxane) under hydrogen at 80 bar pressure and 180 °C, with additives to improve the reaction rate and selectivity.[9] The best selectivity (100%) for 1,2-propanediol, obtained by hydrogenolysis of an aqueous solution of glycerol in the presence of CuO–ZnO catalysts, also gives a low yield. Similarly, hydrogenolysis of glycerol over a Ni–Re catalyst over 4 h at 230 °C under hydrogen at 82 bar yields 44% 1,2-propanediol and 5% 1,3-propanediol, along with 13% ethylene glycol.[10]

In 1985 Celanese patented the hydrogenolysis of an aqueous glycerol solution under 300 bar of syngas at 200 °C in the presence of a homogeneous rhodium complex $[Rh(CO)_2(acac)]$ and tungstenic acid, producing 1,3- and 1,2-propanediol in 20% and 23% yield, respectively.[11] Shell developed the use of a homogenous palladium complex in a water–sulfolane mixture in the presence of methanesulfuric acid. After 10 h reaction, 1-propanol, 1,2-propanediol and 1,3-propanediol were present in the ratio 47 : 22 : 31.[12] A series of recent investigations into glycerol hydrogenolysis using Ru–C,[13] $Rd–SiO_2$[14] and an ion-exchange resin (Amberlyst) at 120 °C and hydrogen at 80 bar was aimed at dehydration of glycerol to acetol, catalyzed by the acidic resin, and subsequent hydrogenation of acetol on the metal catalyst; this showed that neither catalyst was sufficiently selective and a variety of products (1-propanol, 2-propanol, ethylene glycol, propylene glycol and degradation products) were isolated. Finally, an additional drawback of these processes is the use of a dilute solution of glycerol for the reaction. Concentrations of glycerol as low as 10–30 wt% are predominantly used, and are further diluted by the water formed in the reaction. This reduces the average space–time yield of the reaction, increasing the energy consumption of the process and in turn decreasing its viability.

3.3 Dehydroxylation to 1,3-Propanediol

1,3-Propanediol (PDO) is currently produced from petroleum derivatives such as ethylene oxide, using chemical catalysts developed by Shell (the Shell route).[15] DuPont, on the other hand, has recently replaced the older acrolein (Degussa–DuPont) route[16] with a biological process starting from glucose, based on genetically engineered *Escherichia coli*.[17] The polyester fiber formed has been described as the "new nylon"[18] and is suitable for carpets and other textiles, since it possesses a unique combination of chemical resistance, light stability, elastic recovery and dyeability.

In 2003 a classical synthetic approach to the production of PDO from glycerol *via* selective dehydroxylation was reported.[19] The process selectively transforms the central hydroxyl group of glycerol into a tosyloxyl group and then removes the transformed group by catalytic hydrogenolysis. The method consists of three steps: acetalysation, tosylation, and detosyloxylation. Compared to the hydroxyl group, the tosyloxyl group is a better leaving group and is easier to replace with a hydride ion. The first step in the conversion of glycerol to 1,3-propanediol is to acetalize the glycerol with benzaldehyde. Its purpose is to protect the first and third hydroxyl groups of the glycerol so that only the center group is tosylated in the second step.

The condensation between glycerol and benzaldehyde is an equilibrium reaction, but it can be driven to completion by removing the water formed. The second step of the conversion is tosylation of the unprotected hydroxyl group of the acetalysed glycerol to transform it into a good leaving group. The final step of the conversion is detosyloxylation, either preceded or followed by a hydrolysis reaction. The detosyloxylation reaction removes the tosylated central hydroxyl group, while the hydrolysis reaction deprotects the first and third hydroxyl groups. The detosyloxylation reaction shown in Figure 3.8 essentially involves hydrogenolysis. According to the proposed conversion approach, this reaction is accomplished using molecular hydrogen in the presence of a transition metal catalyst.

3.4 Biological reduction to PDO

Glycerol can serve as a feedstock for the fermentative production of PDO. The fermentation uses bacterial strains from the groups *Citrobacter*, *Enterobacter*, *Ilyobacter*, *Klebsiella*, *Lactobacillus*, *Pelobacter* and *Clostridium*. The harmless microorganism *Clostridium*, widely disseminated in nature, was shown to convert glycerol to PDO as early as 1881,[20] and has been widely investigated due to its appreciable substrate tolerance and the yield and productivity of the process. In each case glycerol is converted to PDO in a two-step, enzyme-catalyzed reaction sequence. In the first step a dehydratase catalyzes the conversion of glycerol to 3-hydroxypropionaldehyde (3-HPA) and water (Equation 3.1). In the second step 3-HPA is reduced to PDO by a NAD^+-linked oxidoreductase (Equation 3.2). The 1,3-propanediol is not metabolized further and as a result it accumulates in the medium. The overall reaction consumes a reducing equivalent in the form of a cofactor, reduced beta-nicotinamide adenine dinucleotide (NADH), which is oxidized to

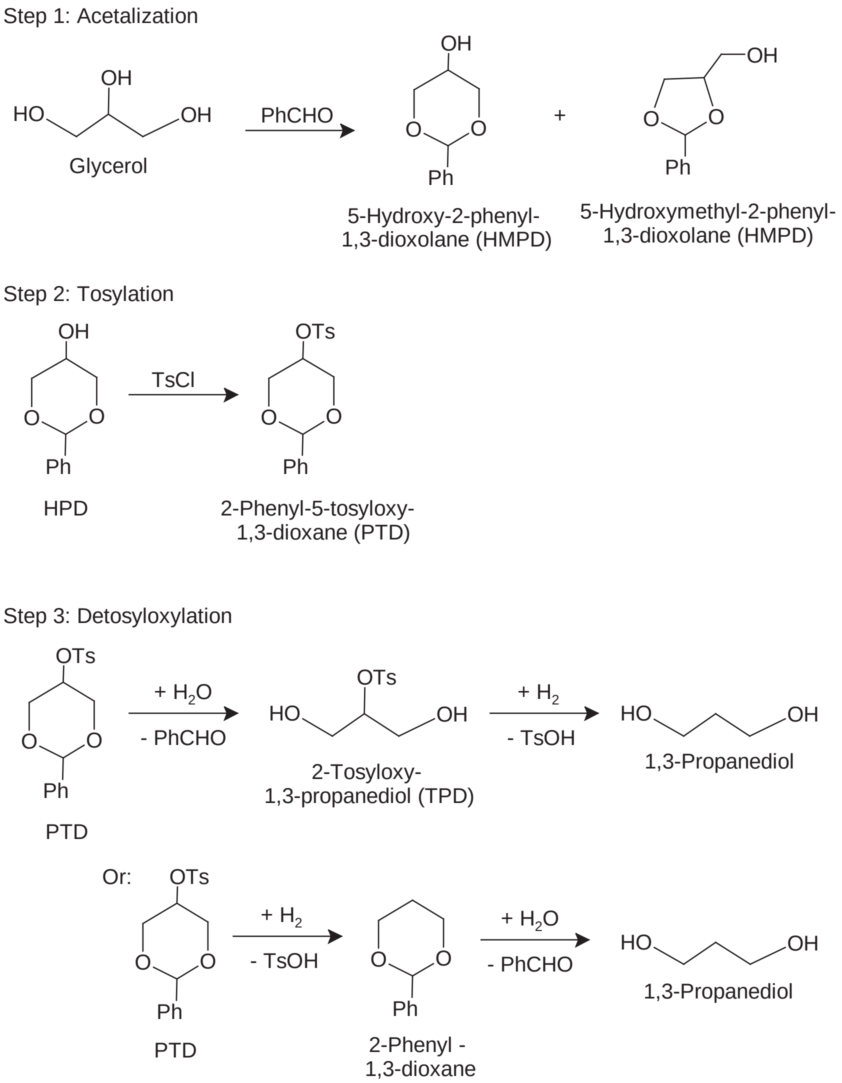

Figure 3.8 Glycerol hydrogenolysis to 1,3-PDO using a protection–deprotection approach (reproduced from Ref. 17, with permission).

Figure 3.9 Integrated production of PDO from glucose and glycerol is being developed in China.

nicotinamide adenine dinucleotide (NAD^+, Equation 3.3).

$$\text{Glycerol} \rightarrow \text{3HPA} + H_2O \tag{3.1}$$

$$\text{3HPA} + \text{NADH} + H^+ \rightarrow \text{PDO} + \text{NAD}^+ \tag{3.2}$$

$$\text{Glycerol} + \text{NAD}^+ \rightarrow \text{DHA} + \text{NADH} + H^+ \tag{3.3}$$

The biological process for the production of PDO has a low metabolic efficiency and uses the relatively expensive glycerol.[21] A less costly method has been developed in China, starting from glucose rather than glycerol. It combines the pathway from glucose to glycerol and the bacterial route from glycerol to PDO (Figure 3.9).[22]

However, under certain conditions, the classic technique based on glycerol can be attractive from both the technical and economic aspect. Extensive screening of new microorganisms and improved process design (fed-batch with pH-controlled substrate dosage) has allowed the product concentrations, which were relatively low at a maximum of 70 to 80 $g\,L^{-1}$ as a result of product inhibition, to be increased to over 100 $g\,L^{-1}$.[23] An additional advantage of this technique and the new bacterial strains isolated is the utilization of low-priced crude glycerol or aqueous glycerol solutions. This is a factor which should not be underestimated, since it has a direct effect on the product cost. A further development is the use of immobilized rather than freely suspended cells, which enables an increase in productivity from about 2 g to 30 g PDO ($L^{-1}\,h^{-1}$). A comparison of existing chemical techniques with the new biotechnical approach, based on different substrates and glycerol qualities (and therefore costs), shows that biotechnology could become a competitive technique if crude glycerol was used.

3.5 Commercial Applications

The position of glycerol as a polyol meant that until the early 2000s it competed in price with other polyols available in the market (Figure 3.10).[24]

As mentioned earlier, conversion of crude glycerol to PDO has resulted in an antifreeze product comprising 70% propylene glycol and 30% glycerol, which can be produced, refined and marketed directly using existing biodiesel facilities.[25] Renewable Alternatives was the first company to focus on creating an antifreeze based on glycerol mixtures with propylene glycol. Indeed, propylene glycol-based antifreezes are already competing with those based on ethylene glycol, all of them approved and ready to use. Products containing propylene glycol are

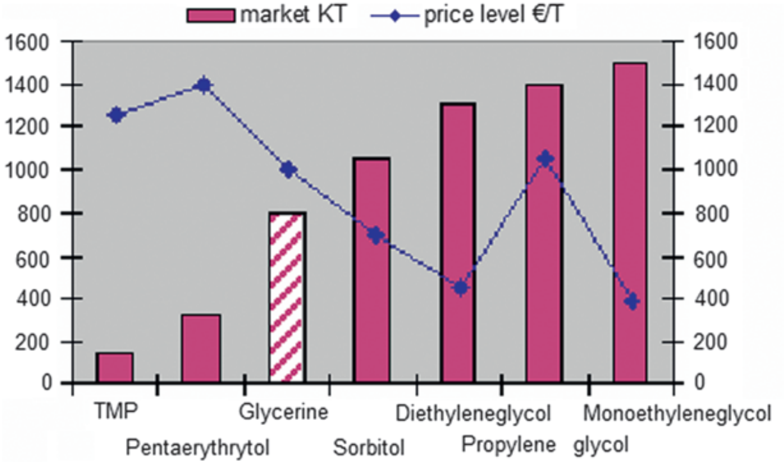

Figure 3.10 Price relationship between glycerol and other polyols in relation to market size (source: Novaol, May 2002; data given in kilotonnes).

slightly more expensive, but the new process will bring the price down and make it the preferred choice. There is also a significant environmental advantage since ethylene glycol, currently in almost universal use, is toxic whereas propylene glycol is not.

However, pressing commercial considerations compelled Renewable Alternatives to aim to produce propylene glycol in a pure condition. As a result, the reactive distillation process now achieves greater than 99.8% purity, which means that the product can be used both as an industrial feedstock and as an antifreeze. Indeed, the practical advantages of the reactive distillation approach are numerous:

- low water content of the feed (70–80%);
- low pressure (200 psi);
- high selectivity (>90%);
- high atom economy (>90%); and
- low-cost catalyst.

Propylene glycol is a major commodity chemical traditionally derived from propylene oxide (and hence from petroleum), with an annual global demand estimated to be between 1.18 and 1.58 billion tonnes.[26] By early 2007 it was selling at about \$1.8 per kg, with a 4% annual growth in market size. However, the steeply increasing petroleum crude oil price has caused the price of propylene oxide to escalate by a factor of four between 2005 and 2008, with a subsequent fall and further rise in 2009. The largest derivative of PO is polyether polyols, taking about

60–70% of PO demand. In general, world demand for polyols is growing at about 5% per annum.[27] Typical uses for propylene glycol are unsaturated polyester resins, functional fluids (antifreeze, de-icing and heat transfer), pharmaceuticals, foodstuffs, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care products, paints and animal feeds.

The first 30 000 tonne/year facility to produce PG from biodiesel-derived glycerol was established in south-east USA, where Senergy Chemical, a consortium of propylene glycol consumers and manufacturers, licensed the Suppes process and built a new plant in 2008.

Another glycerol hydrogenolysis process in course of commercialization has been developed in the UK by Davy Process Technology, a Johnson Matthey company (Figure 3.11). Davy is using its new glycerol to propylene glycol process in a joint venture with biodiesel manufacturer Ashland–Cargill. The new company began producing 65 000 tonnes per annum of propylene glycol at a European location in early 2009.[28]

In the Davy process glycerol is reacted with hydrogen over a heterogeneous copper catalyst under relatively moderate conditions (20 bar, 200 °C). The glycerol, together with a recycle stream, is vaporized in a recirculating stream of hydrogen, typically from a pressure-swing adsorption unit. Glycerol conversion is around 99%, and by-products are removed by distillation. The refining process shown in Figure 3.11 delivers propylene glycol at high purity (the water produced in the reaction is high enough in quality for biological treatment). The propylene glycol in fact meets the specification required for producing unsaturated polyester resins and functional fluids, and pharmaceutical grade material can also be produced if required. The relatively small by-product streams are of high quality and can be used as solvents or, in the case of mixed glycols, in functional fluids.

Finally, Dow in 2007 began production of propylene glycol from glycerol at a Haltermann plant in Texas with a pilot-scale facility of

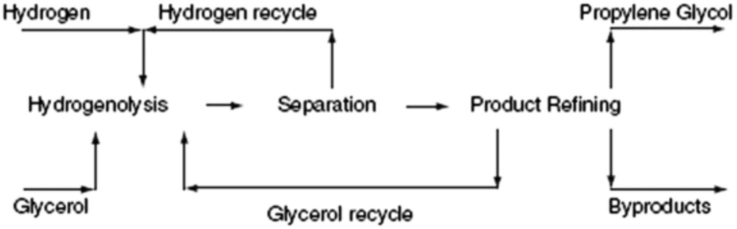

Figure 3.11 Glycerol hydrogenolysis process to propylene glycol developed by Davy in the UK (reproduced from Ref. 25, with permission).

about 15 000 tonnes per annum. However, the company dropped its initial plans for larger-scale production of renewable PG due the high price of glycerol in 2008 at a time when US vegetable glycerol rose to over $330 per kg, against March 2007 contract prices averaging $120 per kg.[29]

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CHAPTER 4

Chlorination

4.1 Chlorination of Glycerol

Studies of glycerol halogenation focus on the formation of 1,3-dichloro-2-propanol, an intermediate in epichlorohydrin synthesis, by direct hydrochlorination. This is produced along with the 1,2-isomer (Figure 4.1).

1,3-Dichloro-2-propanol (α,γ-chlorohydrin) is the isomer of choice because epichlorohydrin, formed by its dehydrochlorination, is so important commercially. By condensation with a polyol such as bisphenol A epichlorohydrin enables a linear structure to be conserved in the ether polymers obtained from it, including the commercially important epoxy resins (Figure 4.2).

Liquid epoxy resins are used in marine, protective, automotive, housing and can coatings and in many other applications.[1] Epoxy resins are applied with over 400 000 tonnes of curing agents annually to produce an estimated 3 million tonnes of products, worth over $20 billion.[2] Epichlorohydrin is also employed for water purification and as a reinforcement agent for paper, for instance in the food industry in the manufacture of tea bags and coffee filters. Epichlorohydrin is however carcinogenic, and its use in food applications should ideally be avoided.

In addition, epichlorohydrin is used in the pharmaceutical industry as a starting point for the synthesis of glycerol monochlorohydrin (1-chloro-2,3-propanediol), employed in the manufacture of products such as cough mixtures. Epichlorohydrin has traditionally been obtained indirectly by the high-temperature reaction of propene (propylene) with chlorine followed by hydrolysis. Annual production in

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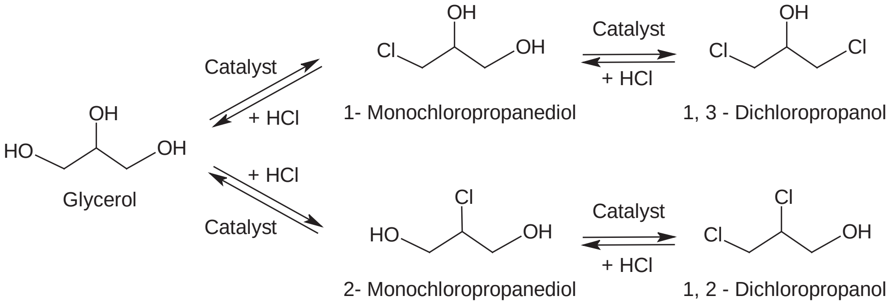

Figure 4.1 Non-selective hydrochlorination of glycerol yields 1,3-dichloro-2-propanol and 1,2-dichloro-3-propanol. Water is a by-product of the reaction.

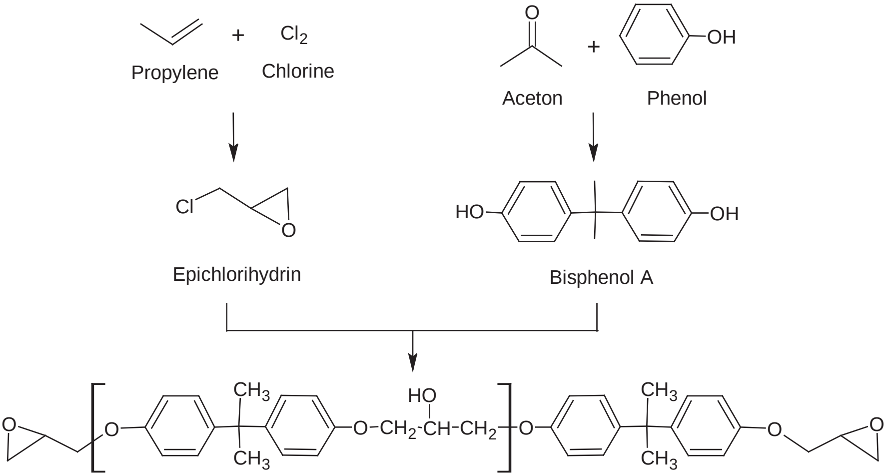

Figure 4.2 Manufacturing process for bisphenol A-based epoxy resins.

2009, the year of the worst post-war recession on record, was around 900 000 tonnes. The first step (Figure 4.3) yields a mixture of 30% 1,2-dichloropropanol and 70% 1,3-dichloropropanol.

The high percentage of 1,2-dichloropropanol formed requires further conversion to the 1,3-isomer, which slows down the process. The overall yield is 97% but large amounts of wastewater are produced, contaminated with chlorinated by-products such as 1,2- and 1,3-dichloropropane, 1,2,3-trichloropropane, penta- and hexachlorohexane, in addition to 1,3- and 1,2-dichloropropanol. Dow Chemical, for instance, produces annually 45 000 tonnes of wastewater using this traditional process (Figure 4.4).[2]

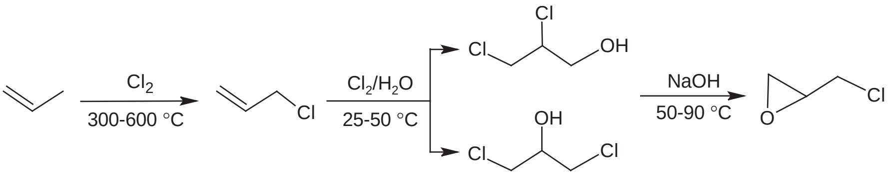

Figure 4.3 The traditional industrial process for epichlorohydrin ("epi" in the industry jargon) based on high temperature chlorination of propene.

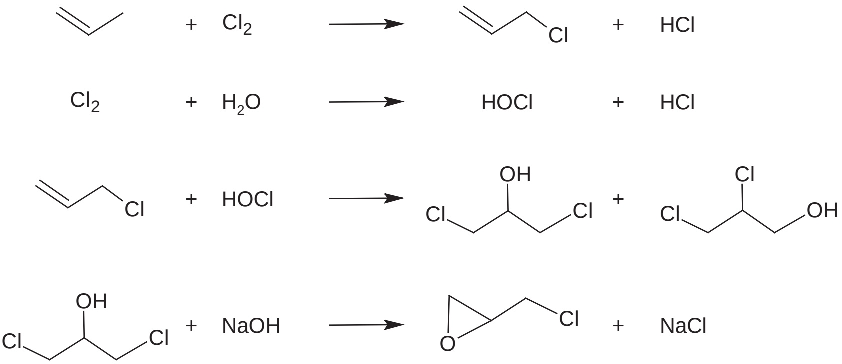

Figure 4.4 In the dominant commercial route to epichlorohydrin starting from propene, of the four equivalents of chlorine atoms employed, only one is retained in the desired product, the remaining three equivalents appearing as by-product HCl or waste chloride ion (reproduced from Ref. 11, with permission).

Described as early as 1931, the alternative process employing hydrochlorination of glycerol had low selectivity and very poor productivity. It involved reaction of glycerol with aqueous hydrochloric acid in the presence of acetic acid as catalyst at a temperature of 80–100 °C. The initial chlorination gave primarily 1-monochloropropanediol and water, along with small quantities of 2-monochloropropanediol. This was followed by a second chlorination, from which 1,3-dichloropropanol was obtained, with modest quantities of 1,2-dichloropropanol as by-product.

A number of later patents describe biphasic processes using water and an organic solvent, in which 1,3-dichloropropanol is rendered soluble by performing the reaction at the boiling point of the mixture; the actual temperature varies according to the particular solvent used.[3] All the traditional processes starting from glycerol have significant drawbacks, including the loss of the acetic acid catalyst during the reaction due to its low boiling point, slowing of the reaction caused by the introduction of water into the reaction mixture in the form of aqueous HCl, and difficulty in recovering the α,γ-chlorohydrin from the reaction mixture.

4.2 Production of Epichlorohydrin

In the traditional process for manufacturing "epi" from propene, only one of the four chlorine atoms involved is retained in the product molecule, the remainder forming hydrogen chloride or waste chloride anion (see Figure 4.4).

The new two-step route to epichlorohydrin employs glycerol of natural origin as feedstock, and comprises initial hydrochlorination of glycerol with hydrogen chloride to give a 30–50 : 1 mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, followed by reaction with a base. Only one equivalent of waste chloride is produced (Figure 4.5).

The conversion starts from either pure or raw glycerol and uses gaseous anhydrous hydrogen chloride in the presence of an organic acid catalyst of low volatility to produce 1,3-dichloro-2-propanol; dehydrochlorination using sodium hydroxide generates epichlorohydrin. The industrial process also employs a system for the continuous removal of the reaction water to improve the efficiency and economy of the process.[4]

The use of hydrogen chloride in the gaseous phase rather than in aqueous solution avoids the introduction of water, which has a negative effect on the reaction balance. As an alternative to acetic acid, the use of catalysts based on carboxylic acids having 3 to 10 carbon atoms and boiling point above 120 °C, compensates for the loss of catalyst due to the reaction temperature, which is close to the boiling point of acetic acid; the concentration of catalyst thus remains constant during the

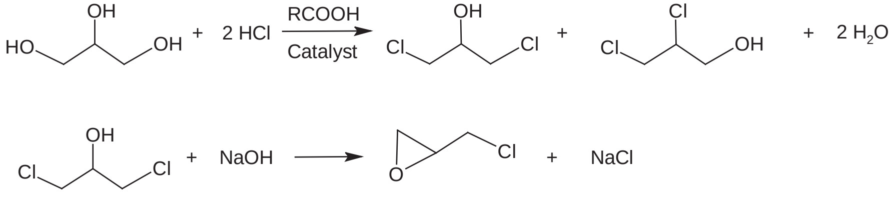

Figure 4.5 In the new glycerol-based route to epichlorohydrin which employs renewable glycerol as feedstock, only one equivalent of waste chloride is produced in a two-step process comprising initial hydrochlorination of glycerin with hydrogen chloride to give a 30–50 : 1 mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, followed by reaction with NaOH (reproduced from Ref. 11, with permission).

reaction. The α,γ-dichlorohydrin is separated, together with the water of reaction, for example by performing the reaction in a continuous stream of hydrogen chloride with stripping, since the α,γ-dichlorohydrin is much more volatile than glycerol or its monochlorohydrins. The reaction temperature is controlled between 80 °C and 180 °C and the pressure of gaseous hydrogen chloride is below 5 bar. The hydrogen chloride pressure has a positive effect on the reaction rate but hinders the stripping of the products; a reasonable compromise is to operate within the range 1 to 5 bar. As an example, anhydrous glycerol and malonic acid (8 mol% based on glycerol) are loaded into the reactor and the temperature increased to 120 °C. Under normal conditions a stream of hydrogen chloride gas is introduced at the rate of 50 L h^{-1}. As the reaction proceeds the products are removed, and after 1 h the glycerol has been completely converted. The desired dichlorohydrin isomers are obtained in 76.5% yield, the remainder being predominantly the monochlorohydrin (Figure 4.6).

The three-step reaction mechanism shown in Figure 4.7 involves a rate-determining esterification step *via* nucleophilic substitution on the

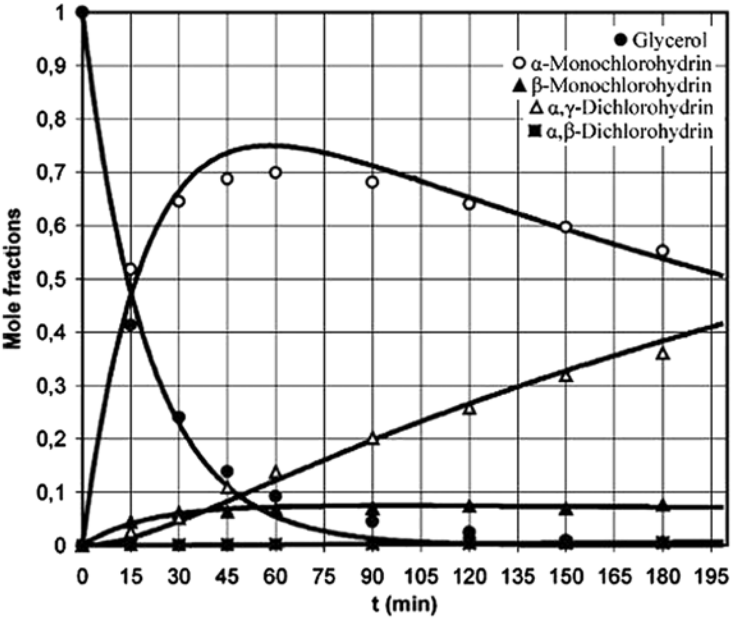

Figure 4.6 Evolution of the composition of a reaction mixture of glycerol and HCl with malonic acid as catalyst at $t = 120$ °C. Comparison between the experimental data and the model behavior is also shown (reproduced from Ref. 5, with permission).

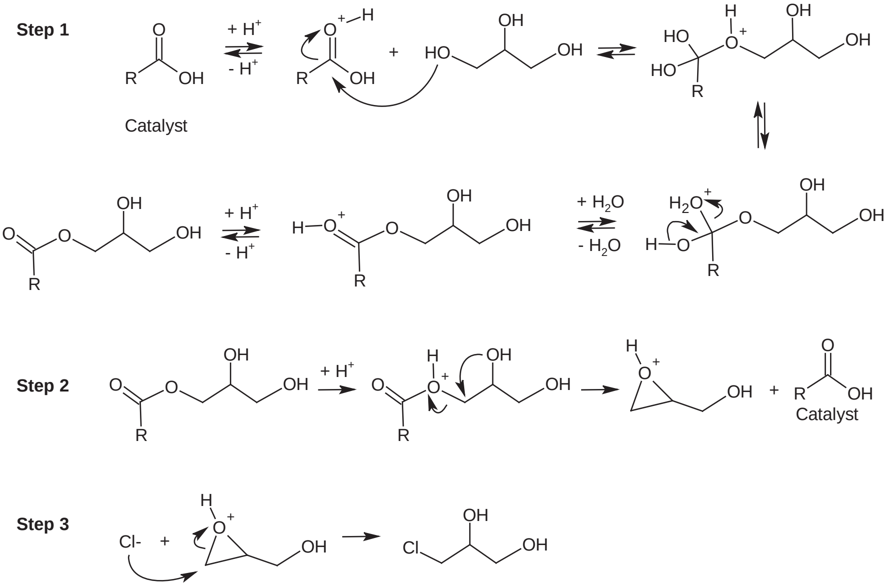

Figure 4.7 The three-step reaction mechanism for glycerol chlorohydrin formation *via* hydrochlorination, explaining the observed reaction path (reproduced from Ref. 5, with permission).

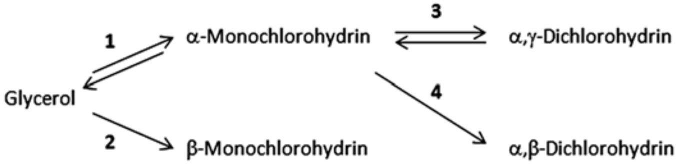

Figure 4.8 Reaction path for hydrochlorination of glycerol (reproduced from Ref. 5, with permission).

acylic carbon with formation of water (**1**), followed by the formation of an oxonium group through alkyl-oxygen bond scission and carboxylic acid release (**2**), and the subsequent formation of the chlorohydrin by chloride addition to either the α- or β-carbon atom (**3**).[5]

This reaction mechanism explains why the formation of glycerol-α-monochlorohydrin is always higher than that of the β-isomer. Since the latter species cannot react further its concentration increases slightly during the reaction until all the glycerol has been consumed, and it then remains almost constant. On the other hand the α-monochlorohydrin is able to undergo a second chlorination by a similar mechanism, giving glycerol-α,γ-dichlorohydrin (Figure 4.8).

The entry of the first chlorine atom in glycerol-α-monochlorohydrin favors the attack of the second chlorine in the γ-position due to an induction effect. Calculations show that substitution by the second chlorine in the γ-position is 7.4 times slower than the first chlorination, whereas attack by the second chlorine in the β-position is 510 times slower than the first chlorination.

Santacesaria and co-workers have recently identified the optimal operative conditions for the chlorination of glycerol using gaseous HCl to obtain 1,3-dichlorohydrin, followed by epichlorohydrin. They have studied the effectiveness of different catalysts, the reaction kinetics, the effect of catalyst concentration and HCl pressure, and the vapor–liquid phase equilibria within the reaction environment, all of which provide useful pointers for the design of an industrial plant.[6]

4.3 Industrial Applications

In 2007 Solvay, a traditional glycerol and epichlorohydrin manufacturer, was the first to start production of epichlorohydrin from glycerol, at their 10 000 tonne plant in France. Glycerol was obtained from a French source as a by-product of the manufacture of biodiesel from rapeseed oil. In the early 2000s Solvay was facing an economically unsustainable situation in the production of chlorinated organics due to soaring propylene prices, which had increased by a factor of four since 1999 with a resulting fall in the price of glycerol. The company therefore halted production of synthetic glycerol from epichlorohydrin in 2005, aiming to reverse the procedure by converting the plant to produce epichlorohydrin from glycerol (Figure 4.9).

The proprietary process is again based on organic acid catalysts. Optimal reaction occurs using anhydrous hydrochloric with 30 mol% caprylic acid as catalyst at above 120 °C, which ensures that only a limited fraction (10%) of the catalyst evaporates from the reactor.[7] Figure 4.10 shows the plots of the hydrogen chloride gas absorbed by 3 mol% carboxylic acid in glycerol at 100 °C and 7.6 bar HCl pressure in the analogous glycerol-to-epichlorohydrin hydrochlorination process.[8] This clearly demonstrates that it is the steric bulk of the catalyst that largely determines the catalyzed rate of hydrochlorination of glycerol.

In order to avoid corrosion of the coated steel reaction vessel, the manufacture of dichloropropanol is conducted while maintaining the inner wall of the vessel lying above the level of the liquid at a temperature of 120 °C, at which corrosion of the enamelled steel

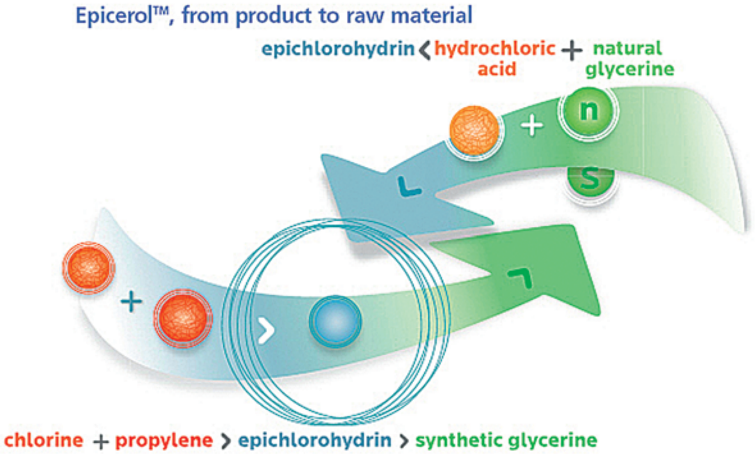

Figure 4.9 Hydrochlorination of glycerol reverses the traditional manufacturing process for glycerol from epichlorohydrin (reproduced from the Solvay website, with permission).

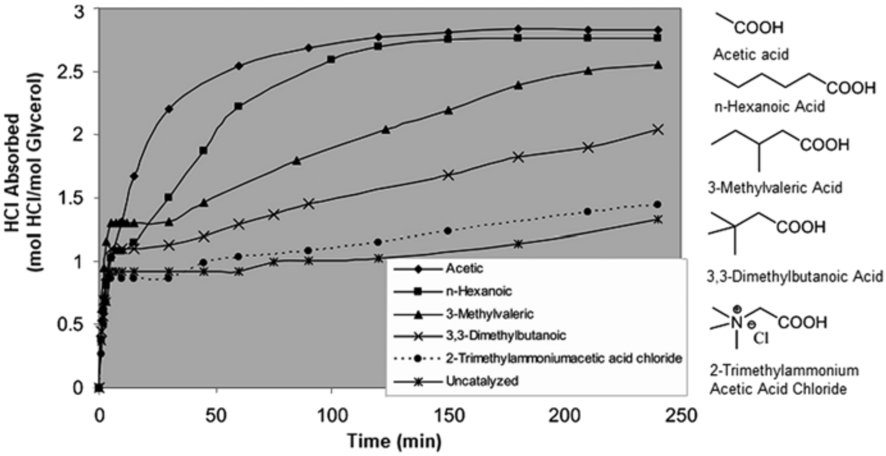

Figure 4.10 As the carboxylic acid catalyst becomes more sterically hindered, the rate of HCl uptake from glycerol declines, suggesting that steric hindrance slows the reaction (reproduced from Ref. 11, with permission).

is minimized.[9] In the subsequent step, producing epichlorohydrin by dechlorination with NaOH, the aqueous fraction rich in NaCl can be recovered and used for the production of chlorine by electrolysis. The fraction rich in water is recycled to provide the aqueous solution needed for hydrodechlorination. This new glycerol-based process shows crucial advantages over the existing propene route:

- it does not require a solvent;
- the size of the reactors can be reduced, thanks to higher selectivity;
- the kinetics are much faster;
- hydrogen chloride is consumed rather than produced;
- chlorine consumption is reduced by 50% and water by 70%; and
- chlorinated residues are reduced by 80%.

Moreover, the process can run either batch-wise or continuously. The company initially planned further investment in a 100 000 tonne epichlorohydrin unit on its integrated site at Map Ta Phut, Thailand, but at the end of 2009 the project was sold to a Thai producer of chlorine and polyvinyl chloride. The start-up of the plant is anticipated towards the end of 2011, as local authorisation has already been granted and the detailed engineering contract signed.[10]

In addition, Dow Chemical has announced the construction of a large glycerol-to-epichlorohydrin plant in China, with production starting in 2010. The company has selected the Shanghai Chemical Industry Park for a 150 000 tonne plant.[11] In this case glycerol will be purchased from local producers of biofuels, which in China are typically obtained from rapeseed and palm oils. Dow has also decided to build a 100 000 tonne liquid epoxy resin plant at the Shanghai location. The Dow production facility will reduce wastewater by more than 70% compared to conventional propylene-based technology and will almost completely avoid the formation of organic by-products.

Again, Dow's glycerol-to-epichlorohydrin process is based on acetic acid-catalyzed hydrochlorination and offers similar advantages to the processes listed above, including fast reaction kinetics, the ability to produce a more concentrated glycerol dichlorohydrin stream, high regioselectivity to 1,3-dichloro-2-propanol, and the formation of very low levels of RCl-type by-products, which reduces environmental and energy costs.[12] The conversion proceeds in two steps. In the first, glycerol is hydrochlorinated using anhydrous hydrogen chloride at 8.2 bar and 120 °C for 90 min, with glacial acetic acid as catalyst. This process yields a mixture of l,3-dichloropropan-2-ol (95.3 wt%) and 2,3-dichloropropan-l-ol (2.6 wt%), with trace amounts of 2-acetoxy-l,3-dichloropropane (0.7 wt%) and l-acetoxy-2,3-dichloropropane (0.1 wt%). Importantly, there is no formation of the highly toxic trichloropropanol, and the glycerol is converted completely. In the second step, the mixture of dichlorohydrins is converted to epichlorohydrin in the presence of a base. In effect, this solventless process can be regarded as an economically and environmentally advantageous, atom-efficient process for an existing commodity chemical, employing a renewable source for its primary feedstock.

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CHAPTER 5

Dehydration

5.1 Dehydration of Glycerol

Two important chemicals can be produced directly by dehydration of glycerol: acrolein and 3-hydroxypropionaldehyde (3-HPA). In addition, oxydehydration of glycerol gives the commercially important acrylic acid. Acrolein is currently produced by the oxidation of propylene. However, as mentioned in Chapter 4, the price of propylene has fluctuated widely over the past ten years, initially increasing by a factor of four between 2005 and 2008 before falling again, and making the production of acrolein from the less expensive glycerol commercially attractive.

Starting from acrolein a number of end-products can be targeted, including plastics monomers, mono-alcohols and energy gases such as propane. All such chemicals have extensive markets but account for no more than a fraction of the glycerol currently available, and therefore have little impact on its cost. By developing multifunctional catalysts, which are able to perform more than one task at the same time, synergies can be obtained which are not possible with conventional catalysts. For instance, by combining catalyst functionalities, reactions that are both endothermic and exothermic can be conducted simultaneously. This allows lower inlet reactor temperatures and more uniform temperature distribution.[1]

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5.2 Dehydration to Acrolein

Older processes for converting glycerol to 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 (Figure 5.1) which makes use of solid acid catalyst ZSM-5 zeolite.[2]

The catalyst and reaction products are separated, and the catalyst is continuously regenerated. The method has a number of advantages because:

- it can process glycerol solution in any concentration;
- it does not need a co-solvent to carry out the reaction; and
- 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 within the process, generating the heat necessary for the process, including water vaporization.

Acrolein can be oxidized to acrylic acid and further polymerized to give acrylic resins (Figure 5.2), and it also forms the basis of superabsorbent polymers, widely employed for instance in the baby hygiene market.[3]

In general, dehydration to acrolein is carried out under acidic conditions since when glycerol is protonated the energy barrier for

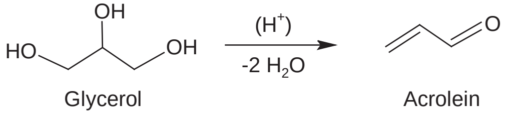

Figure 5.1 Acid-induced dehydration of glycerol to acrolein proceeds smoothly at 250–340 °C over a heterogeneous acidic catalyst.

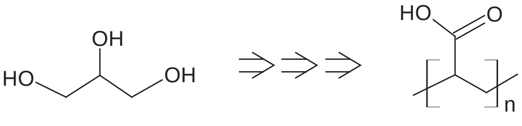

Figure 5.2 Acrolein produced from glycerol is further oxidized to acrylic acid, which can in turn be polymerized to poly(acrylic acid).

dehydration is greatly reduced, falling from about 60 to 20 kJ mol^{-1} (Figure 5.3).[4]

Recently, in an optimized small-scale experiment over 60 h on an acidic catalyst, the reaction gave a yield of 90%. As a general rule the hydration reaction is favored at low temperatures and the dehydration reaction at higher temperatures. To obtain acrolein it is thus necessary to use a sufficiently high temperature, and/or partial vacuum, to shift the reaction towards dehydration. The reaction may be performed in the liquid or the gaseous phase and is catalyzed by acids.

Acrolein is an explosive and toxic chemical whose handling requires the highest safety standards (Figure 5.4).

Its most significant direct application is as a herbicide for the control of aquatic plants. It kills plant cells by the destruction of cell membrane integrity, and additionally due to its affinity for sulfhydryl groups, which causes the denaturation of vital enzymes. Furthermore, it is used in the manufacture of 3-methylthiopropionaldehyde (MMP), a precursor (by reaction with HCN) of methionine, an essential amino acid required by animals to satisfy the nutritional requirements for proper growth, health and reproduction.

In the mid-1990s Degussa introduced a method based on the dehydration of glycerol on solid acidic catalysts.[5] For example, reacting a gaseous glycerol–water mixture, with a glycerol content of 10 to 40 wt%, at 250 to 340 °C on a solid acidic catalyst with a Hammett acidity function (H_0 value) below 2, resulted in complete conversion of the glycerol to acrolein. In this process, however, the dehydration of glycerol to acrolein is accompanied by side-reactions giving by-products such as hydroxypropanone, propanaldehyde, acetaldehyde, acetone, adducts of acrolein with glycerol, glycerol polycondensation products and cyclic glycerol ethers. These cause the formation of coke on the catalyst, resulting in its deactivation, reduction in yield and in selectivity towards acrolein. By-products present in the acrolein such as hydroxypropanone or propanaldehyde are difficult to remove and necessitate separation and purification steps which increase the cost of the purified acrolein. Moreover, it is necessary to regenerate the catalyst regularly in order to maintain its activity. As a result, the process has not been commercialized, and the oxidation of propylene with a mixed Bi–Mo oxide catalyst is more economically attractive. In practice, the technique used for manufacturing acrolein is normally based on the oxidation of propylene derived from petroleum.[6]

An improved process for manufacturing acrolein uses the gas-phase dehydration of glycerol over solid catalysts with H_0 between -9 and -18.[7] Such catalysts are more active and are less quickly deactivated,

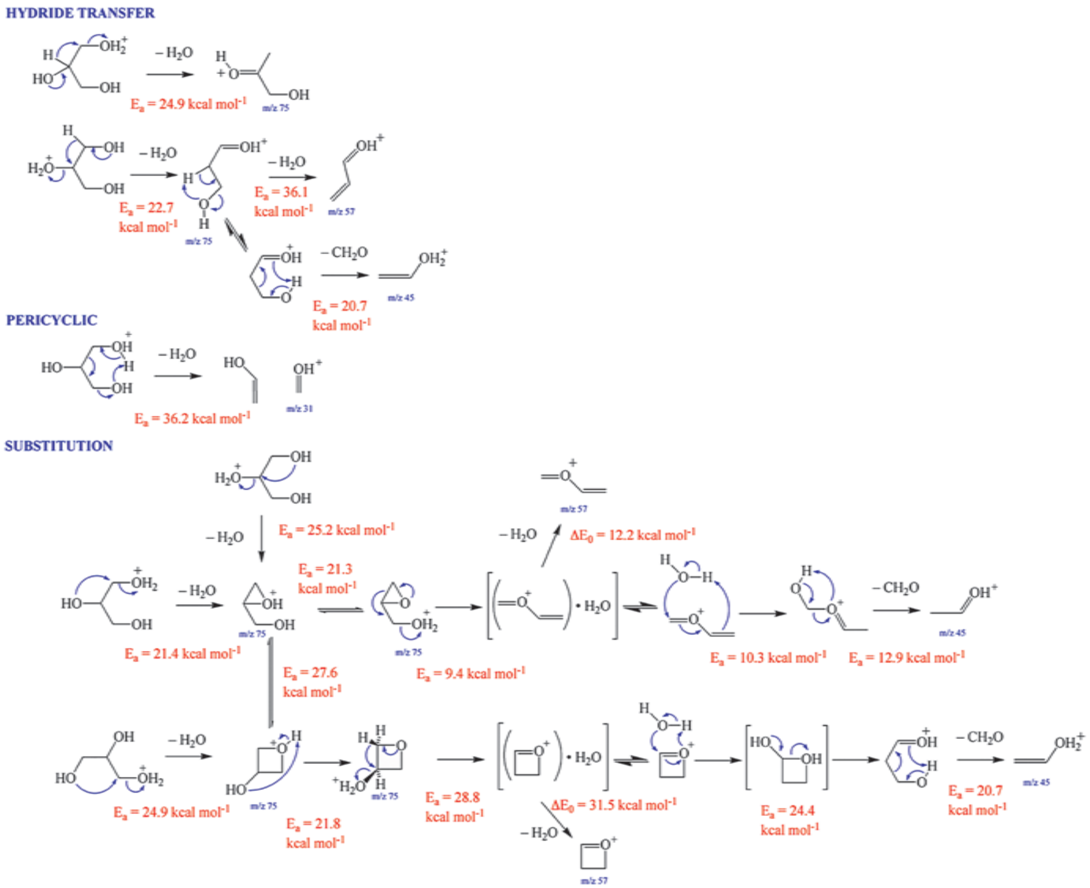

Figure 5.3 Mechanisms of acid-catalyzed dehydration of glycerol as suggested by quantum mechanics calculations (reproduced from Ref 2, with permission).

Figure 5.4 Acrolein, a deadly toxin, is also a powerful explosive. This photograph from 11 December 1982 shows the aftermath of a tank containing acrolein which exploded at a Taft, Louisiana, plant. Windows a mile and a half from the plant were blown out and 17,000 people were evacuated. Photo courtesy of Isaac CC on Flickr.com.

allowing longer cycles and a smaller reactor volume. In a typical reaction, a reactor comprising a tube 85 cm long with an interior diameter of 6 mm is used to carry out the dehydration of glycerol in the gaseous phase at atmospheric pressure. The reactor contains a solid tungstated zirconia (ZrO_2–WO_3) catalyst ground to a particle size of 0.5 to 1.0 mm and maintained at 300 °C. Tungstated zirconia oxides of this type are more active than sulfated oxides, and are typically also more stable.[8]

The reactor is fed with an aqueous solution containing 20 wt% of glycerol (flow rate, 12 mL h^{-1}). After 7 h, corresponding to the passage of about 80 mL of aqueous glycerol solution over the catalyst, 84% of the glycerol has been converted and acrolein is obtained in 35% yield, along with smaller quantities of hydroxypropanone (14%), acetaldehyde (3.4%) and propanaldehyde (7.8%).

If the reaction is carried out in the presence of oxygen it is possible to obtain higher glycerol conversion by inhibiting, firstly, the formation of by-products, particularly those originating from the hydrogenation of dehydrated products such as propanaldehyde and hydroxypropanone, and, secondly, the deactivation of the catalyst by reducing the formation of coke.[9] The proportion of oxygen is chosen to lie outside the flammability range at all stages; in practice this means not allowing oxygen to exceed 7% of the gases involved the reaction, which comprise a mixture of glycerol, water, oxygen and inert gases.

In a typical conversion the tubular reactor containing the ground tungstated zirconia catalyst is placed in a heated chamber at 300 °C. The reactor is fed with a 20 wt% aqueous glycerol solution at a flow rate of $12\,\mathrm{mL\,h^{-1}}$ and oxygen at $0.8\,\mathrm{L\,h^{-1}}$. In this instance the relative proportions of oxygen : vaporized glycerol : steam is 6 : 4.5 : 89.5. The aqueous glycerol solution is vaporized in the heated chamber and then passes over the catalyst. The calculated contact time is about 2.9 s. After 7 h, which corresponds to about 80 mL of aqueous glycerol solution having passed over the catalyst, all the glycerol has been converted and acrolein is obtained in 53% yield along with by-products such as acetaldehyde (10%) and propanaldehyde (*ca.* 4%). In general, the most selective catalysts for the dehydration reaction have H_0 in the range -8.2 to -3.0.[10] Loss of water from glycerol through substitution results in either oxirane or oxetane intermediates, which can interconvert with a low energy barrier. Subsequent decomposition of these intermediates proceeds either due to a second dehydration step or by loss of formaldehyde.

Dehydration of glycerol also occurs in the gaseous phase over silica-supported heteropolyacids. Silicotungstic acid, $H_4SiW_{12}O_{40}.24H_2O$ (HSiW), supported on silica with mesopores of 10 nm displays the highest catalytic activity, with acrolein selectivity at 275 °C and ambient pressure, greater than 85 mol% at complete conversion.[11] Silica Q10, having the largest mesopores, is the most appropriate support for the reaction (Figure 5.5).

Deactivation is caused by the deposition of coke on the support; the color of the catalyst changes from white to black, with a weight increase in the Q10–SiW–30 catalyst after 5 h of 7.8%. This discovery is of fundamental practical importance since supported Keggin-type heteropolyacid catalysts display high thermal stability, are less harmful to the environment than mineral acids and are increasingly employed industrially for reactions such as the dehydration of 2-propanol.[12]

The reaction route involves individual reaction mechanisms revealed by quantum mechanical computation (Figure 5.6).[2] When protonation occurs at the secondary hydroxyl group of glycerol a water molecule and a proton are eliminated from the protonated glycerol, and 3-hydroxypropanal is then formed by tautomerism.

In practice 3-hydroxypropanal is not detected, however, since this compound is unstable and is rapidly dehydrated to acrolein. In contrast, when protonation occurs at a terminal hydroxyl group in glycerol, hydroxyacetone is produced through dehydration and deprotonation, accompanied by tautomerism.

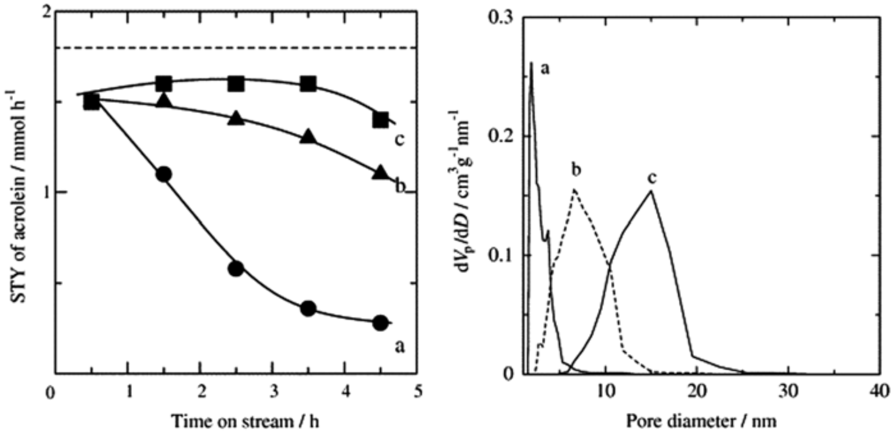

Figure 5.5 Changes (*left*) in space–time yield of acrolein in the dehydration of glycerol at 275 °C catalyzed by silicotungstic acid supported on silica of three different pore sizes: (a) Q3–SiW–30; (b) Q6–SiW–30; and (c) Q10–SiW–30 (*right*, pore size distribution). The broken line indicates the maximum theoretical yield. Reproduced from Ref. 9, with permission.

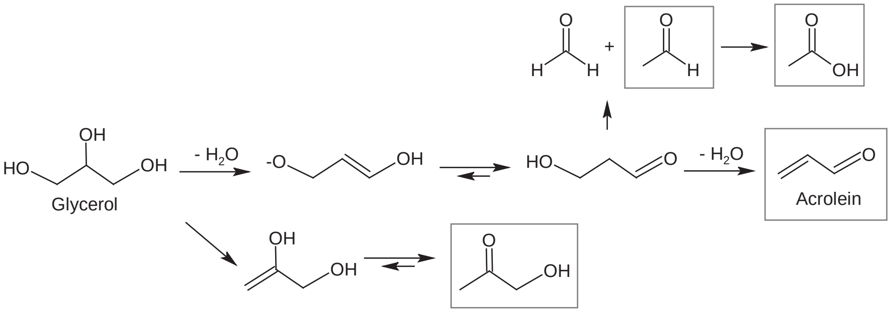

Figure 5.6 Glycerol dehydration route involving the individual reaction mechanisms revealed by quantum mechanical computation (reproduced from Ref. 2, with permission).

Another synthetic approach to acrolein is based on reaction in sub- and supercritical water as reaction medium; this follows from the discovery that acrolein can be obtained with 84% selectivity and 40% conversion from glycerol by adding 5 mM H_2SO_4 to water at 623 K and 34.5 MPa.[13] In an improved version of this method, the reaction catalyzed by zinc sulfate in sub- and supercritical water (573–663 K, 25–34 MPa, 10–60 s) gives 75% maximum selectivity for acrolein at 50% glycerol conversion.[14] Finally, approximately 80% selectivity for acrolein at 90% glycerol conversion has been obtained by carrying out the reaction in pressurized hot water under supercritical conditions (673 K and 34.5 MPa) using H_2SO_4 as catalyst.[15] The yield of acrolein can be enhanced by increasing the pressure and the concentrations of glycerol and H_2SO_4.

A detailed kinetic model for analyzing the dehydration reaction in near- and supercritical water at 622–748 K and 25–45 MPa without additives has concluded that conversion of glycerol progresses competitively through both ionic and radical mechanisms.[16] The respective predominance of the ionic or the radical pathway can be controlled by temperature and pressure—the ionic reaction is preferred in subcritical water (liquid state), whereas the radical mechanism is favored in the supercritical region. This kinetic model also suggests that dehydration of glycerol to acrolein occurs mainly *via* ionic reactions, whereas the competitive dehydration into allyl alcohol, and bond scission to acetaldehyde and formaldehyde, preferentially follows the radical mechanism (see Figure 5.6, above).

5.3 Propane from Acrolein

Once acrolein has been formed it can be converted to propane, with an overall theoretical yield from glycerol of 48 wt% (Figure 5.7).[17] This reaction has been investigated in depth by Biofuel–Solution, a Swedish research organization, with the objective of producing green LPG.

Specifically, propanol can be produced either using acrolein as starting material, or from glycerol (combining the first and second step), with yields of 70–80% in the first case and 65–70% in the second. The propanol is then dehydrated to propene, with a yield of 70–75%. By using a

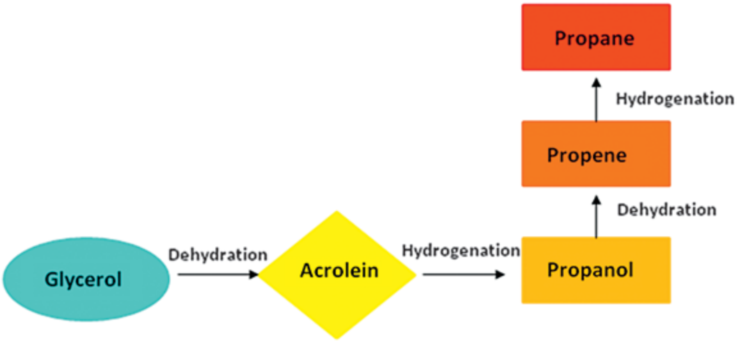

Figure 5.7 Reaction pathways from glycerol to propane (from Biofuel–Solution, reproduced with permission).

proprietary purpose-developed catalyst the propene is hydrogenated to propane (85% yield from propanol). The work continues with further development of multifunctional catalysts and an attempt to combine the two reaction steps.

A thorough economic analysis carried out by Biofuel–Solution shows that the feasibility of the proposed process is once again crucially affected by supply of bioglycerol at a predictable and affordable price. One factor might be the possible exemption of renewable fuels from taxation. The feed usually consists of a 10–20% aqueous solution of glycerol, acrolein or propanol. The inlet liquid is heated and vaporized. Depending on the reaction, one or more reactors are employed in series, with different catalysts and space velocities. The first reaction, independent of the desired end-product, is the conversion of the glycerol feedstock into acrolein. Two water molecules are removed from the glycerol molecule (dehydration) on an acidic catalyst. In this case the reaction is performed in the gaseous phase, at a temperature of approximately 250–300 °C. A glycerol solution (20 wt% in water) at a rate of 18 g h^{-1} was used in this experiment. In the preheater the liquid is heated and gasified before entering the dehydrogenation reactor, with 25 g of catalyst (Z–1152 10–20 mesh). A small carrier gas stream of 50 mL min^{-1} of N_2 is added to the gas stream before entering the reactor. The reactor inlet temperature is 265 °C and the run is performed at atmospheric pressure. The results for a 60 h run are shown in Figure 5.8.

The next step in obtaining propane from glycerol is the reaction of the acrolein formed to 1-propanol. In this experiment, the production of 1-propanol is demonstrated using acrolein as a starting point. In Reactor 1, 14 g of hydrogenation catalyst was used (BF–1015). A feed of 18 g h^{-1} of 10 wt% of acrolein in water was used. Hydrogen of was added at 400 mL min^{-1} to the inlet stream in the pre-heater. Inlet temperature to the reactor was 230 °C and a total pressure of 5 bar(a) was used. Full conversion of acrolein was obtained and in Figure 5.9 it can be seen that a yield of 70–80% was obtained.

Under these reaction conditions a 20% yield of propionaldehyde was obtained as a by-product; this can subsequently be converted to propanol, or recycled to enhance the yield.

Finally, propanol is converted to propane. Reactor 1 was loaded with 30 g of the dehydration catalyst (Z–1152 10–20 mesh) and Reactor 2 with 14 g of the purpose-developed Biofuel #1014 catalyst (10–20 mesh). 18 g h^{-1} of 10 wt% aqueous propanol was fed to the unit and 400 mL min^{-1} of hydrogen was added in the pre-heater. The inlet temperature was 280 °C in Reactor 1 and 270 °C in Reactor 2 and the

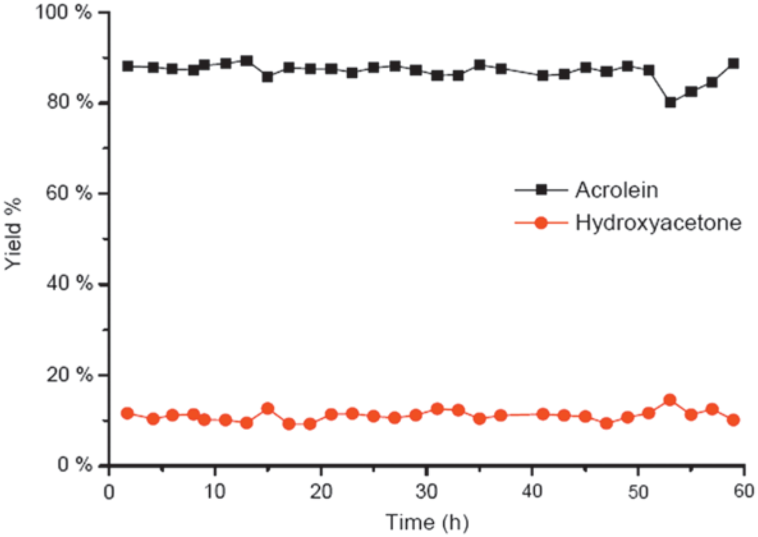

Figure 5.8 Conversion of glycerol to acrolein, normalized carbon balance (from Biofuel–Solution, reproduced with permission).

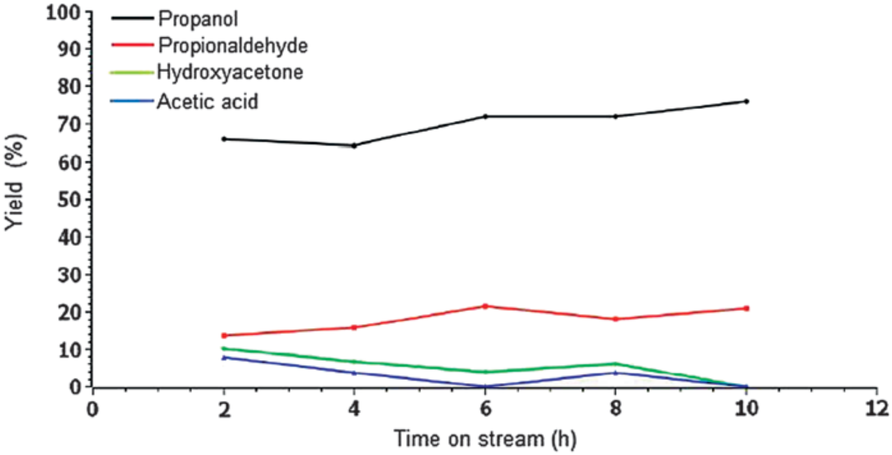

Figure 5.9 Conversion of acrolein to 1-propanol, normalized carbon balance (from Biofuel–Solution, reproduced with permission).

experiment was run at 5 bar(a) pressure. The results of a 7 h run are shown in Figure 5.10.

The yield of propane increases during the first 6–8 h and is then stabilizes around 85%. After 14 h the inlet temperature of Reactor 1

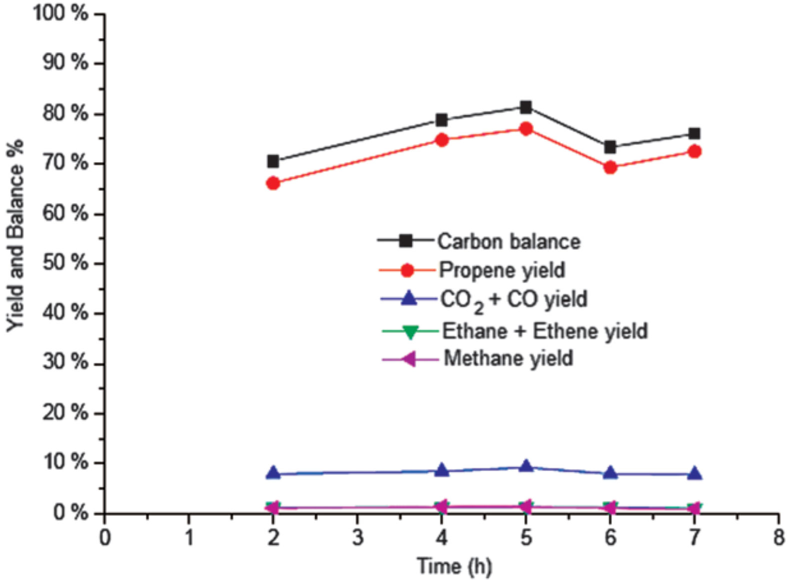

Figure 5.10 Conversion of propanol to propene (from Biofuel–Solution, reproduced with permission).

(dehydration) is decreased from 280 °C to 230 °C. This results in a sharp decrease in propane production. As the temperature of the dehydration reactor (Reactor 1) falls the dehydration of propanol decreases and the yield tails off. However, after 22 hours the inlet temperature of Reactor 1 is restored to 280 °C and the propane yield returns to approximately 85%. The above mentioned experiments were performed during 2007–2008 without extensive optimization, and there is therefore plenty of room for improving the yields of both products by optimizing the catalyst compositions and other process conditions. In any case, however, the idea is to combine the *endothermic* dehydration reaction with the *exothermic* hydrogenation reaction by using a multifunctional catalyst, with consequent energy and capital savings (Figure 5.11). During 2009 substantial improvements have been made to the catalyst, and further details of the project are available at www.Green-LPG.com.

5.4 Oxydehydration to Acrylic Acid

Acrylic acid can be produced by a one-step oxydehydration reaction of glycerol in the presence of molecular oxygen.[18] The dehydration reaction is followed by aerobic oxidation of the resulting acrolein directly to

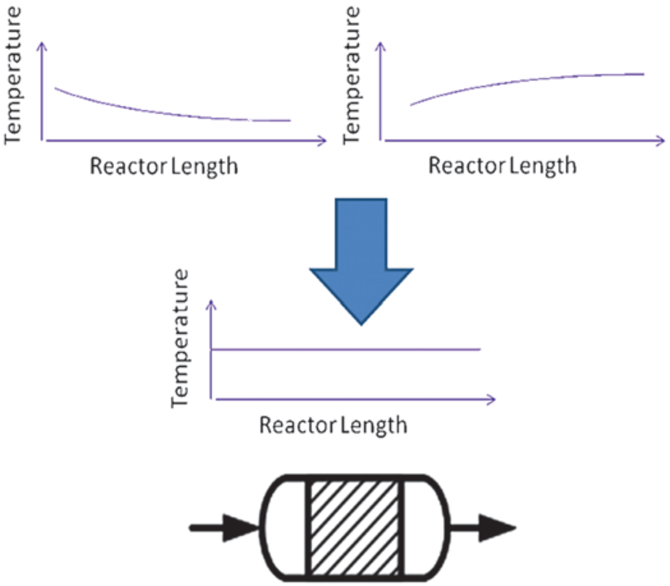

Figure 5.11 A multifunctional catalyst replaces two monofunctional catalysts, with considerable energy and capital savings (from Biofuel–Solution, adapted with permission).

acrylic acid (Equations 5.1 and 5.2):

$$\mathrm{CH_2OH{-}CHOH{-}CH_2OH \rightarrow CH_2{=}CH{-}CHO + 2H_2O} \tag{5.1}$$

$$\mathrm{CH_2{=}CH{-}CHO + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CH{-}COOH} \tag{5.2}$$

The exothermic oxidation reaction is thus coupled with the endothermic dehydration reaction, which provides a better thermal balance for the overall process. In a typical conversion the tubular reactor comprises a tube 85 cm long with inside diameter 6 mm, and this is used to perform the glycerol oxydehydration in the gaseous phase at atmospheric pressure. The reactor contains two catalytic beds, the first with a ground solid tungstated zirconia catalyst, and the second with an industrial mixed W–Sr–V–Cu–Mo oxidation catalyst with the addition of acetic acid as binder. The gas mixture fluxes consecutively through the first and the second beds. The reactor is placed in a heated chamber at 280 °C and is fed with an aqueous solution containing 20 wt% of glycerol (flow rate, $9\,\mathrm{g\,h^{-1}}$) and oxygen (flow rate, $14\,\mathrm{mL\,min^{-1}}$). The time of contact is about 2.9 s, after which sampling confirms that all the glycerol has been converted. Acrylic acid is obtained in 74% yield.

5.5 Dehydration to 3-Hydroxypropionaldehyde

3-Hydroxypropionaldehyde (3-HPA) is a precursor for many important chemicals, including acrolein, acrylic acid and 1,3-propanediol, and is also used for polymer production. It can be efficiently produced from renewable glycerol. Biotechnological production has several advantages compared to chemical methods, and can be carried out using aqueous glycerol solution either at room temperature or at 37 °C under normal pressure.

The transformation to 3-HPA is a one-step enzymatic reaction (Figure 5.12), and the yields of 85–87 mol% 3-HPA/mol glycerol are higher than those achieved by chemical synthesis.

To date, a number of genera of bacteria have been identified as being suitable, including *Klebsiella* (*Aerobacter*), *Citrobacter*,[19] *Enterobacter*,[20] *Clostridium* and *Lactobacillus*.[21]

5.6 Industrial Applications

The first facility for producing acrolein from glycerol is expected to be soon established by Arkema at Beaumont, Texas (Figure 5.13).

This is a hybrid process in which the oxidation of propylene to acrolein is coupled with the dehydration of glycerol. The first glycerol

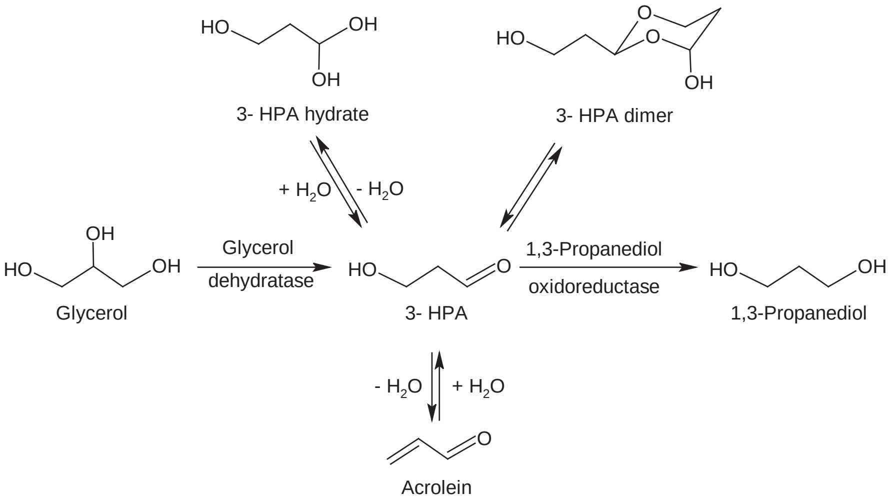

Figure 5.12 Formation of 3-hydroxypropionaldehyde (3-HPA), 1,3-propanediol and acrolein.

Figure 5.13 At Beaumont, Texas, where Arkema is due to manufacture acrolein and acrylic acid from a mixture of glycerol and propene, oil used to gush from the ground in the early 1900s (photo courtesy of the W D Hornaday Prints and Photographs Collection, Texas State Library and Archives Commission).

dehydration step is performed in the presence of the reaction gas originating from the oxidation of propylene to acrolein.[22]

This has the advantage that the endothermic dehydration reaction is coupled to the exothermic oxidation of propene, with considerable energy savings, in contrast to the traditional propene oxidation in which cooling of the reaction gas is required to isolate the acrolein formed. Remarkably, the acrolein produced in the endothermic glycerol enhances the productivity of the process and its commercial potential. Biofuel–Solution has developed an IP-portfolio around gas-phase glycerol conversion into medium value chemicals like propane and ethane and is currently scaling up its multistep process in a pilot plant.[23]

A similar coupling has been used in the production of acrylic acid.[24] Instead of electrically cooling the reaction gas originating from the oxidation of propene to acrolein prior to its oxidation to acrylic acid, which requires a lower temperature, the oxidation of propylene to acrolein is coupled to the oxidation of acrolein to acrylic acid by including endothermic glycerol dehydration.

3-HPA is of considerable industrial interest as an intermediate, because it is relatively easily converted into a number of large-scale commodity chemicals, including acrolein, 3-hydroxypropionic acid, acrylic acid, malonic acid and acrylamide. 3-HPA itself exhibits antimicrobial activity towards a wide range of pathogens and food spoilage organisms, and finds use as a food preservative and as a therapeutic auxiliary agent in the pharmaceutical industry. Currently 3-HPA is produced by synthesis from petrochemicals. Two chemical processes are employed to produce it as an intermediate in the production of 1,3-propanediol, the Degussa and Shell processes.[25] The Degussa process starts with the catalytic transformation of propylene into acrolein, which is hydrated to 3-HPA and then further reduced to 1,3-propanediol. The yield of 1,3-propanediol in this process is however only 43%. The Shell process starts from ethylene, then proceeds *via* ethylene oxide, which is transformed by a hydroformylation reaction with syngas at high pressure (150 bar) into 3-HPA. Ethylene is inexpensive and the intermediate products are not toxic, but the 3-HPA has to be recovered from the organic phase. The yield of 1,3-propanediol in this case is in the region of 80%. Biochemical production of 3-HPA from glycerol is being intensively studied in Germany[26] and commercial production is expected to start at Danisco Deutschland in the near future.

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CHAPTER 6

Etherification

6.1 Etherification of Glycerol

Glycerol ethers of interest include the compounds resulting from reaction with isobutylene or *tert*-butanol, including polyglycerols and glycosyl glycerol. Oxygenated molecules such as methyl *tert*-butyl ether (MTBE, now banned in many US states) are used as additives for fuels due to their antidetonant and octane-enhancing properties.[1] In general, the addition of ethers has a positive effect on the performance of diesel fuels and reduces the quantity of fumes and particulates, oxides of carbon and carbonyl compounds present in engine exhausts.

However, biodiesel has a disadvantage due to its high cloud point (around 0 °C for biodiesel, compared with –16 °C for petroleum-based diesel). However, the addition of glycerol di- and tri-tertiary butyl ethers lowers the cloud point of diesel.[2] These ethers also decrease the emission of particulate matter, hydrocarbons, carbon monoxide and unspecified aldehydes; they also reduce biodiesel viscosity and thereby act as cold flow improvers.[3] For example, a mixture of 1,3-di-, 1,2-di- and 1,2,3-tri-*tert*-butyl glycerol, which are soluble in nonpolar fuels, can be incorporated into standard diesel fuel containing 30–40% aromatics and significantly reduces emission of particulate matter, hydrocarbons, carbon monoxide and miscellaneous aldehydes.[4]

6.2 Butylation of glycerol *tert*-butyl ethers

Glycerol alkyl ethers are readily synthesized by etherification (O-alkylation) of glycerol using alkenes, particularly isobutylene (Figure 6.1), in

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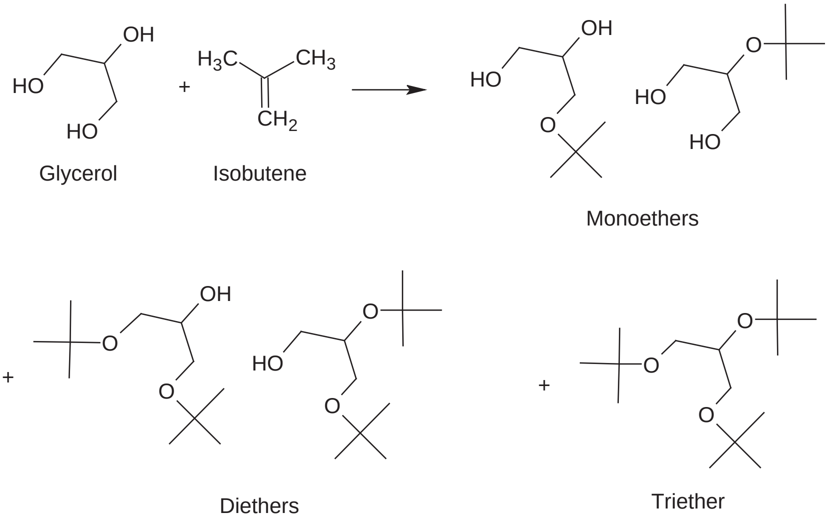

Figure 6.1 Reaction products from the *tert*-butylation of glycerol with isobutene.

the presence of an acid catalyst at temperatures from 50 °C to 150 °C and at molar ratios of glycerol : isobutylene of 1 : 2 or higher.[5] The catalytic reaction of glycerol with isobutene was first investigated in 1992 by Behr and Lohr at the Henkel.[6] They discovered active homogeneous and heterogeneous catalysts, for instance *p*-toluene sulfonic acid, acidic ion exchangers like Amberlyst 15 and several synthetic zeolites. The yield can be improved by optimizing the reaction conditions, such as temperature, molar ratio, and type and amount of catalyst. Initially the reaction mixture comprises a two-phase system, one being a glycerol-rich polar phase (containing the acidic catalyst and mono-*tert*-butyl glycerol ether) and the other an olefin-rich hydrocarbon phase, also containing glycerol diethers and triether. As the reaction proceeds the reaction products accumulate in one or other of the phases according to their solubility, which changes as their concentration increases. Once the glycerol conversion reaches 60–70% the two phases coalesce and form a single phase.

A recently discovered optimal etherification procedure of isobutylene and glycerol makes use of heterogeneous sulfonic-modified mesostructured silica catalysts (Figure 6.2).[7]

Under the optimized conditions identified in Table 6.1, mesostructured catalysts give complete glycerol conversion, with a combined selectivity towards di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) up to about 90% (Figure 6.3). There is no formation of undesirable isobutylene oligomers.

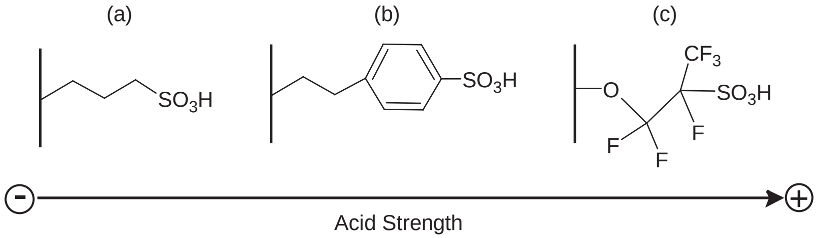

Figure 6.2 Sulfonic acid moieties in the functionalized mesostructured samples: (a) propyl-, (b) arene-, and (c) perfluoro- (reproduced from Ref. 16, with permission).

Table 6.1 Comparison of sulfonic-functionalized mesostructured silicas for the etherification of glycerol with isobutylene (reproduced from Ref. 15, with permission).

Catalyst	*Reaction time (h)*	χ_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

Note: χ_G = glycerol conversion; $S_{DTBG+TTBG}$ = selectivity to di- and triethers, calculated as moles of glycerol reacted to form DTBG and TTBG with reference to total moles of reacted glycerol. *Reaction conditions*: 5 wt% of catalyst with reference to glycerol, isobutylene: glycerol molar ratio = 4 : 1, temperature = 75 °C.

The acidic strength of the sulfonic acid sites is the crucial factor determining the catalytic effectiveness of these materials. The di- and triethers of glycerol are the most desirable products, and the distribution indicated in Table 6.1 shows that the catalyst Ar–SBA–15 gives the highest yield of DTBG and TTBG. The selectivity towards di- and triethers over Ar–SBA–15 is 77% after 1 h and reaches 92% after 4 h.

Over Ar–SBA–15 catalyst, the amount of the undesirable MTBG decreases to 5 wt% after 4 h of reaction. In contrast to the macroporous commercial sulfonic acid resins used, for example, by the Dutch consortium Procede Group BV for the tert-butylation of glycerol,[8] no oligomerization products can be detected over either Ar–SBA–15 or Pr–SBA–15 catalysts, even after 4 h of reaction. The use of a silica matrix reduces isobutylene oligomerization—an important benefit since isobutylene oligomers must be removed from the fuel additive before use, thereby increasing its cost, since during combustion they form deposits which clog the engine.

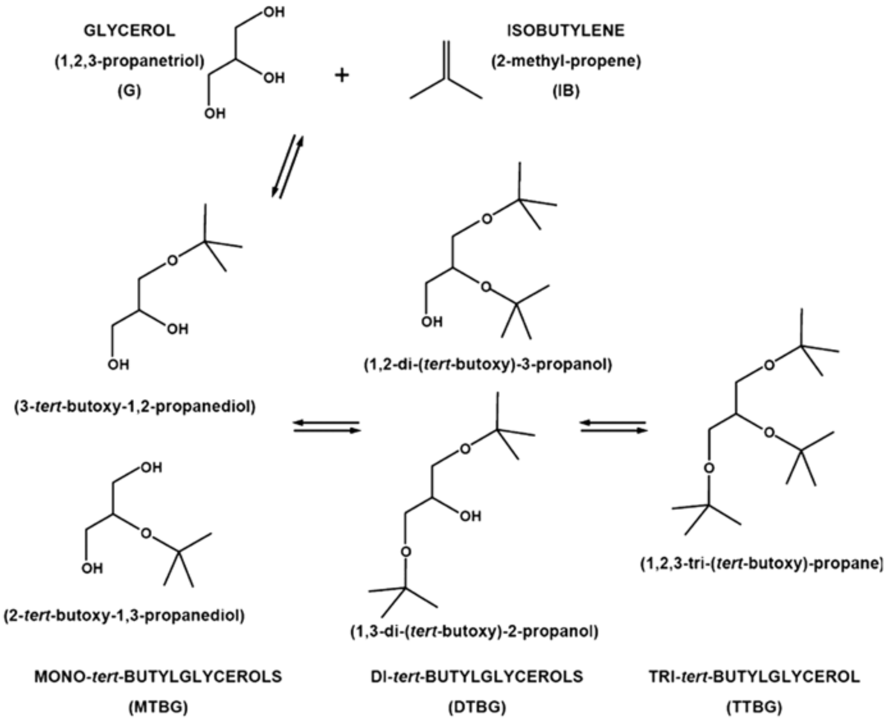

Figure 6.3 Main reaction products in the etherification of glycerol with isobutylene (reproduced from Ref. 16, with permission).

As an extension to this approach, the same sulfonic-functionalized mesostructured silicas show excellent catalytic behavior in the acetylation of glycerol using acetic acid, yielding acetylated compounds (Figure 6.4) with similarly interesting properties as bio-additives for petroleum fuels.[9]

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

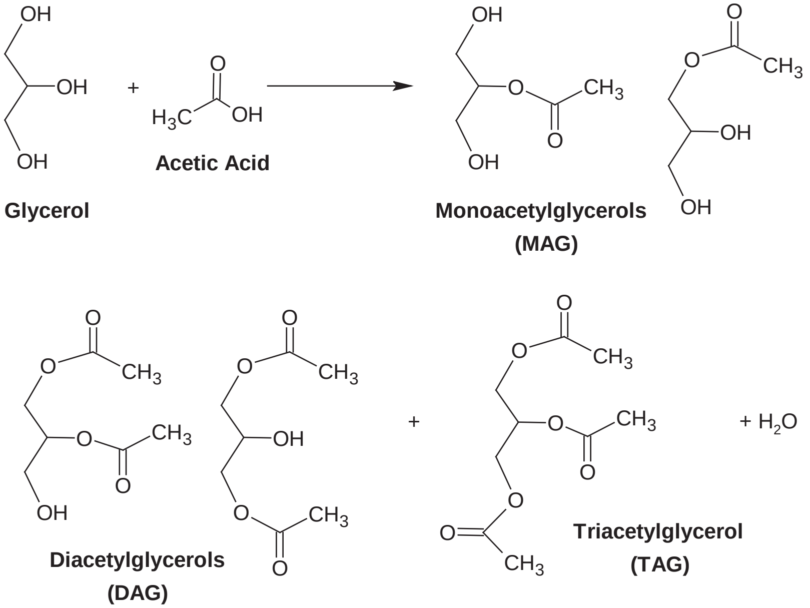

Figure 6.4 Esterification of glycerol with acetic acid (reproduced from Ref. 18, with permission).

Despite the high acid capacity (20.4 mmol H^+/g) of H_2SO_4 and its liquidity, which avoid mass transfer limitations, its catalytic behavior is not as good as that of Ar–SBA–15 and F–SBA–15. Indeed, the superior catalytic performance shown by Ar–SBA–15 and F–SBA–15 after 2 h of reaction compared with liquid H_2SO_4 suggests the presence of interesting *confinement* effects when a sulfonic acid group is supported over a mesostructured material. The solid mesostructure does not hinder molecular diffusion during the reaction process, giving in all cases a roughly similar equilibrium distribution, and selectivity to DAG and TAG after 4 h remains almost identical for the three catalytic systems. On the other hand the use of heterogeneous catalysts avoids the environmental, technical and economic problems associated with catalyst recovery and reuse. Indeed, the catalytic performance of these mesostructured materials used in a typical reaction of glycerol with acetic acid at 125 °C (molar ratio of acid : glycerol = 9 : 1) was completely regenerated after a mild solvent-washing step (Figure 6.5).

The etherification of glycerol with isobutylene in the liquid phase without solvent, catalyzed by strongly acidic resins such as Amberlyst or large-pore zeolites, gives complete conversion of glycerol.[10] Macroreticular resins are highly active due to their large pore diameter, which

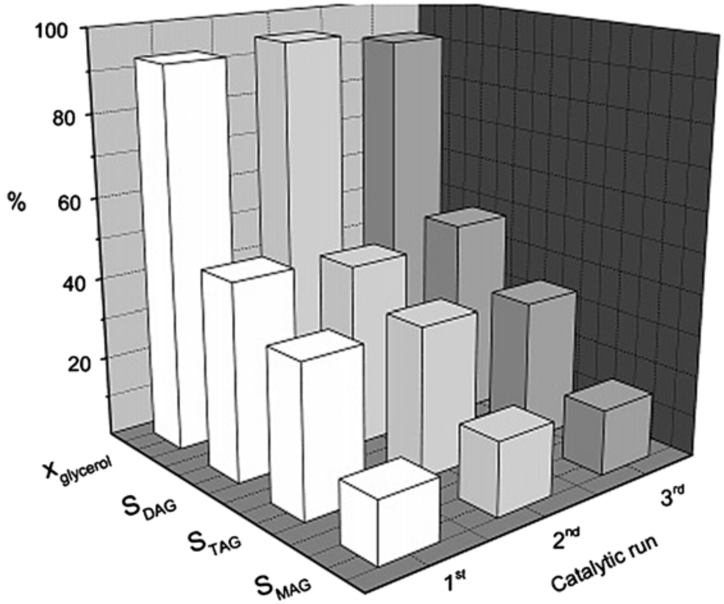

Figure 6.5 Catalyst reuse: Glycerol conversion and selectivity to MAG, DAG, and TAG after 4 h, in three consecutive catalytic runs reusing catalyst Ar–SBA–15 (reproduced from Ref. 18, with permission).

remains constant due to the high level of crosslinking after swelling in the reaction medium.

Complete conversion of glycerol, with selectivity to di- and tri-ethers above 92%, is also obtained over acidic Amberlyst 35 at 60 °C (Figure 6.6). Five ethers are formed in the process, and optimal selectivity toward ethers is achieved at 80 °C with an isobutene : glycerol molar ratio around 3 : 1.[11] The mono, di- and tri-*tert*-butyl ether reaction products have been characterized using MS, NMR, IR and Raman molecular spectroscopy.[12] A drawback to the use of Amberlyst ion-exchange resins is that the methanol, salt and water present in crude glycerol originating from biodiesel production must be removed in order to avoid poisoning the catalyst.[13]

A technical process for the production of the higher GTBE makes use of *p*-toluene sulfonic acid (p-TSA) as catalyst in a stirred batch reactor at 90 °C with a molar ratio of isobutene to glycerol of 2 : 1.[6] 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 equilibrium is achieved, yielding a mixture of about 45 wt% diethers, 30 wt% monoethers and 5 wt% of unconverted glycerol.

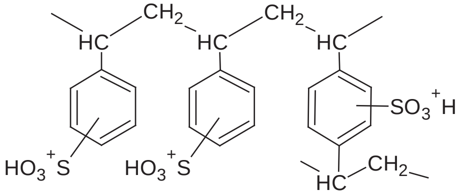

Figure 6.6 Amberlyst 35 is an excellent catalyst for glycerol alkylation with isobutene, but it requires the use of pure glycerol.

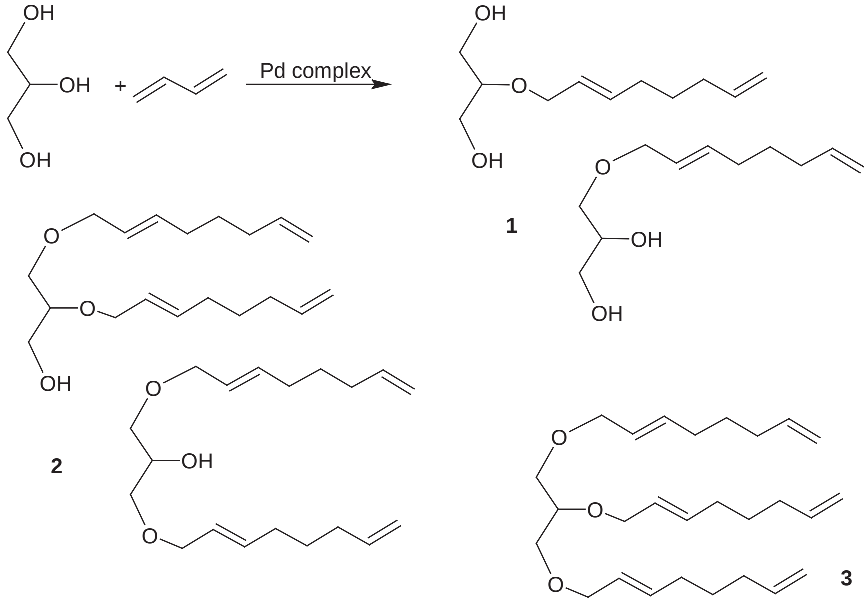

Figure 6.7 Telomerization of glycerol with butadiene to form glycerol ethers **1, 2** and **3** (reproduced from Ref. 13. with permission).

6.3 Direct Telomerization and Etherification over CaO

Direct telomerization of either pure or crude glycerol with 1,3-butadiene mediated by a palladium-based molecular catalyst has recently been described (Figure 6.7).[14] The process employs methoxy-substituted triphenylphosphine ligands, and is a promising technology which makes C8-chain mono-, di-, and triethers of glycerol available as chemical building blocks.

The resulting C8-chain ethers 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, but rather less on whether pure or crude glycerol is used as substrate. The reaction mechanism has been deduced following a study of the effect of different metal precursors and the ligand/metal ratio (Figure 6.8).[15] Formation of di- and triethers of glycerol would require the mono- and diethers to re-enter the catalytic cycle, which is sterically very demanding and therefore not favored.

Similarly, glycerol is attractive as a renewable building block for the synthesis of di- and triglycerols, which have numerous applications in the cosmetic and pharmaceutical industries. In a recent study the selective etherification of glycerol to di- and triglycerol in the presence of alkaline earth metal oxides was compared with the results obtained using Na_2CO_3 as homogeneous catalyst.[16] The best selectivity values for di- and triglycerol ($>90\%$ at 60% conversion) were obtained over CaO, SrO or BaO. Glycerol conversion increases with increasing catalyst basicity in the order: MgO < CaO < SrO < BaO. In no case was substantial formation of acrolein observed. Furthermore, at the start of the reaction mainly linear diglycerol was produced, but as conversion proceeded branched diglycerol began to form. In another series of experiments different types of CaO materials were prepared in order to provide an understanding of the relationship between the structure of Ca-based

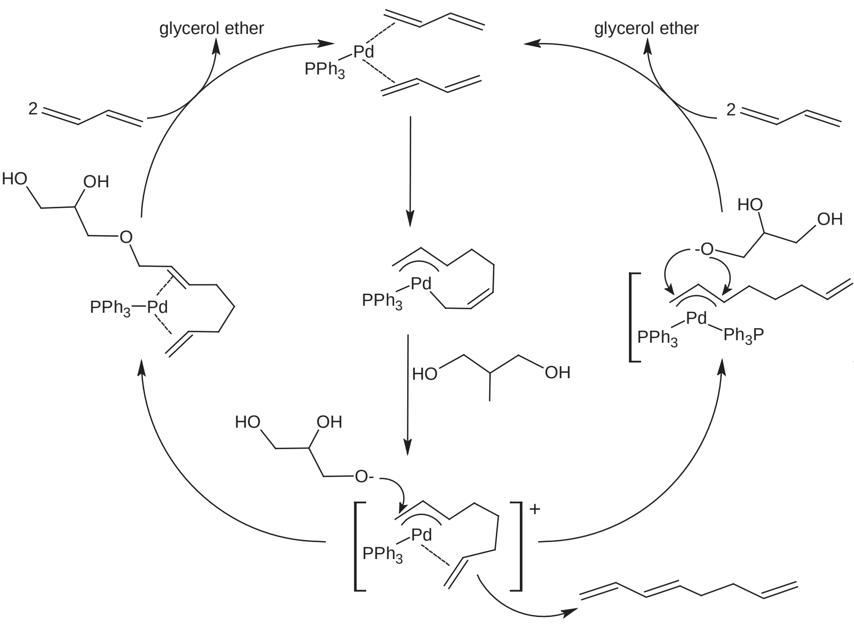

Figure 6.8 Proposed reaction mechanism for the telomerization of 1,3-butadiene with glycerol (reproduced from Ref. 14, with permission).

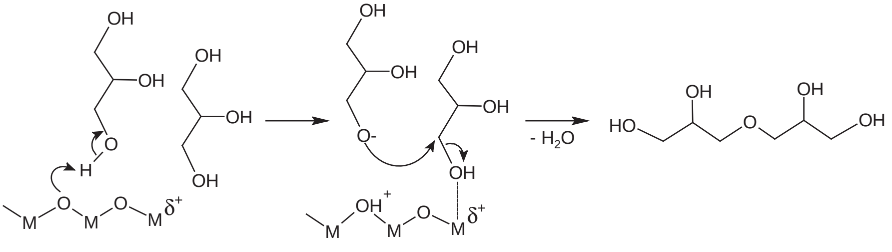

Figure 6.9 Potential reaction mechanism for the base-catalyzed glycerol etherification involving Lewis acidity (reproduced from Ref. 15, with permission).

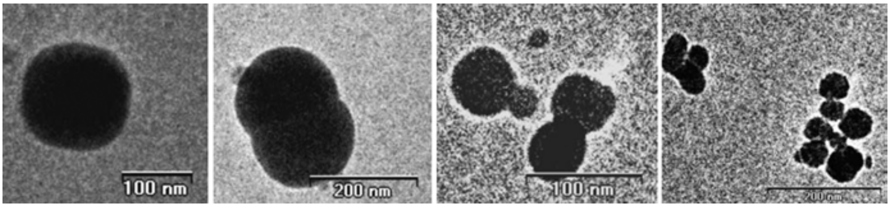

Figure 6.10 Cryo-TEM micrographs of colloidal particles formed during the glycerol etherification over CaO–C (*left* pair of images) and CaO–B (*right* pair of images) (reproduced from Ref. 15, with permission).

colloids and their activity. The CaO material possessing the strongest Lewis acid sites had the greatest catalytic activity, comparable to that of BaO, pointing towards the important role of Lewis acidity in the etherification reaction. Using these observations, an alternative reaction scheme for glycerol etherification was suggested based on an enhanced hydroxyl leaving process (Figure 6.9).

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 about 50–100 nm in size are spontaneously generated and their quantity gradually increases with increasing reaction time (Figure 6.10). Catalytic assessment of these CaO colloids reveals very pronounced etherification activity.

In terms of practical applications, researchers are looking for a suitable method of immobilization, since such supported colloidal systems would take advantage of both their homogeneous and their heterogeneous nature.

6.4 Polymerization to Polyglycerol

Polyglycerol is a highly branched polyol (Figure 6.11). It is a clear viscous liquid, highly soluble in water and polar organic solvents such as methanol, and is essentially non-volatile at room temperature.

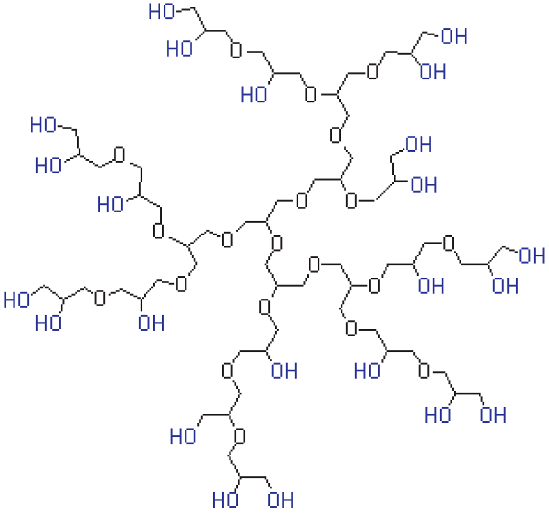

Figure 6.11 Polyglycerol is a highly branched polyol with a range of advanced applications.

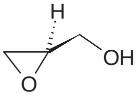

Figure 6.12 Glycidol, a glycerol derivative, is used in the controlled synthesis of polyglycerol.

At room temperature it is highly viscous, and its viscosity increases with molecular weight. Its high functionality, in combination with the versatile and well-investigated reactivity of its hydroxyl functionality, forms the basis of a variety of derivatives. A number of polyglycerols are commercially available (*e.g.*, from Hyperpolymers GmbH, Germany), with applications ranging from cosmetics to controlled drug release. Biocompatibility is an attractive feature of aliphatic polyether structures containing hydroxyl end-groups, including polyglycerols or linear polyethylene glycols (PEGs), which are approved for a wide variety of medical and biomedical applications. Controlled etherification of glycerol to form polyglycerols occurs *via* anionic polymerization of glycidol (Figure 6.12) through a rapid cation exchange equilibrium, producing polyglycerol with a narrow molecular weight distribution (polydispersity M_w/M_n usually below 1.5) and molecular weight within the range 1000 to 30 000 g mol^{-1}.[17]

Partially deprotonated (10%) 1,1,1-tris(hydroxymethyl)propane (TMP) is used as an initiator for the anionic polymerization, carried out under slow addition conditions, when polymerization or cyclization is minimized in the absence of initiator.

Hyperbranched polyglycerol possesses an inert polyether scaffold. Each branch ends in a hydroxyl function, which renders hyperbranched polyglycerol a highly functional material; for example, a molecule with a molecular weight of 5000 g mol^{-1} possesses 68 hydroxyl end-groups. This high functionality, in combination with the reactivity of hydroxyl functions, forms the basis for a variety of derivatives. Partial esterification of polyglycerol with fatty acids[18] yields amphiphilic materials which behave as nanocapsules.[19] Such nanocapsules can for example incorporate polar molecules as guests and solubilize them in a nonpolar environment. Selective modification can be achieved utilizing the reactivity of 1,2-diol units, located preferentially at the periphery of the molecule.

6.5 Glycosylation to Glucosyl Glycerol

O-α-D-Glucosyl glycerol (Glc–GL) is found in traditional Japanese fermented foods such as sake, miso and mirin.[20] For example, Glc–GL contributes to the flavor of sake, which contains approximately 0.5% of this compound. Glc–GL is a non-reducing glucoside exhibiting about half the sweetness of sucrose; it has high thermal stability, low heat-discoloration, low Maillard reactivity, low hygroscopicity, high water retention capacity, high digestibility, and it is non-carcinogenic. Its use for sweetening foods and beverages is expected to increase since it reduces caloric intake.[21] Glc–GL is produced by an enzymatic process based on *Candida tropicalis*, an α-glucosidase with starch as donor substrate,[22] or cyclodextrin glucanotransferases,[23] which transfer the Glc residue of starch and dextrins to the 1- or 3-position of glycerol. Concentrations of 30% (w/v) glycerol and 20% (w/v) soluble starch are the most effective for ensuring efficient transglycosylation.

6.6 Industrial Applications

Glycerol ether formulations are already commercialized as oxygenate fuel additives for use in gasoline engines. For example, the US-based company CPS converts glycerol by-products originating from both the biodiesel and ethanol industries to ethers, using olefins supplied by petrochemical producers (Figure 6.13).[24] The company believes that a combination of low molecular weight olefins and glycerol, and the

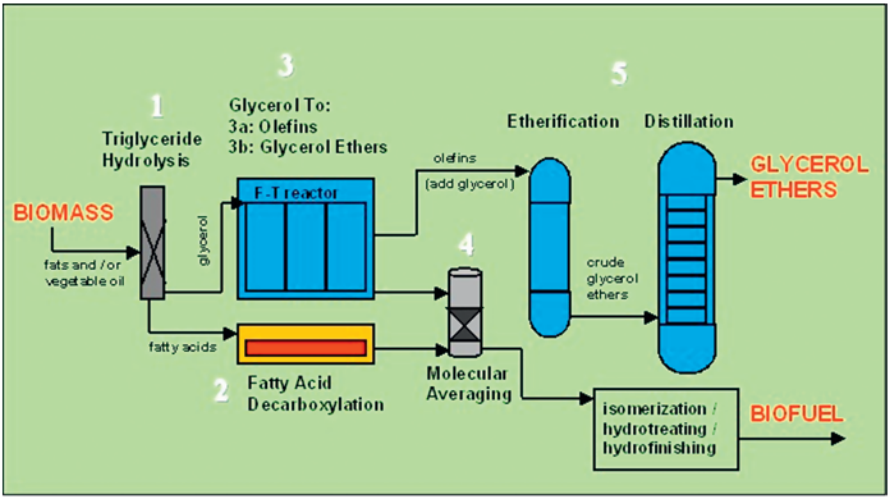

Figure 6.13 In the US, CPS Biofuels uses glycerol produced as a by-product of biodiesel for the synthesis of glycerol ethers.

paraffins derived from decarboxylated fatty acids, should provide greater market penetration than either on its own.

According to an EU directive 5.75% of the total quantity of fuel consumed within the Union by 2010 has to originate from renewable sources. In Germany alone this would be equivalent to 30 million tonnes of biodiesel, and hence 3 million tonnes of glycerol, or 10 million tonnes of GTBEs. If achieved, this could be easily absorbed by the market since large quantities of isobutylene are already available due to its use as a starting material for MTBE which, although banned in California, New York, and 18 other US states, is still permitted in the EU.

Unlike the unpleasant tasting and water-soluble MTBE, GTBEs are insoluble in water and are only modestly toxic. For this reason optimization engineering is being carried out on GTBE, both in Europe[25] and in the USA.[26] In Europe, the company Procede Twente is conducting what is described as a "GTBE project". The GTBE acronym for the commercial product has been trademarked and the company has joined another partner to form the GTBE Company NV in order to commercialize the technology. A demonstration plant was built in 2008 within the context of the EU-funded project, *GTBE: A renewable remedy for diesel soot emissions*.

Currently, both esterification and etherification reactions of crude glycerol from production of fatty acid methyl esters (FAME) over the mesostructured silica catalysts developed by the research group of Juan Hernández are under investigation at a Repsol plant in Spain. The

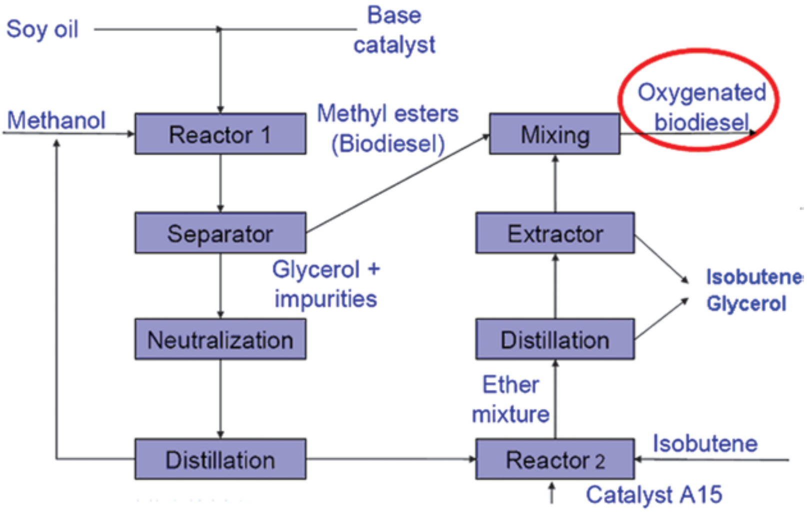

Figure 6.14 Integrated etherification will take place in the same plant as biodiesel production (Ref. 2).

long-term stability of such solid catalysts is being evaluated due to the high hygroscopicity of glycerol. SBA–15 and related materials exhibit higher thermal stability than conventional silica-based catalysts, but they are still unstable in the presence of water or alcohols.

Once glycerol has been converted into an additive the overall economics of biodiesel improves considerably, since glycerol converted to GBTE can be recovered in its entirety, thereby enhancing the viability of blended biodiesel. One might envisage a situation in which the original homogeneous manufacturing process for biodiesel could be replaced by the more efficient heterogeneous conversion, such as that of Yellow Diesel (Chapter 1). This process produces a stream of pure glycerol which can be converted to GBTE and used as a biodiesel fuel additive within a single plant (Figure 6.14).

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CHAPTER 7

Esterification

7.1 Esterification of Glycerol

Esterification of glycerol gives rise to a variety of useful products and in recent years has been an active area of research. The reactions employ both chemical catalysts and lipases and can be divided into three types: esterification with carboxylic acids, carboxylation, and nitration.

7.2 Esterification with Carboxylic Acids and Glycerolysis

Esterification of glycerol with carboxylic acids results in monoacylglycerols (MAGs) and diacylglycerols (DAGs) (Figure 7.1). MAGs are amphiphilic molecules and are useful as nonionic surfactants and emulsifiers.

Both MAGs and DAGs are widely used as food additives in bakery products, margarines, dairy products and sauces. They assist in combining certain ingredients, for example those based on oil or water which would otherwise be difficult to blend.[1] In the cosmetic industry they are employed as texturing agents for improving the consistency of creams and lotions.[2] In addition, owing to their excellent lubricant and plasticizing properties MAGs are used in textile processing oils on various types of machinery.[3] They are currently manufactured industrially either by continuous chemical glycerolysis of fats and oils at high temperature (220–250 °C), employing alkaline catalysts under a nitrogen atmosphere, or by the direct esterification of glycerol with fatty acids.[4] These catalytic

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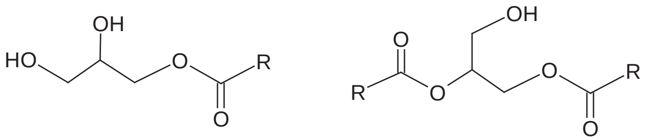


1 **2**

Figure 7.1 Monoacylglycerol and diacylglycerol structures.

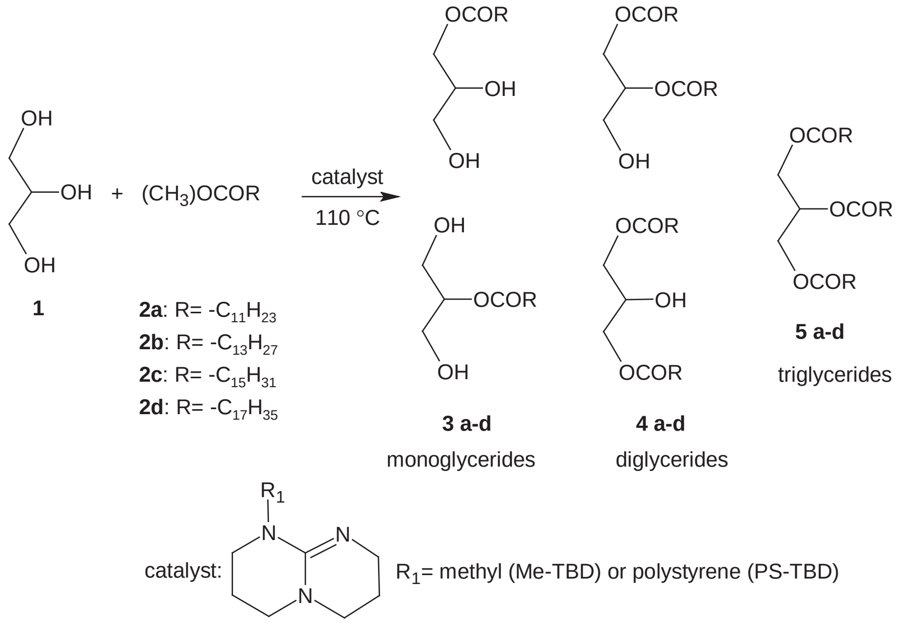


Figure 7.2 Catalytic esterification of unprotected glycerol over guanidine derivatives (reproduced from Ref. 6, with permission).

processes require strongly basic catalysts such as KOH, NaOH or $Ca(OH)_2$ and lead to the formation of monoglycerides of limited purity, due to the presence of by-products such as di- and triglycerides and soaps. For this reason MAGs destined for food use must undergo a distillation step.[5] An alternative approach uses a supported guanidine catalyst to provide a one-pot glycerol ester synthesis with high yield and high monoglyceride selectivity, starting with a glycerol : methyl ester molar ratio of 1 : 1 (Figure 7.2).[6]

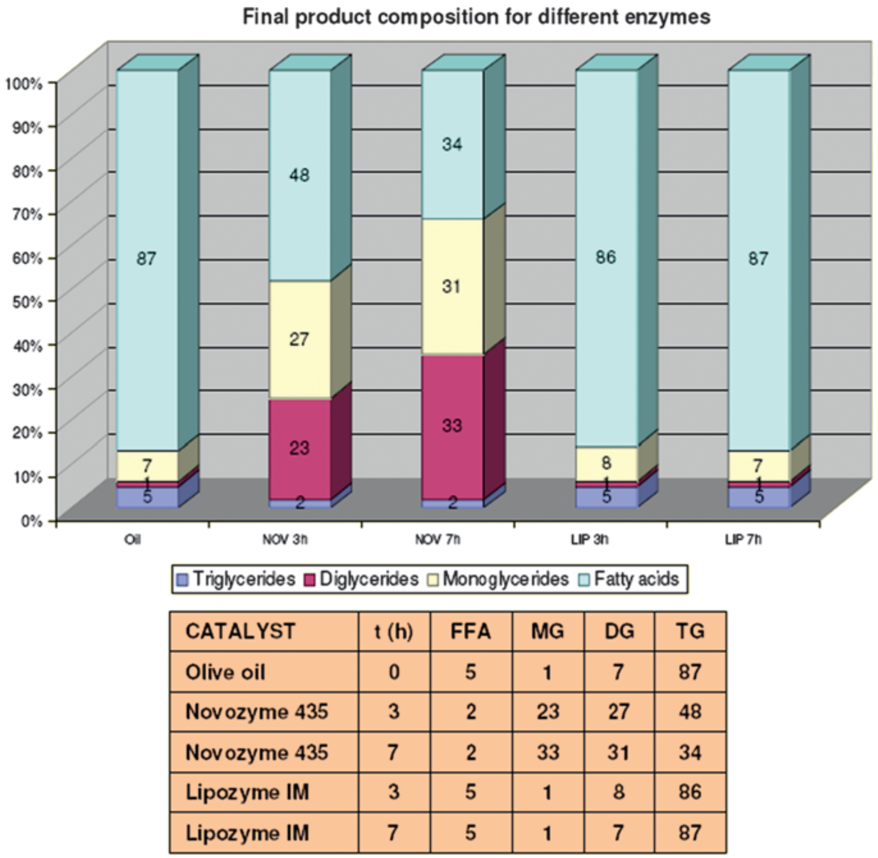
In Figure 7.2, starting from **2a,** after 50 h reaction glycerol esters were produced at more than 98% yield with very high 78% selectivity, to give **3a**. Alternative methods involve immobilized lipases. An example is the synthesis of MAGs using *Staphylococcus simulans* lipase immobilized on $CaCO_3$ in a solvent-free system,[7] yielding 70.6% of pure MAGs suitable for food use.

Catalytic glycerolysis of a tryglyceride yields mono- and diglycerides (Equations 1 and 2, respectively):

$$\text{triglyceride} + 2\ \text{glycerol} \leftrightarrow 3\ \text{monoglyceride} \tag{1}$$

$$2\ \text{triglyceride} + \text{glycerol} \leftrightarrow 3\ \text{diglyceride} \tag{2}$$

Olive oil and glycerol, for example, react over immobilized Nozyme lipases at 80 °C and atmospheric pressure with good yields of glycerol dioleate (Figure 7.3).[3]



CATALYST	t (h)	FFA	MG	DG	TG
Olive oil	0	5	1	7	87
Novozyme 435	3	2	23	27	48
Novozyme 435	7	2	33	31	34
Lipozyme IM	3	5	1	8	86
Lipozyme IM	7	5	1	7	87

Figure 7.3 Comparison between different lipases in the transesterfication reaction between olive oil and glycerol (reproduced from Ref. 3, with permission).

Table 7.1 Comparison between lipase- and base-catalyzed transesterification of olive oil with glycerol (reproduced from Ref. 8, with permission).

Processes	*Reaction Conditions*	*Downstream processes*	*Refined processes*
Base-catalyzed transesterification (Glycerol mono-oleate)	180 °C Atm. pressure 0.2 wt% catalyst	1. Decanting 2. Washing	Short path distillation
Enzyme-catalyzed transesterification (Glycerol mono-oleate)	60 °C Atm. pressure 1.5 wt% catalyst	Crystallization (3 steps)	1. Deodorization 2. Drying

On the other hand, an excess of glycerol does not result in a significant increase in monoglyceride yield, as similar product distributions are obtained for glycerol : oil mole ratios of 3 : 1 and 6 : 1.

Comparison of the traditional and enzymatic processes for the production of MAG clearly shows the key advantages of the bioprocess in terms of higher selectivity (and less waste) and lower temperature and pressure (Table 7.1). Since the enzyme costs can be reduced by a factor of three by economies of scale, this and similar lipase-based processes will find commercial application for large-scale transesterification reactions.[8]

Generally speaking, the methodology is versatile and can be applied to the preparation of both MAGs and DAGs from fatty acids. For example, esterification of glycerol with linoleic acid in hexane over 15% (w/w) lipase from *Rhizomucor miehei* gives 80% esterification to 1,3-diacylglycerol and 1-monoacylglycerol in 8 h at 50 °C in a system containing a 1 : 2 molar ratio of glycerol : free fatty acids. Similarly, esterification levels $>80\%$ are obtained in 8 h at 40 °C using lipase from *Candida antarctica*.[9]

DAG is present naturally as a minor component of edible fats and oils from various sources.[10] It can exist as either 1,3-DAG or 1,2(2,3)-DAG. DAG has been employed as a cocoa butter blooming agent and as an intermediate for the synthesis of structural lipids.[11] Recent studies of its nutritional properties and dietary effects suggest that DAG in which 1,3-DAG is the major component plays a role in reducing serum triacylglycerol (TAG) levels, and as a result can decrease body weight and visceral fat mass.[12] Consequently, oils with a high DAG content have gained attention for the prevention of obesity and other lifestyle-related conditions.[13] State of the art production of 1,3-DAG using lipases is based on the esterification of glycerol with fatty acids using a

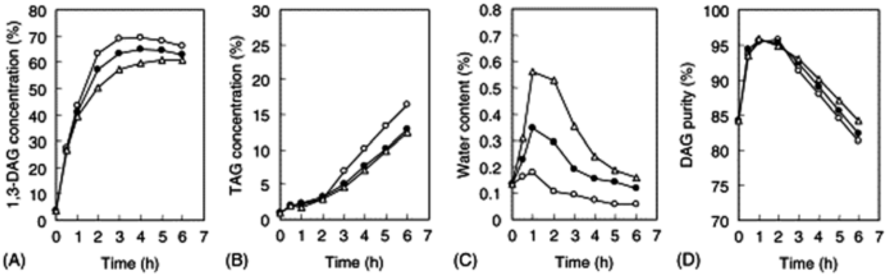


Figure 7.4 Effect of vacuum conditions on the production of 1,3-DAG: (**A**) 1,3-DAG; (**B**) TAG; (**C**) water content in the reaction mixture; and (**D**) DAG purity. The reaction was performed at 50 °C with a molar ratio of fatty acids to glycerol of 2.0 and a residence time of 60 s. The Lipozyme RM IM concentration was 5% (dry weight basis): (○) 0.4 kPa; (●) 0.8 kPa; and (Δ) 1.3 kPa. Reproduced from Ref. 14, with permission.

solvent-free approach (Figure 7.4).[14] This is an advance on traditional esterification in organic solvent.[15]

On the laboratory scale an 84% yield of DAG with a purity of 90% is obtained in a solvent-free system using 1.29 mM glycerol and 2.59 mM fatty acid with a 1,3-regioselective lipase. Due to the low temperature of the reaction (25 °C), non-solvent esterification requires a relatively long time (*e.g.*, 12 h) to produce dilinolein (71.7%). A better approach for production on the industrial scale is to use a temperature of 50 °C with continuous removal of water (Figure 7.4).[16] In particular, a packed bed reactor containing an immobilized 1,3-regioselective lipase, connected to a water removal vessel under optimized vacuum conditions of 0.4 kPa and 50 °C, yields a maximum 1,3-DAG content around 70%, provided the molar ratio of fatty acid to glycerol is above 2.0.[17]

Under 0.4 kPa the DAG purity reaches a maximum of 95.4% after 2 h reaction, and then gradually decreases to 81.2% after 6 h (**D** in Figure 7.4) due to increasing TAG concentration in the later stages of the reaction. Although the rate of production of 1,3-DAG appears to be constant in the initial stages of the reaction, regardless of the vacuum conditions, its concentration in the later stages increases under higher vacuum (**A**). Water is thus removed more effectively under higher vacuum conditions. For example, the water content after 6 h reaction is 0.057% at 0.4 kPa (**C**). The lower rate of 1,3-DAG synthesis in the later stages of the reaction under lower vacuum is due to an increase in the reverse reaction (hydrolysis).

7.3 Carboxylation to Glycerol Carbonate

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one; GC) is a colorless protic polar liquid. Being nontoxic and having a high boiling point, GC is a useful solvent for plastics and resins such as cellulose acetate, nylon, nitrocellulose and polyacrylonitrile. It also has potential as a biolubricant, due to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis and pressure. It can be prepared directly in high yield from glycerol and dimethyl carbonate in a reaction catalyzed by lipases (Figure 7.5).

An alternative method of obtaining the carbonate derivatives of glycerol is by catalytic reaction between equimolar amounts of urea and glycerol using a mineral zinc sulfate catalyst. This produces GC with good yield and selectivity (92%) by carbamoylation–carbonation at temperatures between 140 °C and 150 °C at a pressure of 40 mbar in the presence of a Lewis acid catalyst.[18] The second, slower, step requires heterogeneous catalysis using a salt such as zinc sulfate (Figure 7.6). In particular, the catalyst $Zn(CH_3.C_6H_4.SO_3)_2$ leads to yields of glycerol carbonate in excess of 80% in a relative short reaction time, about 1 h.[19]

The reaction is carried out at a pressure of 40–50 mbar in order to shift the equilibrium by eliminating ammonia in the gaseous phase. Synthesis and purification of glycerol carbonate in a thin-film separation 2 L thermal reactor has given yields of 94% and 97%.[20] Other methods involve transesterification with ethylene carbonate or dialkyl carbonates.[21] For example, in a reaction with ethylene carbonate carried out

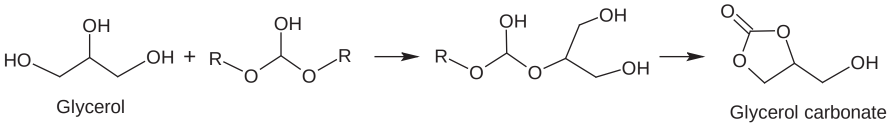


Figure 7.5 GC can be produced from the reaction of dialkylcarbonate (R = alkyl) with glycerol, with the intermediate ester undergoing a second esterification.

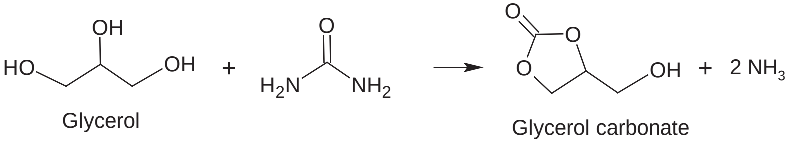


Figure 7.6 Reaction of urea and glycerol catalyzed by Zn^{2+} at reduced pressure yields GC (reproduced from Ref. 18, with permission).

at 125 °C in the presence of sodium bicarbonate, GC was formed in 81% yield.

When heated, GC reacts readily with phenols, alcohols, amides and carboxylic acids to form ethers or esters of glycerol, including polymers such as polyesters, polycarbonates, polyurethanes and polyamides. Being relatively inexpensive, GC could serve as the source of new polymeric materials based on glycidol, which is readily obtained in high yield from GC by catalytic reaction within the pores of zeolite A. Reaction at 180 °C and pressures as low as 35 mbar produces glycidol in 86% yield and 99% purity, by contraction of the five-membered cyclic carbonate unit to a three-membered epoxy unit (Figure 7.7).[22]

Glycidol is a clear, slightly viscous liquid and has a variety of industrial uses. It is used in surface coatings, as a gelation agent in solid propellants, as a stabilizer for natural oils and vinyl polymers, and as a

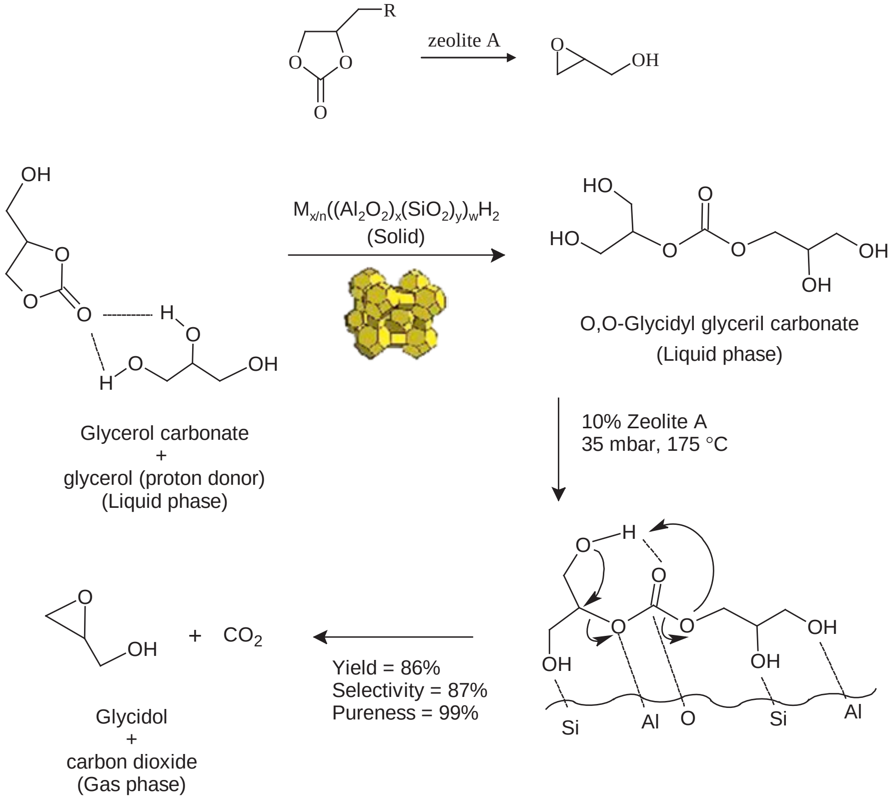


Figure 7.7 Glycidol is readily formed by oligomerisation of GC, catalyzed under reduced pressure over zeolite A or γ-alumina (reproduced from Ref. 18, with permission).

demulsifier. It is also an intermediate in the synthesis of glycidyl ethers, esters and amines and can form a high-value component in the production of epoxy resins and polyurethanes. For example, glycidyl carbamates, synthesized by the reaction of polyfunctional isocyanate oligomers and glycidol, combine the excellent properties of polyurethanes with the crosslinking chemistry of epoxy resins.[23] Finally, glycidol is itself commercially polymerized to polyglycerol (Chapter 6).[24]

7.4 Nitration

The explosive nitroglycerine, currently produced in modular plants, is also successfully employed as an antianginal drug (Figure 7.8).

When treated with nitrating agents glycerol forms a solution containing dinitroglycerol. If the solution is then treated with a cyclizing agent the dinitroglycerol is converted into glycidyl nitrate, which can be polymerized to poly(glycidyl nitrate) (PGN).

The polymer PGN is potentially suitable for use in propellants, explosives, gas generators and pyrotechnics. Its industrial synthesis typically follows a three-step procedure, involving nitration of epichlorohydrin (now obtained from glycerol), followed by cyclization of the nitrated epichlorohydrin using a base to form glycidyl nitrate. In the third step the glycidyl nitrate is polymerized cationically to form PGN. This method of producing of glycidyl nitrate is, however, dangerous and is not economically feasible for large-scale commercial production. A

Figure 7.8 Nitroglycerine, currently produced in modular plants (*left*) is also successfully employed as an antiangina drug (*right*) (reproduced from Novartis.com, with permission).

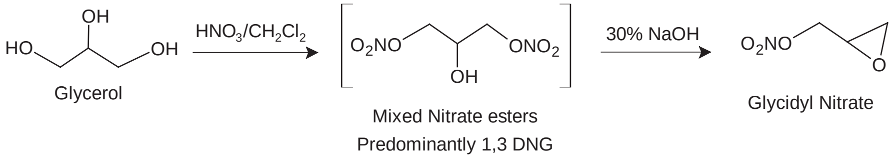


Figure 7.9 The continuous process for the production of glycidyl nitrate, and thus PGN, from glycerol involves consecutive nitration and caustication.

safe and relatively inexpensive process for producing glycidyl nitrate in large quantities, at sufficient purity for conversion to PGN without further distillation, has therefore been developed (Figure 7.9).[25]

In a first reaction vessel glycerol and nitric acid are reacted continuously to produce 1,3-dinitroglycerol in high yield (at least 50%), assisted by the asymmetric kinetics of the continuous process. In a second reaction vessel the outflow is reacted with an excess of NaOH to neutralize the excess nitric acid and form glycidyl nitrate. The outflow from this vessel passes into a decanter in which the immiscible organic phase is separated from the basic aqueous solution. The temperature of the nitration reaction is around 5 °C and the preferred temperature for causticization and separation is about 25 °C. This offers significant advantages over conventional processes for glycidyl nitrate, typically carried out at temperatures as low as – 10 °C to – 70 °C. The addition of an organic solvent such as dichloromethane dilutes and moderates the reactions, and provides a significant measure of safety to the process by absorbing the heat of reaction, since it boils before a dangerous temperature can be reached. In addition, the boiling organic solvent drives off the catalyst decomposition product, oxides of nitrogen (NO_x), stabilizing the reaction and making it suitable for commercial use. The glycidyl nitrate produced is pure enough for direct use in the production of PGN. This avoids the hazardous and costly purification required with other glycidyl nitrate processes.

7.5 Industrial Applications

Glycerol esters such as MAGs and DAGs have well established industrial applications, particularly in the food and oleochemical industries. In 2006 the world market for food emulsifiers was estimated to be around 400 000 tons, approximately 10% of which was monoolein. Of the 40 emulsifier units across the world, 25 are located in the United

Figure 7.10 1,3-DAG content of Kao Econa cooking oil is 80% (reproduced from Kao.com, with permission).

States. DAG has the advantage of being stable to decomposition at cooking temperatures. It is produced by the Japanese company Kao from soybean and canola oil using a lipase[16] and marketed under the tradename "Healthy Econa Oil" for use in cooking, frying and dressings (Figure 7.10).[26]

DAG is in fact present at a level of a few percent in virtually all edible oils, whether vegetable or animal, and has been long ingested by man.[10] Research concerning the human nutritional characteristics of DAG oil compared to triacylglycerol (TAG) oil clearly demonstrates the significant suppressive effect of DAG on body fat accumulation.[27] This is due to the reduced possibility of synthesis of TAG in the small intestine following DAG oil digestion. This has led Kao to start production of DAG-based oil, aimed at an affluent population of 128 million for which obesity had become a serious issue. Since its introduction in 1999 Econa has become the best selling vegetable oil in the Japanese market, due to its health benefits and its mild flavor. In a joint venture with Kao, Archer Daniels Midland manufactures and markets it in the Americas, Europe, Australia and New Zealand.

The new process for production of glycidyl nitrate is already in use in the USA by the weaponry manufacturer, Alliant Techsystems. The continuous nature of the process reduces labor costs, and the conventional equipment used, its inherent safety, increased nitration yields, lack of hazardous waste streams, thermal savings and the improved purity of the product, all combine to make it technically and economically attractive. Finally, in France the company Condat is about to commercialize products in the form of glycerol polycarbonates and glycerol carbonate polyesters, obtained as the result of three one-pot reactions: carbonation, oligomerization and acylation. This opens the way to new multifunctional plant-based polymers, which have already proved themselves effective as industrial lubricants and biodegradable hydraulic fluids that are nontoxic and fire-resistant. With their anti-wear properties, even at high pressures, as well as their anti-friction characteristics, they will find applications in metal working and machining.

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CHAPTER 8

Selective Oxidation

8.1 Selective Oxidation of Glycerol

Selective oxidation of glycerol is of particular interest due to the commercial importance of oxygenated glycerol derivatives. During the last decade a whole arsenal of chemical, electrochemical and biological oxidation methods has been explored for creating a market outlet for the large surplus of biodiesel glycerol. As the result of this effort, human ingenuity has now arrived with the series of glycerol derivatives shown in Figure 8.1. Previously this versatility was entirely absent, with biological transformation producing only a single product, dihydroxyacetone, for a global annual market of no more than 2000 tonnes.

As an example of recent progress, newly developed gold catalysts now provide the basis for a highly selective process for the human metabolite, glyceric acid (Figure 8.2).

This interesting bifunctional molecule has not yet been fully developed as a chemical intermediate owing to the lack of a large-scale preparative method. On the other hand novel food supplements or medicinal products containing D-glyceric acid are now commercialized for improving ethanol metabolism.[1] In addition, conventional platinum and palladium catalysts, in newly developed bi- and polymetallic systems, are useful tools for the intensive oxidation of glycerol to tartronic and mesoxalic acids. As a further example, the electrochemical oxidation of glycerol in fuel cells will without doubt provide an important large-scale outlet for glycerol, completing the cycle of conversion of renewable seed oil to energy. The use of glycerol in biofuel cells has

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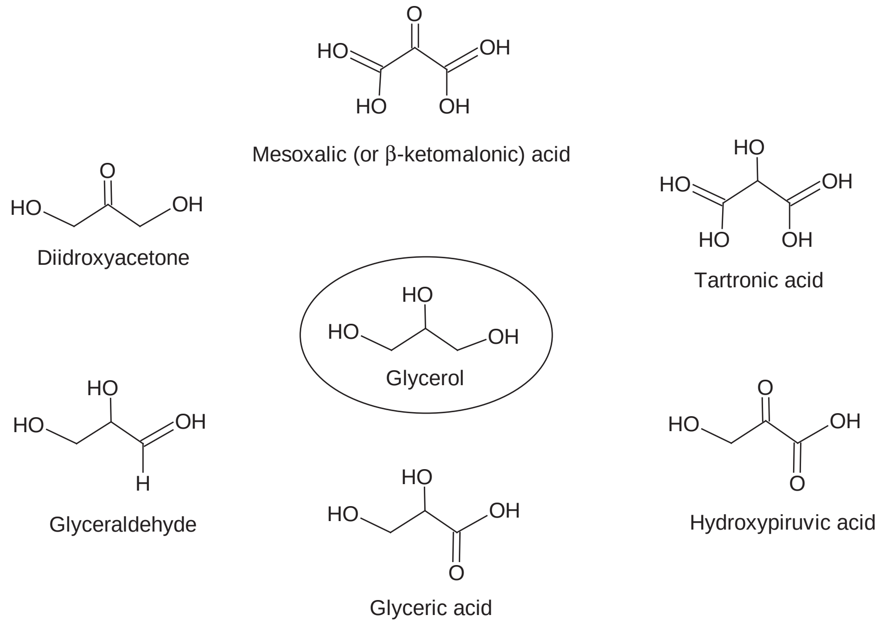


Figure 8.1 Oxidized glycerol derivatives.

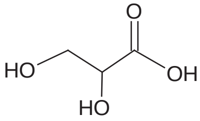


Figure 8.2 Glyceric acid is a synthon of largely unexplored potential, whose D-enantiomer is an anticirrosis agent.

considerable advantages over ethanol and methanol, which have been the traditional first choice for biofuel cells in portable devices (Figure 8.3).[2]

Progress in oxidation technology marks the irreversible decline of so-called stoichiometric oxidants such as chromates, permanganates and hypochlorites, which produce unacceptable types of waste, in favor of clean processes carried out under mild conditions using molecular oxygen in aqueous solution. An example of this challenging approach is the use of heterogeneous catalysis in which a solid catalyst is stirred with liquid reagents in the presence of oxygen or, even better, air. This avoids the large-scale use of soluble catalysts, it simplifies separation of the catalyst from the products, and finally, it speeds purification.

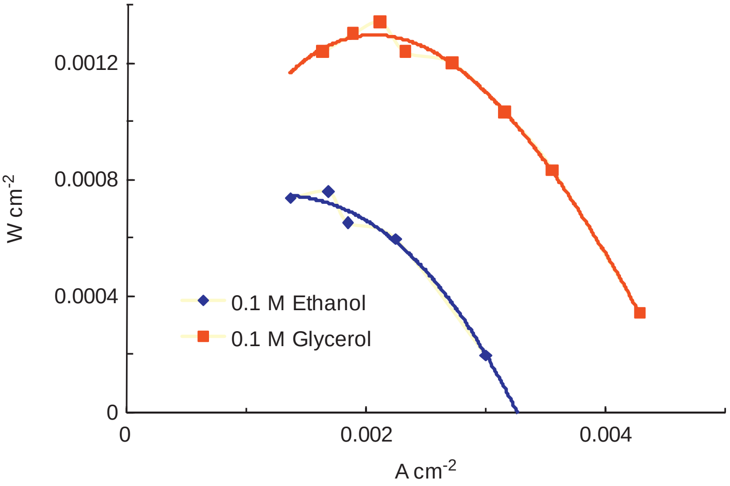


Figure 8.3 Comparison of the power curves for a single biofuel cell with two different analyte fuels (100 mM ethanol and 100 mM glycerol) at room temperature (adapted from Ref 2, with permission).

The aerobic oxidation of alcoholic hydroxyl groups was developed in the early 1990s with the use of conventional Pt- and Pd-supported catalysts and has since evolved into sophisticated polymetallic systems and organocatalysis, which increase selectivity and limit catalyst deactivation.[3] Owing to the presence of three oxidizable hydroxyl groups, a range of glycerol derivatives becomes available by adding oxygen and removing hydrogen atoms. A selection of stable, commercially relevant oxygenated products are shown above in Figure 8.1. Thanks to the current low price of glycerol, the economy of each product is governed to a large extent by its processing cost, in which the selectivity–conversion balance plays a crucial role. While simple oxygenated derivatives of glycerol such as peroxides are practically unknown, oxidative dehydrogenation is the common route to carbonyl derivatives, which may then undergo further oxygen addition to carboxylic derivatives. Glyceraldehyde (glycerose) is of scientific interest due to its choice as a standard for relative enantiomeric configurations and to the role of its 3-phosphate derivative as an intermediate in carbohydrate metabolism. In addition, this simple aldose undergoes the Lobry de Bruyn–Alberda van Ekenstein rearrangement, producing a mixture of glyceraldehyde and dihydroxyacetone in the biogenesis of animal organisms.[4] Owing to its high reactivity with molecular oxygen, however, glyceraldehyde itself is rarely observed among the products of the aerobic oxidation of glycerol. Dihydroxyacetone, a highly valued chemical used in artificial tanning and as a synthon for organic synthesis, is at present produced by fermentation of glycerol in the presence of *Gluconobacter oxidans*.[5] Glyceric and β-hydroxypyruvic acids are promising monomers for new polymeric materials and chelating agents, but their use in the food industry[6] is at present limited by the lack of a low-cost synthesis. Tartronic acid is available on the small scale *via* malonic acid ozonization,[7] whereas the naturally occurring mesoxalic acid, an interesting pharmaceutical precursor,[8] can be prepared by both catalytic and electrochemical methods.[9] The last two products are the precursors of interesting polyketomalonate materials.[10]

8.2 Thermodynamic and Kinetic Aspects of Aerobic C–OH Oxidation

From a thermodynamic point of view, dioxygen can be considered a high-energy molecule which reacts exothermically with organic compounds. However, activation of dioxygen is of fundamental importance in selective oxidation, in fact most organic molecules are stable in the presence of dioxygen owing to the high activation energy. The stability of organic molecules towards dioxygen is a kinetic property. Molecular oxygen is characterized by its paramagnetic and electrophilic character, which can be interpreted as a feature of the molecular orbital of its fundamental state (Figure 8.4).

As a radical it can easily react with other paramagnetic species, and as an electrophile it forms charge transfer complexes which can be reduced by accepting up to four electrons in the high-energy orbitals. To overcome kinetic inertness two mechanisms are available. The first is the promotion of the organic substrate to the upper triplet state, and the second consists of the so-called dioxygen activation. The latter can be achieved either by light-induced promotion to an O_2 singlet state, or more commonly by interaction with a metallic atom or ion. The M–O_2 bond produces sufficient energy to overcome the kinetic barrier of spin coupling, whereas the spin orbit coupling energy in the metal–dioxygen complex reduces the kinetic barrier of the spin change.

Dioxygen and the hydroxylated molecule are activated on a solid catalyst surface, producing a dehydrogenation process which leads to carbonylic species. The process requires temperatures in the region 60–80 °C, and the carbonyl intermediates behave either as kinetically inert species or they are oxidized further, depending on the experimental conditions. Whereas in the absence of water the oxygen attack on the aldehydic carbon is a slow process, the *gem*-diol derived from water addition readily undergoes dehydrogenation (Figure 8.5).

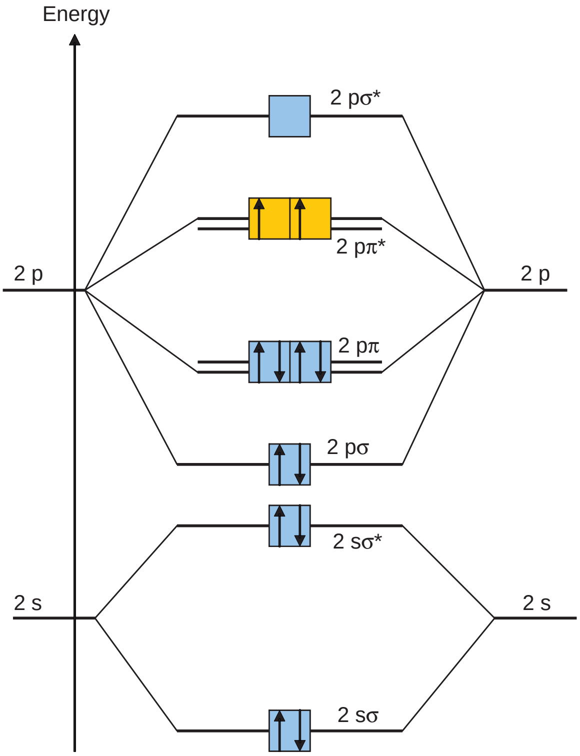


Figure 8.4 Molecular orbital scheme of O_2 fundamental state.

Hydration of the intermediate aldehyde is crucial for generating a carboxylated species. Thus the selectivity can be towards carboxylates in aqueous solution with alkali as hydration catalyst, whereas in organic media or under solvent-free conditions carbonylic species are the main products.

8.3 Platinum-Group Metal Catalysis

In general, platinum and palladium are highly active aerobic catalysts for the oxidation of glycerol. High yields of dihydroxyacetone can be obtained by the aerobic oxidation of glycerol on bismuth-promoted platinum in acidic media (Figure 8.6).[11]

Oxidation at the primary carbon to produce glyceric acid is favored on platinum or palladium catalysts. A fairly good selectivity (80%) to glyceric acid is obtained at 100% conversion with a Pd/C catalyst at pH 11, whereas a Pt/C catalyst produces a lower yield (50%). By

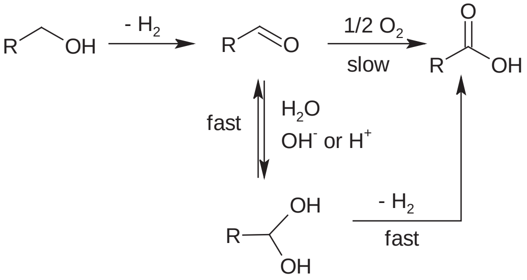


Figure 8.5 The *gem*-diol derived from water addition undergoes ready dehydrogenation.

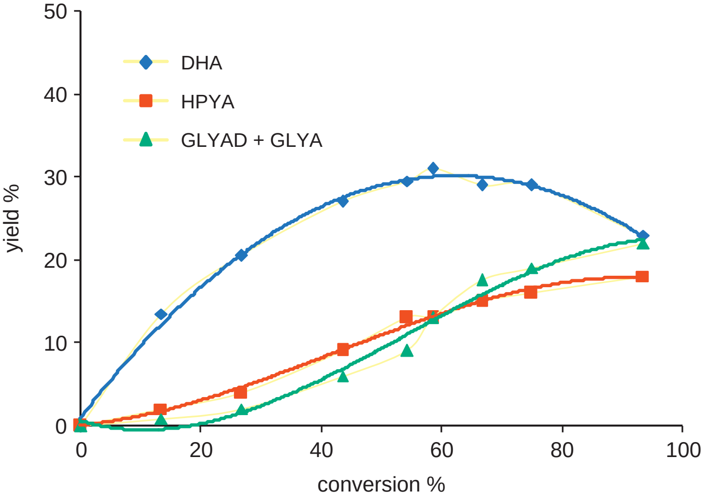


Figure 8.6 Oxidation of glycerol over Pt–Bi/C catalyst at pH 2 yields mainly DHA (adapted from Ref 11, with permission). GLYA = glyceric acid; GLYAD = glyceraldehyde

prolonging the oxidation glyceric acid is further oxidized to tartronic acid, with a reaction rate increasing with pH, the optimal yield being observed at pH $\geq$ 9.

In addition, tartronic acid can be further oxidized to mesoxalic acid with air in acidic media on a Pt–Bi on carbon catalyst, but the yield of this step is modest (60% yield at 80% conversion). To avoid the complex separation of mesoxalic acid from tartronic acid it may be advantageous to sacrifice some yield in order to drive the conversion to 100%. In this case a 50% yield of mesoxalic acid, contaminated by trace amounts of oxalic acid, is finally obtained.[12] In its turn, bismuth-promoted platinum at low pH values catalyzes the conversion of glyceric acid to β-hydroxypyruvic acid (64% yield at 75% conversion).[13]

While a Bi–Pt catalyst shows high selectivity to dihydroxyacetone, a three-component Ce–Bi–Pd catalyst supported on carbon allows the formation of tartronic acid in high yield under acidic conditions, and its disodium salt under basic conditions.[10] Subsequent oxidation of tartronic acid over a Bi–Pt catalyst produces ketomalonic acid. Following this with a multifunctional four-component Ce–Bi–Pt–Pd catalyst, the ketomalonic acid resulting from one-pot glycerol aerobic oxidation is readily polymerized to form the corresponding polyether, polyketomalonate, in the presence of a cationic or anionic initiator (Figure 8.7). Polyketomalonate, prepared by anionic polymerization in NaOH solution, is an unusual polymer owing to the absence of hydrogen atoms on the polyether carbons. Acidification readily causes decarboxylation to poly(oxymethylene).[10]

Deactivation of the catalyst due to overoxidation is the most important obstacle to the large-scale application of platinum group metals in liquid-phase oxidation. High temperatures and a low partial pressure of oxygen are required in order to stabilize the catalytically active zerovalent species. Strong adsorption of by-products is also responsible for the deactivation of platinum group metals. Mobility of metal atoms at

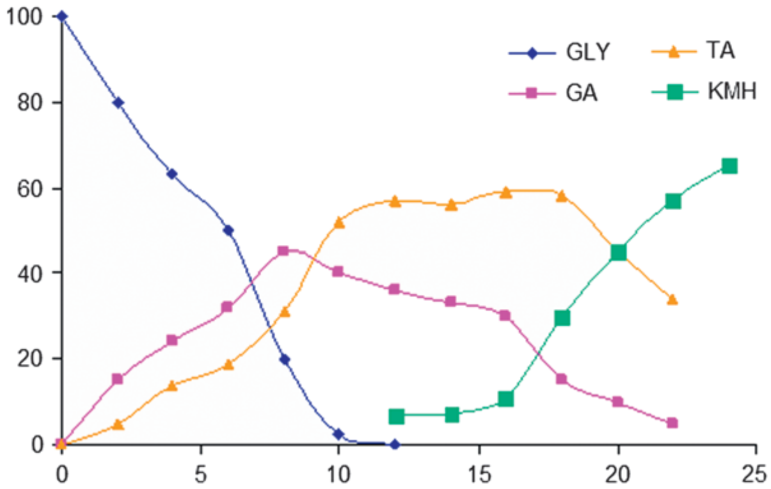


Figure 8.7 One-pot consecutive oxidation of glycerol to ketomalonic (mesoxalic) acid over a multifunctional Ce–Bi–Pt–Pd catalyst (adapted from Ref 10, with permission). (GLY = glycerol; TA = tartronic acid; GA = glyceric acid; KMH = ketomalonic acid hydrate).

the catalyst surface causes the metal particles to grow, thus decreasing their specific surface area and the consequent turnover frequency (TOF). The latter phenomenon occurs *via* a reversible metal dissolution–precipitation, favored by strongly coordinated products, whereas irreversible dissolution results in loss of precious catalyst as it is leached into solution.

8.4 Gold and Organocatalysis

Supported gold catalysts are a true second generation class of supported metal catalysts in the oxidation of glycerol. Indeed, great improvements in selectivity and stability have been achieved since the early 2000s. Firstly, the high electrode potential ($E^\circ = +1.69\,V$) of gold is responsible for its well known inertness, which in catalytic terms indicates high stability, greater resistance to oxygen, and tolerance against poisoning chemical groups such as aliphatic and aromatic amines. A second feature concerns the kinetic aspect of gold catalysis, namely that the TOF is strongly related to the size of the metallic gold particles.[14] Many investigations into the liquid-phase oxidation of polyols have in fact confirmed that it is only the smaller gold particles that are catalytically active.[5]

With the new gold-based catalytic systems a valuable new general method for organic synthesis has arrived: primary alcohols and terminal diols can readily be oxidized to carboxylates in aqueous solution in the presence of alkali with almost 100% regioselectivity.[15] Activation of dioxygen and alcohol molecules occurs *via* adsorption on the solid catalyst according to the general pattern shown in Figure 8.8. In the case of polyhydroxylated molecules, the size of particles within the range 2–7 nm correlates linearly to the kinetics, the smaller being the more active, whereas particles larger than 10 nm are virtually inactive.

A great advantage of gold catalysis is the absence of metal overoxidation and leaching. In the presence of a stoichiometric amount of NaOH (1 : 1 with respect to the reagent), the aerobic oxidation of glycerol at 60 °C over 1 wt% Au/C under a moderate pressure of oxygen

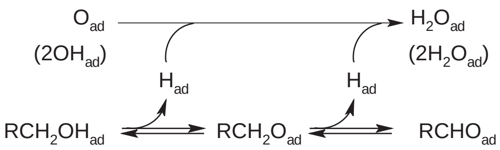


Figure 8.8 Activation of dioxygen and alcohol molecules.

(3–6 bar) produces glycerate with up to 100% selectivity at 54–56 % conversion with a glycerol : Au molar ratio of 538.[16] Newer catalysts containing relatively large particles (> 20 nm) show constant selectivity throughout the reaction, giving 92% selectivity to glycerate at full conversion, by oxidizing glycerol at 30 °C with a NaOH : glycerol ratio of 4 and a glycerol : Au molar ratio of 500.[17] Furthermore, a bimetallic Au–Pd/C catalyst enables kinetic control of the oxidative dehydrogenation, producing high selectivity to glyceric acid (69% at 90% conversion), with no overoxidation.[18] Again, relatively large metal particles ensure that glycerate remains stable at higher temperatures, avoiding the formation of tartronate, with a progressive increment in selectivity towards glycerate as the mean diameter of the particles increases from 2 to 16 nm.[19] Figure 8.9

Kinetic investigation of glycerol oxidation under high oxygen pressure over an Au/C catalyst points to a Langmuir–Hinshelwood mechanism in which the adsorption step of the main compounds, glycerol and glyceric and tartronic acids, is that of kinetic relevance.[20] Hutchings, who first reported the gold catalyzed oxidation of glycerol, has demonstrated the advantage of using *continuous* flow reactors for the oxidation of glycerol under mild conditions. Both monolith and meso-scale structured downflow slurry bubble column designs lead to a significant enhancement in the reaction rate compared with use of an autoclave (which is one order of magnitude greater for the Au/carbon coated monolith, and two orders of magnitude larger for the meso-scale

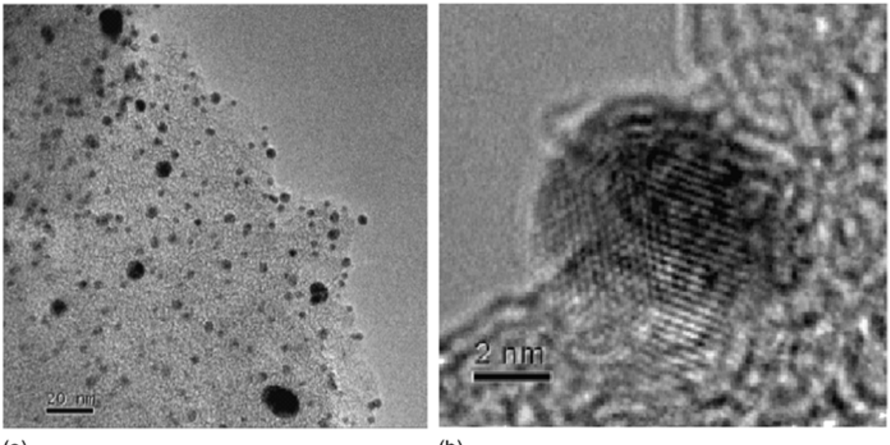


Figure 8.9 (*a*) and (*b*) Au/C catalysts of 6 and 12 nm particle size, respectively (reproduced from Ref 20, with permission).

structured downflow slurry bubble column reactor).[21] The monolith and autoclave data show high selectivity to glyceric acid, whereas under similar conditions the thin channel slurry bubble column yields almost equal quantities of dihydroxyacetone and glyceric acid. This difference in selectivity can be attributed to enhanced interaction between bubbles and particles by structuring gas–liquid–solid reacting flows in thin channels or capillaries.[21] The strategic importance of reactor configuration in improving the selectivity has also be pointed out by Zope and Davis, who found similar results: the unique hydrodynamics of the fixed bed system leads preferentially to secondary oxidation products such as tartronic acid and oxalic acid, unlike the lower production observed in a batch system.[22] The ultimate scientific developments of gold-catalyzed oxidation of glycerol and other alcohols have been reported in a critical review.[23]

Organocatalysis by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is a suitable technique for the selective oxidation of glycerol to mesoxalic acid.[24] Coupled to an inexpensive NaClO–Br regenerating oxidant, the catalytic cycle typical of nitroxyl-mediated oxidation selectively produces ketomalonate (98%) along with a small amount of dihydroxyacetone (2%). The reaction can conveniently be carried out over microporous sol–gel silica glass doped with the TEMPO radical moiety. This enables rapid separation of the product from the catalyst, which can be recycled (Figure 8.10).

Most recently, the oxidation of glycerol with TEMPO in the presence of the laccase enzyme has been found to cause its sequential oxidation to glyceraldehyde, glyceric acid and tartronic acid, and finally to mesoxalic acid.[25] The number and nature of the oxidation products depends on the concentration of TEMPO. At lower TEMPO concentrations (<6 mM) the major initial reaction products are glyceraldehydes, while at higher concentrations considerable amounts of glyceric acid are formed (Fig 8.11).

In this study, during 24 h of incubation at TEMPO concentrations below 30 mM there was less overoxidation, at the expense of low conversion, with glyceraldehyde the predominant product. Use of 3 mM TEMPO led to a conversion of 35%, with glyceraldehyde and glyceric acid the major oxidation products. Raising the concentration of TEMPO from 3 to 6 mM increased the conversion to 55%. At this substrate/TEMPO ratio the formation of glyceraldehyde and glyceric acid was almost in balance. For TEMPO concentrations greater than 6 mM the oxidation was driven to lower selectivity but higher conversion rates. When the incubation time for 6 mM TEMPO was extended to 48 h the conversion of glycerol (64%) was comparable to that for 30 mM of TEMPO incubated for 24 h, which gave 70% conversion.

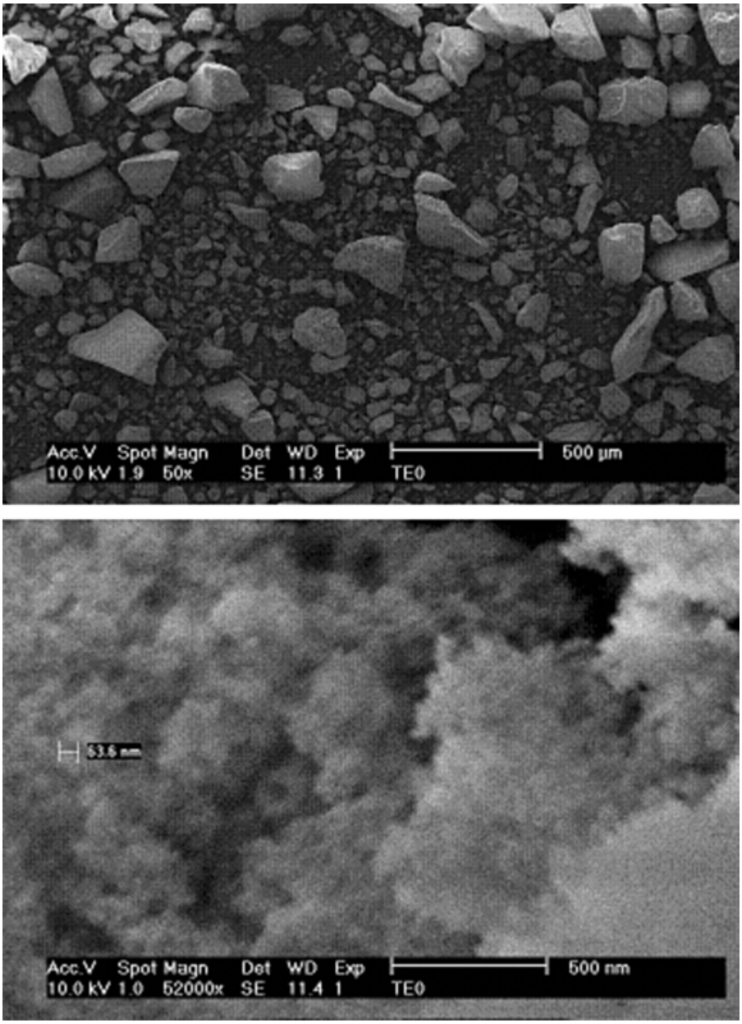


Figure 8.10 SEM photographs of sol–gel entrapped silica catalysts doped with TEMPO (reproduced from Ref 21, with permission).

8.5 Oxidation Using an Iron Catalyst

A new potentially large-scale use for crude glycerol has recently been reported in the patent literature. According to researchers from Lignotech USA, crude glycerose, the technical name for 2,3-dihydroxypropanal, or glyceraldehyde, can be synthesized by partial oxidation of glycerol at 50–60 °C. Under acidic conditions, using hydrogen peroxide as oxidant and ferrous sulphate (500-3000 ppm) as catalyst, a liquor is produced containing glyceraldehyde and other side-products of the

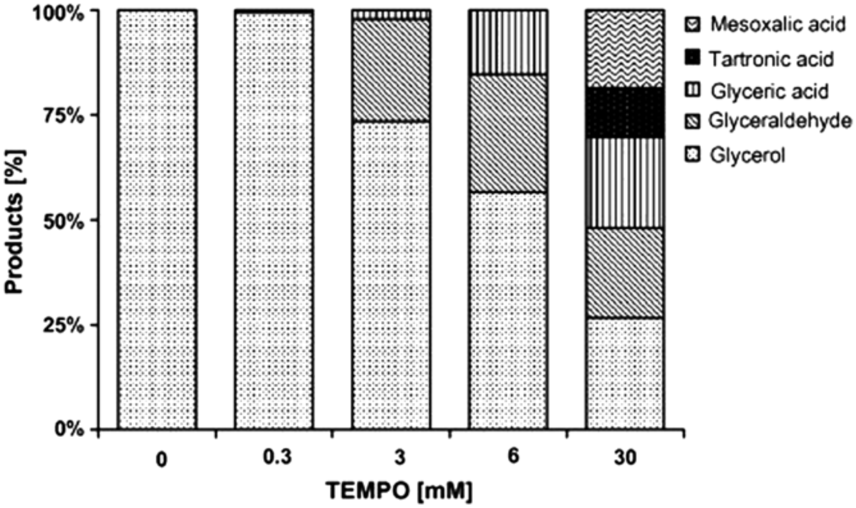


Figure 8.11 Oxidation of 100 mM glycerol with different amounts of TEMPO in the presence of laccase (reproduced from Ref 25, with permission).

oxidation.[26] It may be recalled that during the aerobic oxidation of glycerol over heterogeneous noble metal catalysts, glyceraldehyde is detected only as a transient species in very small amounts. In this new study the high-yield oxidation to glyceraldehyde seems to depend on a quite different catalytic arrangement, namely the combination of hydrogen peroxide oxidant with homogeneous iron. According to this process, starting from crude glycerol the glycerose liquor may be combined with a protein-containing fodder without further isolation, purification or drying to provide a ruminant feedstuff.

8.6 Electrochemical Oxidation

The catalytic system employing TEMPO as catalyst for the oxidation of glycerol by NaClO can also be used in the electrochemical conversion of glycerol to 1,3-dihydroxyacetone (DHA).[27] Thus, one-pot waste-free oxidation of glycerol to DHA has been achieved by simply applying a small electric potential (1.1 V *vs* Ag–AgCl) to a glycerol solution in water buffered at pH 9.1 in the presence of 15 mol % TEMPO at the surface of a glassy carbon anode. Prolonging the reaction time gives comparable amounts of hydroxypyruvic acid (Figure 8.12).

The catalytic cycle indicated in Figure 8.13 shows how DHA is formed by TEMPO, which is reduced to the hydroxylamine

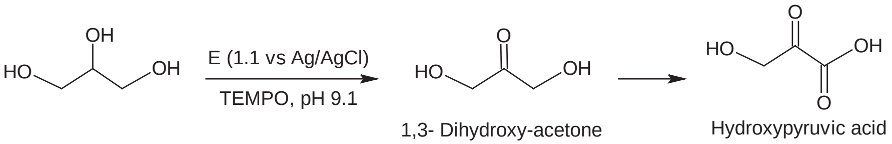


Figure 8.12 Electrochemical oxidation of glycerol to DHA takes place smoothly in aqueous solution (reproduced from Ref 22, with permission).

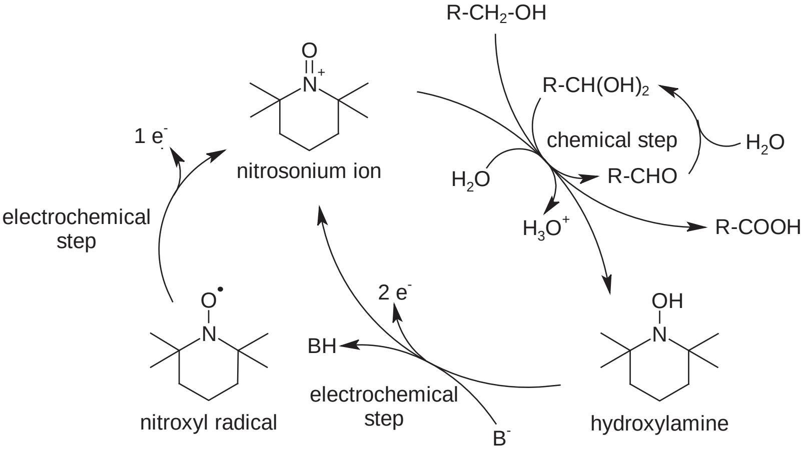


Figure 8.13 Electrochemical oxidation of alcohols mediated by TEMPO.

intermediate. The key point of this process is the reoxidation of the latter to TEMPO through parallel electrochemical pathways.

Apart from the oxidation of glycerol to high-value chemicals ranging from DHA to mesoxalic acid, great attention is being paid to the energy produced by direct conversion of glycerol to carbon dioxide and to electrical energy resulting from its oxidation in fuel cells. Films of polyaniline electrodeposited on gold and glassy carbon electrodes,[28] and doped with Pt, Pd or Ru,[29] show good activity in the electro-oxidation of glycerol in acidic media. In such partial oxidations, however, the main product is glycerate, which only results in 28.6% oxidation of the glycerol fuel and limits the amount of energy produced.

Recently, a new pH-controlled electrochemical oxidation of glycerol has been reported which makes use of a thin-film cell.[30] According to the process, the relative formation of glyceraldehyde, dihydroxyacetone and glyceric acid can be controlled by use of appropriate supporting electrolytes.

Potentially, however, the most relevant contribution arising from the electrochemical oxidation of glycerol is expected to be its use in power-producing devices, since this would make waste glycerol a valuable fuel suitable for large-scale application. Encouraging results from the electro-oxidation of glycerol in acidic and alkaline media show that, compared to ethanol, the current density reached in glycerol oxidation on the anode containing a Ru–Ni catalyst significantly exceeds that in ethanol oxidation, the result being increased by a factor of 3–4.[30,31]

8.7 Biological Oxidation

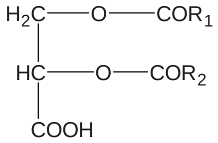
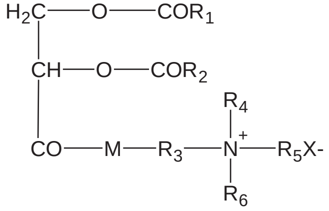
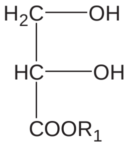
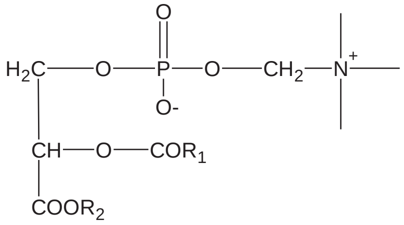
Industrial fermentation of glycerol has been applied to the synthesis of DHA since the late 1920s. DHA is the main active ingredient in artificial tanning agents,[32] and manufacturers today obtain it by the bioconversion of glycerol extracted from colza or palm oil.[33] A variety of microorganisms and derived enzymes can be employed, producing a range of selectivities. A range of bacterial cells, including *Acetobacter* (*A. suboxydans* ATCC 621, *A. xylinum* A9, *A. kuetzingianus* OUT 8296, *A. pasteurianus* OUT 8299, *A. rancens* OUT 8300, *A. suboxydans* IFO 3254, *A. suboxydans* IFO 3255, *A. suboxydans* IFO 3291 and *A. suboxydans* IFO 3432); *Gluconobacter* (*G. melanogenus* IFO 3293, *G. melanogenus* IFO 3294, *G. capsulatus* IAM 1813, *G. cerinus* IAM 1832, *G. dioxyacelonicus* IAM 1814, *G. glyconicus* IAM 1815 and *G. roseus* IAM 1838); and yeasts (*Candida valida* and *Neurospora crassa*), all show high selectivity to DHA.[34] Batch fermentation can be used with *G. oxydans* or *A. suboxydans*. A troublesome feature of microbial fermentation is however the tedious inoculation required for each cycle, and improved systems adopt a semi-continuous process in which part of the fermentation broth is allowed to remain in the reactor as the inoculate for the next cycle. Moreover, DHA has an inhibitory effect on bacterial growth, and single-stage production restricts DHA concentration to $60\,\mathrm{kg\,m^{-3}}$. A two-stage process based on *G. oxidans* has recently been developed to increase DHA productivity,[35] along with a heterogeneous process using cells immobilized on polyvinyl alcohol beads.[5] The first stage provides the source of a durable non-product-inhibited culture, and the second stage is a high concentration DHA reactor. Under these conditions, a DHA threshold value of $82\,\mathrm{kg\,m^{-3}}$ has been reached in the first stage and $161\,\mathrm{kg\,m^{-3}}$ in the second reactor.

As disclosed by Daicel Chemical Industries in 1989, acetic acid bacteria members of the *Gluconobacter* species are able to usefully metabolize glycerine into glyceric acid.[36] It has also recently been recognised by Habe's group that a large excess of the optically active D-GA is generated by the aid of *Gluconobacters*.[37] This behavior is in contrast to the chemical oxidation route, which produces only the racemic mixture, DL-GA. The availability of large quantities of glyceric acid, and even more importantly, in form of the pure enantiomer (D-GA), is an important step towards providing a cheap and versatile building block for pharmaceuticals and other fine chemicals, and will be exploited commercially in the near future. The importance of glyceric acid as a chemical feedstock for new derivatives and their functions is summarized in Table 8.1.

With a view to providing an outlet for the glycerol by-product of biodiesel, however, the most promising biological oxidation process has been the recent employment of glycerol in fuel cells using membrane-immobilized enzymes.[38] Two oxido-reductase enzymes (PQQ-dependent alcohol and aldehyde dehydrogenase, respectively) are immobilized at the surface of a carbon anode 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 over months, or even years. These glycerol bioanodes have been incorporated into a glycerol–oxygen biofuel cell which enables multi-step oxidation of glycerol to mesoxalic acid; this utilizes 86% of the energy density of the glycerol and results in power densities of up to $1.21\,\mathrm{mW\,cm^{-2}}$ at room temperature. This is very different from metallic electrodes, which give glycerate as the only detectable oxidation product of glycerol, and it demonstrates that the biofuel cell can allow deeper oxidation of the glycerol fuel, increasing overall efficiency and energy density (Figure 8.14).

This technology has been licensed to the company Akemin Inc., and is progressing towards commercialization.[39] The key to commercial development will lie in improving the lifetime and performance of enzymes over a range of temperatures. Fuel cells convert the energy stored in the fuel directly into usable electrical power. They are in effect batteries which can be recharged merely by refilling a small fuel tank. One of the their main drawbacks is that they are limited to simple fuels such as hydrogen or methanol, each of which give 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 and non-flammable, and a given volume contains three times more energy 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

Table 8.1 Glyceric acid and its derivatives (adapted from Ref 30, with permission).

Compound	*Derived from*	*Use*
Glyceric acid	Fito-extract	Hepatic therapy
Calcium D-Glycerate	Chemical synthesis	Demineralisation agent
C_{14}-C_{18} fatty acids dialkylglycerate 	Biosynthesis	Antritrypsin activity
Ammonium salts 	Chemical synthesis	Biodegradable fabric conditioning
Monoalkylglycerates 	Chemical synthesis	Surfactant
Phospholipids 	Chemical synthesis	Biologically active phospholipids

amount of glycerol produces almost four times as much power as methanol, and it is the main alternative at present being considered for portable electronics such as cell phones and laptops. Biofuel cells have the further advantage that they avoid the use of expensive precious metals. On the other hand their use is restricted by the fact that they can only be used between freezing temperatures and 90 °C, so they are unsuitable for high temperature applications such as automobile engines and household generators.

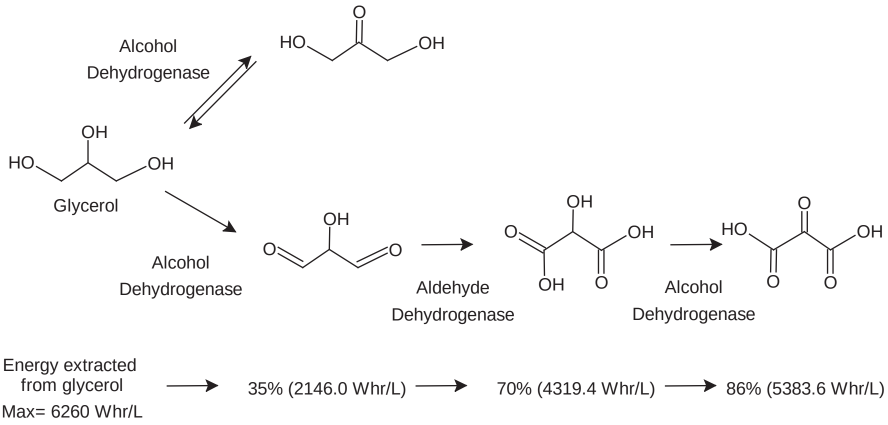


Figure 8.14 Oxidation sequence for glycerol at a PQQ–ADH/PQQ–AldDH-modified bioanode (reproduced from Ref 2, with permission).

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39. According to the inventor it will take about three further years before glycerol clips could be used to power mobile phones (Professor S. F. Minteers, personal communication).

CHAPTER 9

Bioglycerol in the Construction Industry

9.1 Polyols as Additives for Cement

The materials employed in the construction of buildings, roads and bridges comprise one of the largest volume markets in the world. Hydraulic cements, for instance, are used in quantities amounting to billions of tonnes per year, and global consumption is expanding rapidly, particularly in China, India and other Far Eastern regions (Figure 9.1).

The concrete industry uses both commercially available blends and topically applied products as evaporation retardants, curing compounds and penetrating sealants. These are designed to reduce cracking, freeze–thaw damage, sulfate attack and chloride ion penetration.

Hydraulic cements are produced by calcining a mixture of calcareous and argillaceous materials, comprising limestone, sand, shale, clay and iron ore, to produce a sintered "clinker". Prior to calcination the raw materials are crushed to below 10 cm in size. In either wet or dry production processes the proportions of each raw material are adjusted to meet the required performance and are fed to a rotating ball mill, with or without water. The resulting material contains the majority of particles below 75 μm (Figure 9.2). The materials discharged from the mill are known as "kiln feed".

Apart from evaporating all the moisture present, the reactions involved include conversion of the limestone to calcium oxide, which

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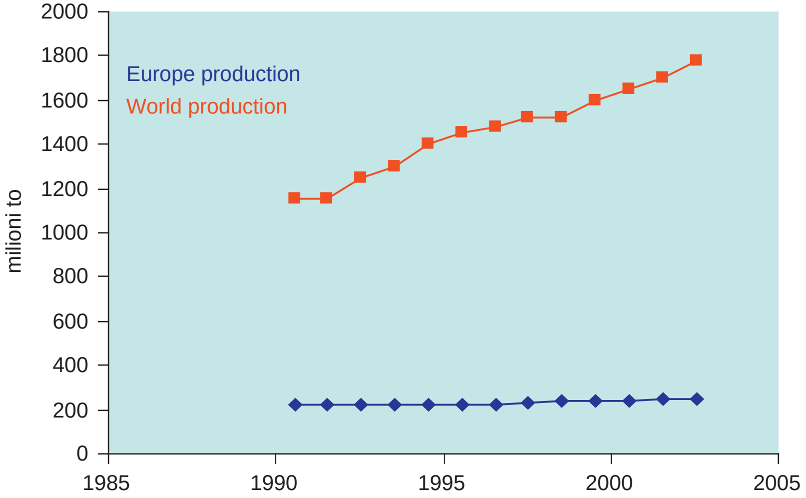

Figure 9.1 World consumption of cement is rapidly on the rise, whereas in Europe it is constant at about 200 million tonnes per annum (source: Grace Construction Products).

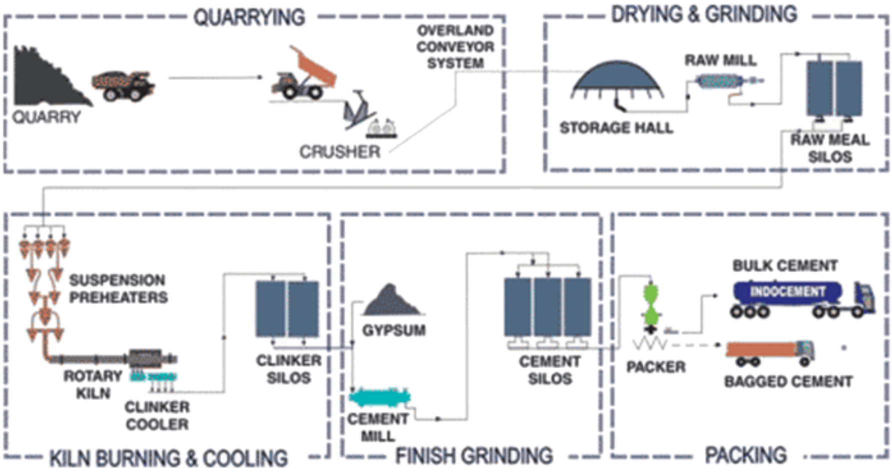

Figure 9.2 Scheme for typical dry process for cement manufacture (source: Indocement).

then reacts with the other materials present, such as sand, shale, clay and iron. Calcination takes place in the intense flame produced by burning coal or petroleum (“pet”) coke and results in a black nodular clinker. The clinker is ground in ball mills along with gypsum and other process additives to form the final cement product. The fineness of the cement powder and the quantities of gypsum and other materials added are controlled to give the required performance to the final product.

In terms of production volume, Portland cements are by far the most important hydraulic cements. In this case the clinker is mixed with gypsum and ground, usually in a ball mill, to a finely divided state, giving a particularly high surface area to the finished cement. Clearly the grinding process consumes a considerable amount of energy, indeed energy costs account for 40% of the overall cost of production. Of this, 80% is accounted for by the calcination and grinding processes and the remaining 20% by the electrical energy required for the cooler (Table 9.1).

While thermal energy consumption has been reduced almost to the theoretical minimum of 3500 MJ per tonne of clinker (Figure 9.3), the overall electrical energy requirement is on the increase due to greater demand for higher grade cements.

It is common practice in the cement industry to add small amounts of grinding additives during milling to lower the friction between particles.

Table 9.1 Electrical energy represents about 20% of the overall energy input for cement manufacture, with typical values in the range 90–130 KWh per tonne.

	kWh per tonne
Crushing	1–3
Grinding of the crude mixture	8–30
Homogenization of the crude	1–2
Cooking	16–18
Grinding finished cement	30–80

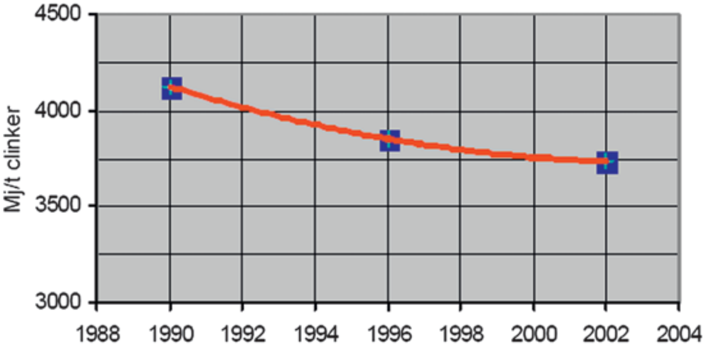

Figure 9.3 Evolution of specific thermal energy consumption for the production of 1 tonne of clinker in Italy. Similar trends are common in Germany and other leading industralized countries (source: Grace Construction Products).

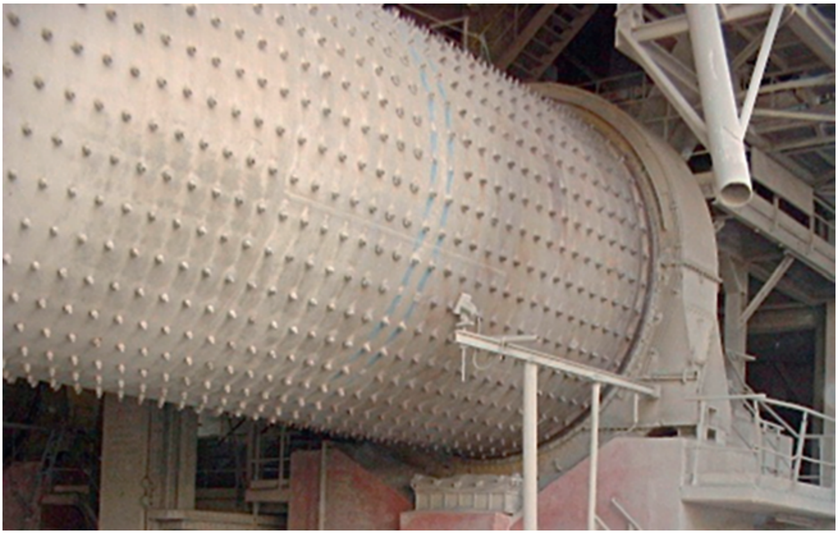

Figure 9.4 A ball mill used to grind clinker and produce cement (photo courtesy of Grace Construction Products).

This has the effect of reducing the energy needed to grind the clinker to the required particle size (Figure 9.4).

An important issue in the handling of cement-like materials is the packaging of the powdered material. After grinding, most cements become semi-rigid when vibrated and compacted and do not flow under a consistent mechanical effort. Lowering the "pack set inhibition", the energy required to initiate flow, is of paramount importance in unloading cement powder from storage silos and trucks.

Water-soluble polyols, mainly glycols and polyglycerols,[1] and the acetic acid esters of glycerol,[2] are useful cement additives for assisting grinding and reducing pack set inhibition.[3] Grinding aids reduce the cost of cement manufacture by decreasing the attractive forces between the particles which cause agglomeration. They are added to the cement during the grinding process, in the range 150–500 g per tonne of cement, resulting in:

- increased cement flowability and reduced pack set;
- increased grinding efficiency and mill output;
- reduced unit power costs; and
- reduced handling and pumping costs.

Materials which assist the grinding process are all strongly polar in nature. Their effect results by decreasing the causes of agglomeration.

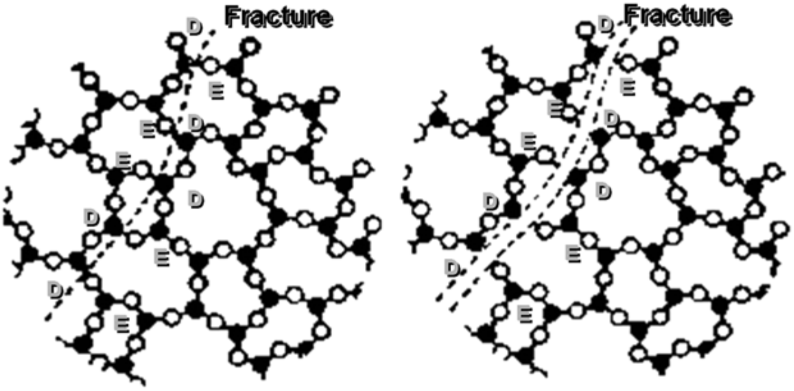

Figure 9.5 Silica crystal structure. Units D and E refer, respectively, to oxygen-deficient (+) and oxygen-excess (–) sites.

The grinding aids are adsorbed on the newly created surface of the particles, neutralising electrostatic charges and hence reducing their tendency to reagglomerate (Figure 9.5). As a result the cement becomes easier to grind into smaller particles.

In addition to polyols, other types of hydroxyl additives may be used, including water-soluble aliphatic alkali carboxylates,[3] nitrogen-containing compounds such as triethanolamine,[4] and sulfonated lignins.[5] A combination of more than one of these is frequently employed.[6]

Of relevance to this book is the recent finding that biodiesel (or fatty acid methyl esters, FAME) from which bioglycerol is mostly obtained, is an effective and economical sealant for concrete. In particular, FAMEs applied to concrete are highly effective without adversely affecting its properties. Results from sorption tests show that cement samples containing FAME–polystyrene (PS) blends reduce water absorption by between 74 and 94%, and chloride ion penetration by as much as 77%. Such a significant reduction in water absorption has a direct effect on the durability of the concrete, and demonstrates the ability of FAME–PS to reduce water transport within cementitious systems without affecting their basic mechanical properties.[7]

9.2 Glycerol as Anticracking and Waterproofing Agent

A third issue deriving help from cement additives is the surface cracking of Portland cement, which appears under the effects of low humidity, wind or high temperature. A further factor is compression strength. Compression strength is the capability of a manufactured cement structure to retain its performance under pressure. When the ultimate compression strength is reached, fractures are generated at the surface and cause the structure to break. Since good compression strength is so important, a variety of additives have been developed to improve this property and are added at the clinker milling step. Glycerol is effective in improving compression strength, but its industrial usage has traditionally been impeded by the high cost of the pure material.

Glycerol has also been employed in conjunction with film-forming polymeric materials for preventing surface cracking.[8] A continuous coating comprising an aqueous alcoholic solution of glycerol and/or a polyglycerol is applied to a fresh uncured concrete surface containing a film-forming polymeric modifier such as a styrene–butadiene copolymer. By comparison with a control experiment, no cracking is observed in the test specimen. Small quantities of glycerol are also employed in the additives used to improve the waterproofing of concrete.[9] A typical additive might for example contain alumina (10%), alkali (4%), fatty acid (3.5%) and glycerol (0.5%). An aqueous slurry of this composition is added to the cement used for repairing old concrete structures.

9.3 Raw Glycerol as Quality Enhancer and Grinding Aid

Crude glycerol from biodiesel production is an excellent quality enhancer for cement, improving its resistance to compression.[10] This discovery, resulting from collaboration between the University of Milan, the National Research Council of Italy and Grace Construction Products, has created a considerable outlet for biodiesel-generated glycerol. Furthermore, since biodiesel production in all continents tends to be found in the same locality as cement production, cement manufacturers can now rely on an abundant and convenient source of this valuable additive.

Additives composed primarily of organic materials and only minor proportions of inorganic ingredients are now used in 60% of world cement production. The organic components are usually derived from ethylene oxide, and thus from fossil oil. Table 9.2 shows the results of industrial tests carried out in Belgium, Italy and Greece on three types of clinker before blending with gypsum to produce cement, to which raw and pure glycerol from biodiesel production has been added in amounts comparable to those used for current additives.

The tests were conducted in accordance with international standards, and the final concentration of additive was usually in the range 200 to

Table 9.2 Granulometry and performance properties of three cement clinkers with addition of pure or raw glycerol.

Cement			*Laser PSD*[a]				*Compressive strength (MPa)*			
Additive	*Ppm*	*Blaine*[b] *($cm^2\,g^{-1}$)*	*R32 (%)*	*R45 (%)*	*R63 (%)*	*R90 (%)*	*1d*	*2d*	*7d*	*28d*
Belgium										
Blank	–	3230	21.9	10.5	3.2	0.1	–	25.9	45.0	58.2
Pure glycerol 50%	400	3290	24.7	12.5	4.1	0.4	–	26.7	45.0	58.8
Raw glycerol 50%	400	3160	26.5	14.2	5.2	0.7	–	28.3	46.9	60.8
Greece										
Blank	–	3570	18.8	8.7	2.6	0.2	16.1	–	41.6	53.0
Pure glycerol 50%	400	3550	22.1	10.8	3.4	0.3	20.1	–	41.6	53.8
Raw glycerol 50%	400	3590	21.5	10.7	3.6	0.5	18.1	–	43.8	56.6
Italy										
Blank	–	3560	27.5	16.4	7.8	2.4	–	22.2	38.0	52.9
Pure glycerol 50%	400	3480	33.6	21.1	10.5	3.2	–	26.3	39.0	49.6
Raw glycerol 50%	400	3590	33.0	21.3	11.1	4.0	–	24.8	40.8	51.8

[a] Laser PSD: granulometry distribution (number of particles with diameter greater than a certain figure, in this case: 32, 45, 63 and 90 µm).

[b] Blaine: measure of cement fineness.

400 ppm, applied as a 50% aqueous solution. In all cases, crude glycerol (containing 5% NaCl and with a color approaching that of lager, due to the presence of natural dyes) was found to produce similar or improved mechanical and chemical properties to those resulting from three other additives, including pure glycerol itself. This is surprising, and points to interaction between glycerol and the inorganic salts present. According to industry experts, initial market consumption of crude glycerol for this application is estimated to be about 1000 tonnes per annum, roughly 2% of Europe's 50 000 tonne market for glycerol as a cement additive.

A second major benefit of glycerol as a cement additive comes from its employment in grinding technology. Using low levels of glycerol, either pure or in raw form as a by-product of biodiesel, gives significant improvements in mechanical properties in the milling of a range of doped cement clinkers. A similar or better performance is obtained in comparison to the more expensive triethanolamine (TEA) and diethylene glycol (DEG) typically used as high-value cement performance enhancers (Table 9.3).

In cement production the energy requirement is dominated by thermal heating of the furnace and the electrical energy required by the mill. As mentioned earlier, these factors account for as much as 40% of total production costs (fuel 3500 MJ per tonne of clinker and electricity 90–120 KWh per tonne of cement). The benefit obtained from grinding additives is in decreasing electrical energy consumption by about 10%, which is a remarkable result.[11] The annual market for grinding aids in continental Europe, not including performance- or quality-enhancing additives, is 25 000 tonnes, amounting to 0.012% of European cement production, which totals 200 million tonnes.

9.4 Bioglycerol as Anticorrosive Lubricant

Glycerol fractions from biodiesel production show excellent anticorrosive and antioxidant properties, a recent finding that generates a new application in lubricant manufacturing.[12] This indicates that most of well known phenolic antioxidants occurring naturally in oils during esterification are transferred to the glycerol fraction, opening new possibilities of usage of the fraction without a very expensive purification process. The results obtained in the course of a project financially supported by an EU grant,[13] show that the mixture of antioxidants with glycerol, could be utilized as anticorrosive soap. This kind of application would only be possible for technical demands such as washing cars, tanks, lorries and trains, as well as external building surfaces, providing

Table 9.3 Properties of clinkers with addition of raw glycerol (GLY), triethanolamine (TEA) or diethylene glycol (DEG). Passing refers to percentage of particles passing through a standard sieve.

	Particle size (μm)						
Sample	*32.0*	*45.0*	*63.0*	*90.0*	*Blaine ($cm^2\,g^{-1}$)*	*RPM (s^{-1})*	*Packset (s)*
Clinker Italy A							
Passing%-	74.8	85.6	94.3	99.0	3620	3200	
Passing% TEA	74.4	86.4	95.2	99.4	3620	2500	
Passing% DEG	74.3	85.9	94.7	99.2	3550	2500	
Passing% GLY	72.0	84.1	93.6	98.9	3720	2500	
Clinker Italy B							
Passing%-	71.2	82.4	91.7	97.8	3580	2200	41
Passing% TEA	73.8	85.3	93.8	98.6	3510	2250	29
Passing% DEG	74.1	84.8	93.3	98.5	3590	2200	28
Passing% GLY	79.9	89.8	96.3	99.5	3590	2050	32
Clinker Greece							
Passing%-	80.0	89.7	96.3	99.5	3610	2350	68
Passing% TEA	77.5	88.1	95.4	99.3	3510	2400	21
Passing% DEG	78.5	89.0	96.0	99.4	3620	2200	38
Passing% GLY	77.3	88.1	95.5	99.3	3530	2400	32

a market huge enough to absorb a major fraction of global glycerol surplus.

Apart from 1,2,3-propanetriol, the glycerol fraction consists of methyl/ethyl esters, soaps, unreacted fatty acids and glycerides. Other natural compounds originating from oils may also be present, for example phenolic antioxidants. Indeed, the EPR spectra of raw glycerol fractions, first measured by the research group of Jerzykiewicz at Wroclaw University, show a typical phenolic/semiquinone radical line (Figure 9.6). Parameter $g = 2.0043–2.0046$ is characteristic of radicals with an unpaired electron centered on an oxygen atom substituted to an aromatic ring. The spectra are not resolved by hyperfine interaction, which could also be associated with this kind of radical. Additionally, lack of hyperfine interaction and the absence of nitrogen-containing groups by elemental analysis proves the absence of Maillard polymers, as are found in products of natural origin. Since stability is one of the most important features of radicals, the signal was measured a number of times. The oldest samples of glycerol fractions were about three years old, and the EPR parameters remained unchanged.

Additionally, scavenging galvinoxyl radical EPR method shows high phenolic antioxidant content in the raw glycerol fractions. The basis of

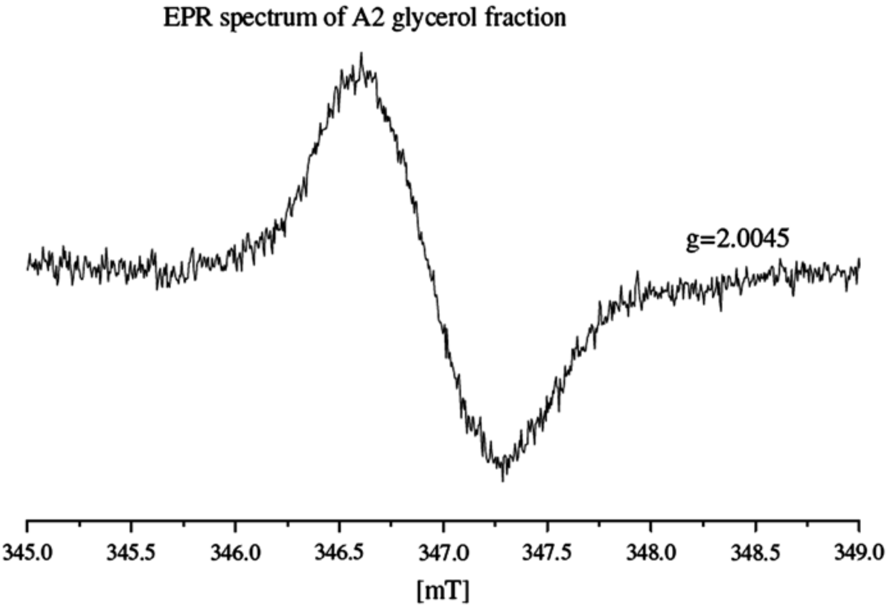

Figure 9.6 EPR spectrum of glycerol fraction (reproduced from Ref. 11, with permission).

the method is the reaction of a galvinoxyl radical with a phenolic system, as a result of which quenching (scavenging) of galvinoxyl radical signal is observed. A short-lived radical is formed, and for some samples was possible to measure this radical; its g parameter was 2.0046, similar to that observed for raw glycerol fractions.

Quantitative studies of phenolic antioxidants obtained using EPR method parallels the UV–Vis results. As standards, gallic acid and caffeic acid were used. The calculated concentration of phenolic systems varied between 0.001 and 1 $\mathrm{g\,L^{-1}}$. This demonstrates that in general the production scale, the type of catalyst and the alcohol employed in biodiesel manufacture does not influence the scavenging activity of free radicals. Similarly, it is difficult to establish a relationship between soap content (or saponification number) and free radical scavenging ability. Nevertheless, antioxidant content differs between biodiesel producers—but within the same producer samples are very consistent.

Corrosivity was measured using the standard Herbert method (PN–92/M–55789). All glycerol fractions assessed by this method exhibited anticorrosive properties. Before measurement all fractions were saponified, and corrosivity was analysed for solutions with a range of initial and final soap content. The corrosivity of all saponified glycerol fractions was shown to decrease with increasing total soap content (Table 9.4), but more importantly the initial soap content had a pronounced influence. For comparison, two examples are given in Table 9.4 of fractions from different producers with varying initial soap content.

Table 9.4 Comparison of Herbert test with free radical scavenging for two different crude glycerol samples (reproduced from Ref 11, with permission).

Glycerol fraction	*Initial soap content (%)*	*Final soap content (%)*	*Corrosivity ($\mathrm{g\,m^{-2}}$)*	*Radical scavenging (% of radical remaining)*
D2	15	0.75	0.28	2
E	34	0.73	0.72	60

Final soap content (%)	*Corrosivity ($\mathrm{g\,m^{-2}}$)*
0.14	1.68
0.27	0.96
0.54	0.56
1.35	0.12

Tab. Herbert test results for D1 samples, initial soap content 27%.

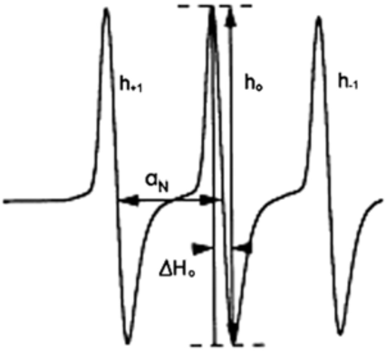

Figure 9.7 EPR spectrum of 16-doxyl radical.

After saponification, the soap content was comparable (about 0.75%), but corrosivity was very different. Samples of the glycerol fraction with high soap content (E) had lower anti-corrosive properties and lower free radical scavenging ability than samples with low initial soap content (D2). In general, radical scavenging (antioxidant) properties obtained from EPR spectroscopy paralleled the anti-corrosivity results, and samples with the highest quenching ability gave the best results on the Herbert test. On the basis of these results the biodegradable antifreeze and washing liquid have been patented by the Wraclaw University's Institute of Heavy Organic Synthesis (Poland).[14]

In the investigation of surfactant properties, the spin labeling method, EPR, is very popular. The rotation time calculated from spectral parameters (τ) enabled fluidity to be established. 16-Doxyl-stearic acid methyl ester (2-ethyl-2-(15-methoxy-15-oxopentadecyl)-4,4-dimethyl-3-oxazolidinyloxy) was used as the spin label. The typical isotropic spectrum of the 16-doxyl spin label with EPR parameters marked is shown in Figure 9.7.

On the basis of the spectral parameters h and H the rotation time was calculated according to Equation 9.1:

$$\tau_R = 6.51 \times 10^{-10}\left[\left(\frac{h_0}{h_{+1}}\right)^{\frac{1}{2}} + \left(\frac{h_0}{h_{-1}}\right)^{\frac{1}{2}} - 2\right]\Delta H_0 \qquad (9.1)$$

The results of the calculation of rotation time *vs* temperature are shown in Figure 9.8:

The longest rotation time was observed for glycerol fractions in which NaOH was used as catalyst. Sodium soaps are more viscous, and rotation of the molecules in these fractions was thus inhibited, especially

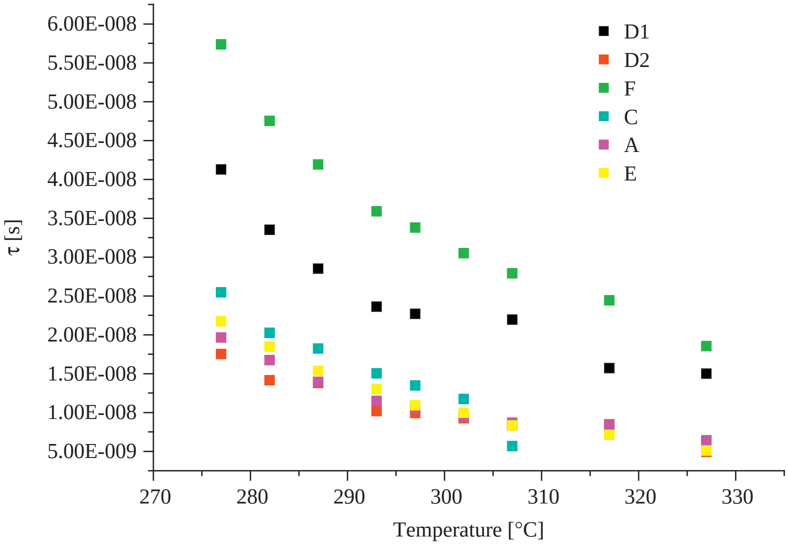

Figure 9.8 Dependence of rotation time on temperature for a range of glycerol fractions.

at low temperatures (Sample F). At higher temperatures the catalyst has a much smaller influence on rotation time, but this parameter depends not only on the type of catalyst. In Figure 9.8 examples of two different samples from the same producer (D1 and D2) are shown. The same technology was used in both of the samples but they differed in soap concentration and saponification number. Sample D2 had higher soap concentration and a higher saponification number.

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CHAPTER 10

Sustainability of Bioglycerol

10.1 Biofuels: A Triple Bottom Line Analysis

To be a viable alternative to conventional fuels, a biofuel must offer a net energy gain, provide environmental benefits, be economically competitive, and available in large quantities without reducing food supplies.[1] Brundtland's definition of sustainability—safeguarding the world for future generations—has three elements: social, economic and environmental. All three aspects must be satisfied if something can be considered truly sustainable. In other words, anything which protects the environment by driving people into poverty, or which supports the economy while undermining environmental services, will inevitably collapse, often with devastating consequences either for people living today or for future generations. Ecosystems, including those involving humans, have maintained themselves for tens of thousands of years and future businesses should manage and measure their success not only in terms of profitability, but rather by a "triple bottom line" of economic, social and environmental responsibility.[2]

Comparing the full life-cycle economics of biodiesel from soybeans and ethanol from corn grain, biodiesel yields 93% more energy than the energy required for its production, while ethanol yields only 25% more.[3] The advantage of biodiesel over ethanol arises from its lower agricultural input and the more efficient conversion of its feedstocks to fuel. Hence, relative to ethanol, biodiesel releases just 1.0%, 8.3%, and 13% as much agricultural nitrogen, phosphorus, and pesticide pollutants, respectively, per net energy gain. Biodiesel also releases less air pollutant

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per net energy gain than does ethanol. Thus, relative to the fossil fuels they displace, greenhouse gas emissions are reduced 41% by the production and use of biodiesel, compared with 12% for ethanol. The results of a study (Figure 10.1) which includes the energy costs of farm machinery and processing facilities, together with recent advances in crop yields and biofuel production efficiency, refute previous assertions[4] that biofuel requires more energy to produce than it yields.

Indeed, the advantages in net energy balance (NEB) of soybean biodiesel is confirmed by five separate methods of accounting for the energy credits of the co-products. Thus biodiesel offers sufficient environmental advantages to merit a subsidy given to otherwise economically uncompetitive biofuels which are justified by their reduced life-cycle environmental impact.

Governments in Europe and the USA provide a subsidy in the form of tax exemption for each litre of biodiesel produced.[5] Furthermore, in both the EU and the USA ethanol and biodiesel producers also benefit from federal crop subsidies, which give lower soybean prices. The main rationale in subsidizing the biodiesel industry is to support the farmer, reduce unemployment, prevent neglect of the countryside and, in democracies, to win the votes of the beneficiaries. Incidentally, it is worth noting that a strain of *Escherichia coli* bacterium (Figure 10.2) could potentially ferment glycerol anaerobically into ethanol and valuable green chemicals, with an estimated operational cost 40% lower than first generation ethanol production from corn.[6]

Since fossil energy usage includes environmental costs not reflected in market prices, whether a biofuel provides a net benefit to society depends not only on whether it is cost competitive but also on its environmental costs and benefits compared with fossil fuel alternatives. Demand, especially of ethanol, is mainly the result of laws and regulations requiring the inclusion of some proportion of biofuel into petroleum and diesel. Moreover, any further increase in the petroleum price above the 2007 average improves the cost competitiveness of biofuels.

As crude oil has skyrocketed in price since the late 1990s (from US$20 a barrel in 1998 to around US$80 a barrel), so also has interest in biodiesel production and usage. For example, in Colombia—the largest palm oil producer in the Americas—oil palm plantations had by 2003 occupied 188 000 hectares and, if fields planted but not yet producing are included, the total is now closer to 300 000 hectares. Palm oil was at one time used entirely for cooking and the manufacture of soap, but 35% of its output now goes into biodiesel fuel. The same trend is taking place in Malaysia, Argentina and other developing countries. US production of biodiesel is 30–40 million US gallons and is expected to grow

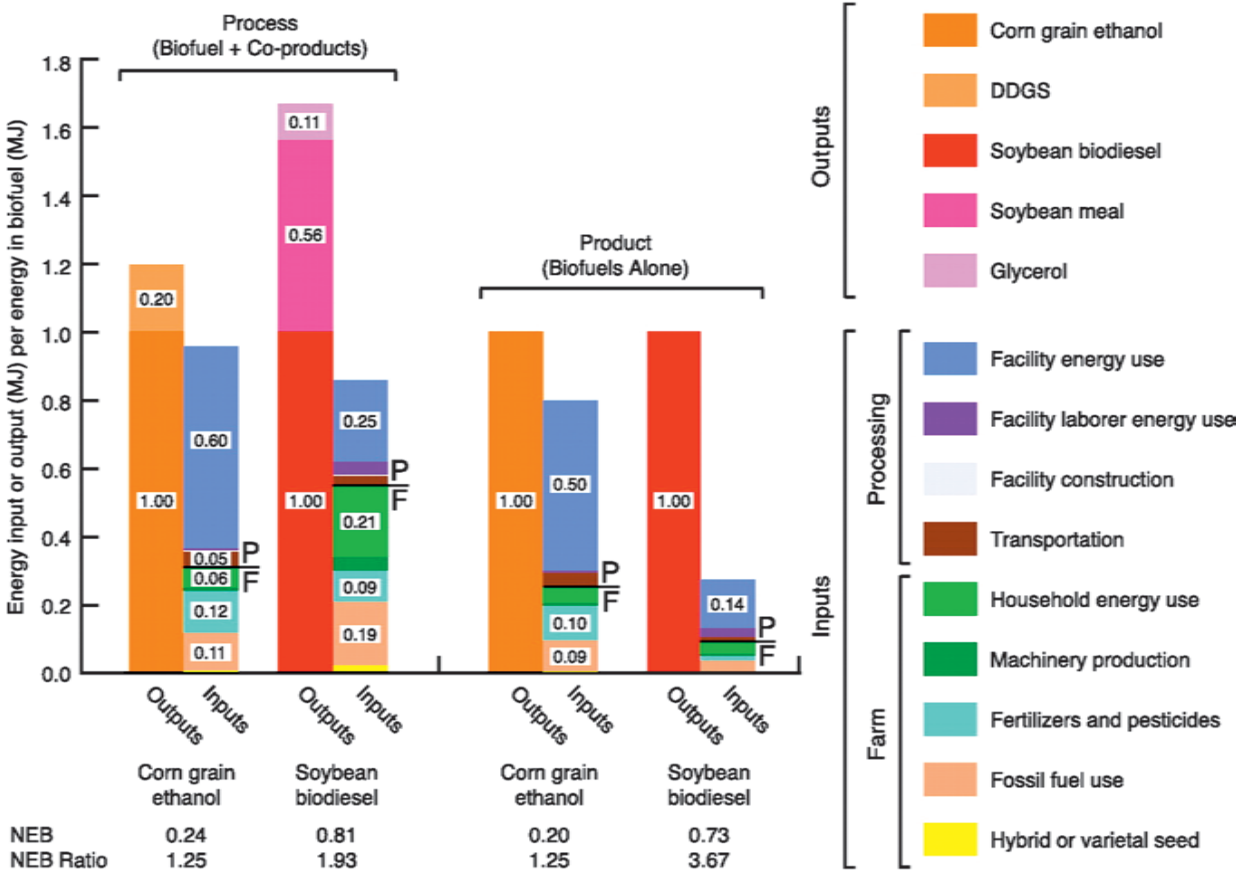

Figure 10.1 NEB (net energy balance) of corn grain ethanol and soybean biodiesel production. Energy inputs (nine categories) are consistently ordered in each set of inputs, as in the legend. Individual inputs and outputs ≥ 0.05 are labeled. The NEB (energy output – energy input) and NEB ratio (energy output/energy input) for each biofuel are presented, both for the entire production process (*left*) and for the biofuel only (*i.e.*, after excluding co-product energy credits and energy allocated to co-product production) (*right*). Reproduced from Ref. 3, with permission.

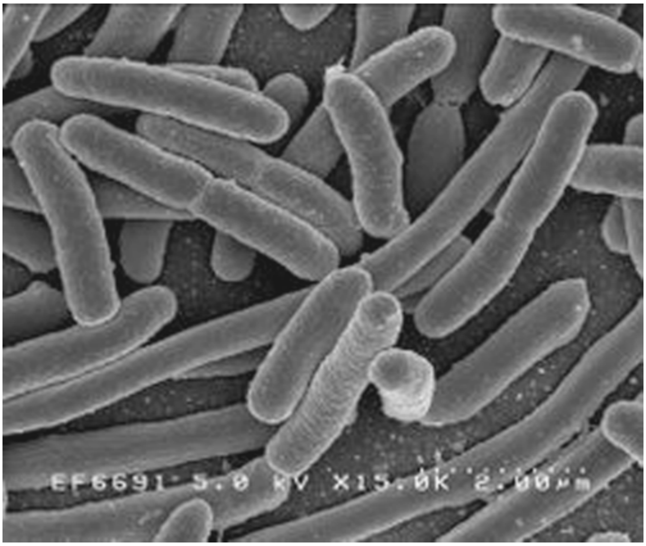

Figure 10.2 The ubiquitous *E. coli* bacteria. These bacteria are widely used in industrial fermentation processes and can efficiently convert glycerol to ethanol (photo courtesy of Wikipedia.org).

at a rate of 50–80% per year, with an anticipated figure of 400 million gallons by the year 2012.

Chemical and petrochemical companies are also beginning to invest heavily in biofuels. Recently published estimates predict that the annual demand for biodiesel will grow within the next few years from 6 to 9 million tonnes in the USA and from 5 to 14 million tonnes in the European Union. As a representative current example, the British company D1–BP Fuel Crops (a joint venture between BP and D1 Oils) intends to invest US$160 million over the next five years to cultivate *Jatropha curcas* (Figure 10.3) as a biodiesel feedstock in Southeast Asia, Southern Africa, Central and South America, and India. This is a drought-resistant, oil-seed-bearing tree and does not compete with food crops for good agricultural land, nor does it adversely impact the rainforest, since *Jatropha* can be grown on land on which other crops struggle, and it has the further benefit of requiring less irrigation. Moreover, inedible oils are not subject to the same competitive market pressures as food oils.

However, no biofuel can replace petroleum to a significant extent without some impact on food supplies. Even if the entire US corn and soybean output was dedicated to biofuel production it would satisfy only 12% of demand for petroleum and 6% of that for diesel. Until the recent increases in petroleum prices, high production costs made

Figure 10.3 *Jatropha curcas* oilseeds (*top*, photo courtesy of Dreamstime); and related commercial projects at the end of 2008 (*bottom*, copyright Emerging Markets Online).

biofuels unprofitable without subsidies. Transportation biofuels such as synfuel hydrocarbons or cellulosic ethanol, if produced from low-input biomass grown on agriculturally marginal land or from waste biomass, can provide much more plentiful supplies and environmental benefits than food-based biofuels. Results of a comprehensive study[1] reveal that over the next 25 years biofuels could provide 37% of US transport fuel and 20–30% of the oil used in the EU.

10.2 Bioglycerol Economics

Developing new industrial uses for glycerol greatly increases the net energy and sustainability of biodiesel. A model based on the production

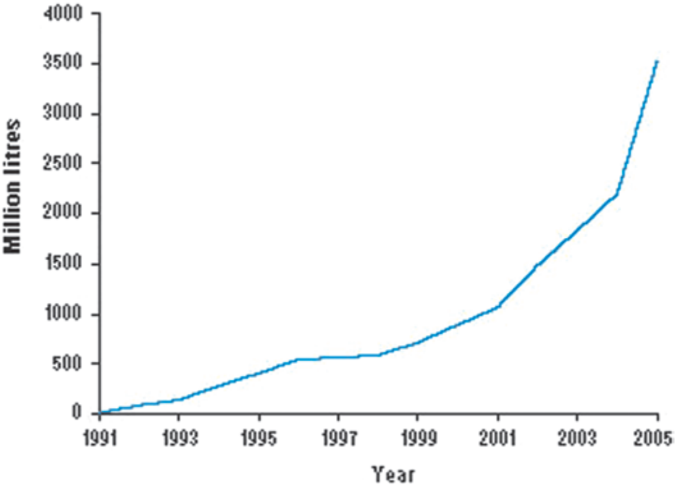

Figure 10.4 Global production of bioglycerol (1975–2005) (source: F. O. Licht).

and sale of 80% glycerol by weight, and assigning it a value of US$0.33/kg (consistent with recent prices), predicts an inverse linear relationship between the production cost of biodiesel and variations in the market price of glycerol, with an increase of US$0.0022 per litre for each US$0.022 reduction in the glycerol price per kg.[7] Hence, in order to expand biodiesel production, it is essential for economical utilization pathways for the glycerol by-product to be developed, either by expanding the existing markets for glycerol or, better still, by establishing new marketable value-added derivatives.

Global production of bioglycerol from biodiesel (Figure 10.4) has climbed from 200 000 tonnes in 1995 to 600 000 tonnes in 2006, progressing further to 1 million tonnes in 2009.

Most of the growth has come in the years since 2005, as a result of the glycerol arising as a by-product of the production of biodiesel.[8] Figure 10.5 shows how world production of biodiesel quadrupled between 2005 and 2008, with a corresponding increase in global glycerol production.[9]

The bioglycerol stream typically contains a mixture of glycerol itself, along 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. To produce USP-grade glycerol, the crude material from biodiesel production must be purified. Cargill, for instance, has built its own refinery in conjunction with its 37.5 million gallon per annum biodiesel plant in Iowa, making it the first company in North America to

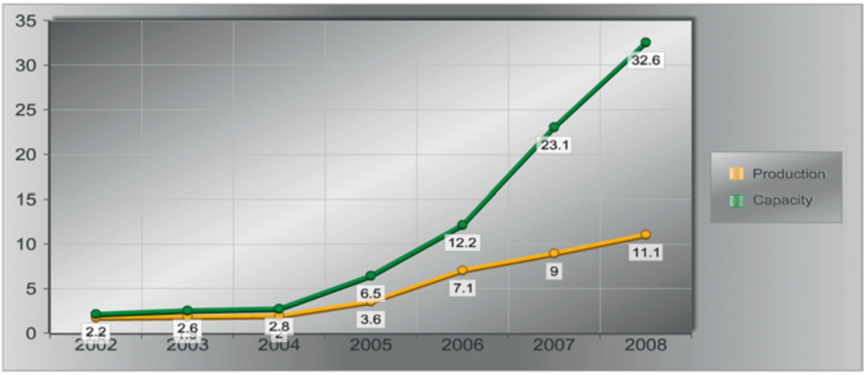

Figure 10.5 World biodiesel production and capacity development, 2002–2008 (source, Biodiesel 2020: A global market survey).

combine soybean crushing, biodiesel and USP-grade glycerol production in a single plant. However, refining crude glycerol is too expensive for small-scale producers, who need a price rise to sell the crude which they currently give away just to get rid of it from their storage tanks. In the USA, for instance, up to mid-2007 it was common practice to market 50% of total crude glycerol and sell the remainder at minimal profit. The alternative process for biodiesel production based on the high-pressure hydrogenation of fatty acids is not likely to alter the availability of crude glycerol.[10] In fact, even though the product outperforms biodiesel produced by conventional transesterification, the high cost of the investment required for the high-pressure unit (for example, approximately €200 million for the two units being built at the Porvoo refinery in Finland, Figure 10.6) implies that biodiesel fuels of both types will remain on the market for the foreseeable future.

We stated in 2007 in the first edition of this book:

> *In today's energy-eager world, the price of oil is high and can only increase, both in the medium and long term. 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 Africa. It will be interesting to cover developments in future editions of this book.*

In the event, many of the most significant developments have indeed taken place in developing countries. Or, as the author of a report on the

Figure 10.6 The first NExBTL production plant at Neste Oil's Porvoo refinery with a rated annual capacity of 170 000 tonnes, on-stream since 2007 (photo courtesy of Suomen Ilmakuva Oy).

biodiesel industry has expressed it: "In the year 2007, there were only 20 oil producing nations supplying the needs of over 200 nations. By the year 2010, more than 200 nations will become biodiesel producing nations and suppliers".[11] Asia is a major global exporter of glycerol, and glycerol is quoted as an active spot commodity, derived mainly from palm oil in Malaysia and Indonesia, and from coconut oil in the Philippines. On the other hand USA is a net importer of glycerol, bringing in refined product from Indonesia, Malaysia, Argentina and Europe.[12]

Asia is in fact both the largest producer and consumer of refined glycerol (accounting for 44% and 35% of world production and consumption, respectively, in 2007), and is expected to remain the largest market into 2012, with increased demand for all applications, including new markets for refined glycerol, such as production of epichlorohydrin.[13]

Figure 10.7 illustrates world consumption of refined glycerol, and it will be seen that Western Europe is the second largest producer and consumer of refined glycerol, accounting for nearly 35% and 28% of world production and consumption, respectively, in 2007. North America was the third largest market. These three regions accounted for nearly 91% of world production and 82% of world consumption in that year.

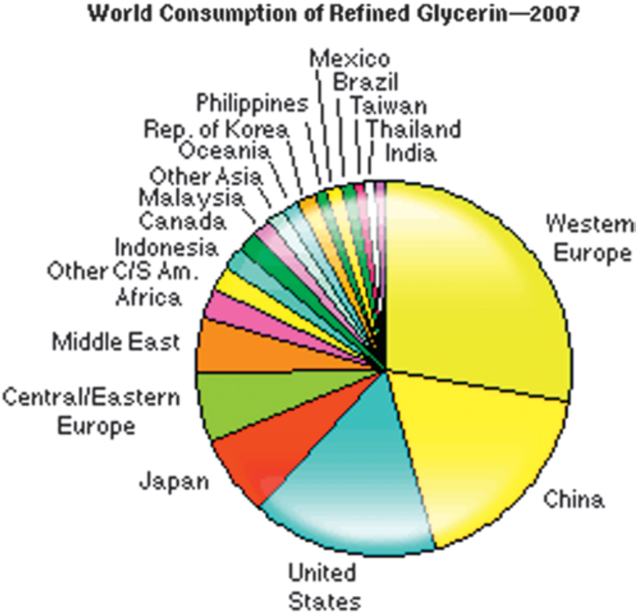

Figure 10.7 World consumption of refined glycerol, 2007 (image: SRI Consulting).

Double-digit growth in consumption in the United States, China and Thailand, and significant growth also in Western Europe, is largely due to increased demand for new applications such as manufacture of epichlorohydrin, syngas and propylene glycol. These outlets for refined glycerol are likely to account for the projected growth in world demand during the period 2007–2012. Table 10.1 lists the main producers of glycerol worldwide.

In Europe an EU directive was adopted in 2003 to promote the use of renewable fuels, including those derived from biomass, and required that by the year 2010 at least 5.75% of the total fuel consumed in the EU must be from renewable sources. Since directives are binding on EU member states, this has naturally given sharp impetus to the production of biodiesel, especially in France and Germany. Over the past decade environmental legislation has progressively lowered the sulfur content of fossil diesel fuel, and the addition of biodiesel within the EU helps this objective, supported by the fact that it also has excellent lubricant properties.

Finally, since the mid-1990s production of natural fatty alcohols in Asia has also increased steadily, adding to the glycerol surplus. For instance, countries such as Malaysia and Indonesia are major producers of glycerol, mostly derived from palm oil, and are able to sell it in China

Table 10.1 Large glycerol producers worldwide (source: *Purchasing*).

Unilever (Malaysia) Holdings
Dial
Cognis
Dow Chemical
PT Sinar Oleochemical International (Indonesia)
Procter & Gamble
Vantage Oleochemicals
Archer Daniels Midland
Henkel
PT Sumi Asih Oleochemical Industry (Indonesia)
Cargill
Kao Corp. (Japan)
Godrej Industries Ltd (India)
PT Cisadane Raya Chemicals (Indonesia)
United Coconut Chemicals (Philippines)

where demand for this chemical is burgeoning. As a result, the global market for glycerol reached 900 000 tonnes in 2006—of which 600 000 tonnes was from biodiesel production—compared to as little as 60 000 tonnes in 2001. Such a rapid surplus of refined glycerol soon caused prices to plummet to US$0.33 per kg, or even below; and the spot market price for refined glycerol collapsed from €1500 to €330 per tonne.

Having become an element of the fuel market, glycerol is now an important component of the global market scene.[14] The graph in Figure 10.8 shows the price trend for refined glycerol up to 2003 and contains the prediction by a US researcher that by 2010 the glycerol price will fall as low as US$0.35 per lb.[15]

Historically the price of glycerol has been dictated primarily by factors as diverse as the weather, regulatory costs, plant shut-downs and politics. Over the past 30 years glycerol prices have oscillated in roller-coaster fashion between the low $0.20s per lb and a record high of $1.20 in 2001. Subsequent history has however shown that the above prediction was if anything conservative (Figure 10.9). The glycerol price has plunged rapidly and since the first quarter of 2005 it has been selling within the range US$0.30–0.55 per lb, depending on the grade, and during 2006 the worldwide glut of glycerol created from biodiesel production drove the price below 2005 levels.[16]

The market is, however, self-correcting. In 2005, a comprehensive market study[17] predicted that glycerol prices in the medium-term (2008) would not fall below €400 per tonne in Europe and $0.30 per lb in the USA. The reasoning was that due to its consistently low price glycerol usage could be expected to expand, especially in replacing propylene

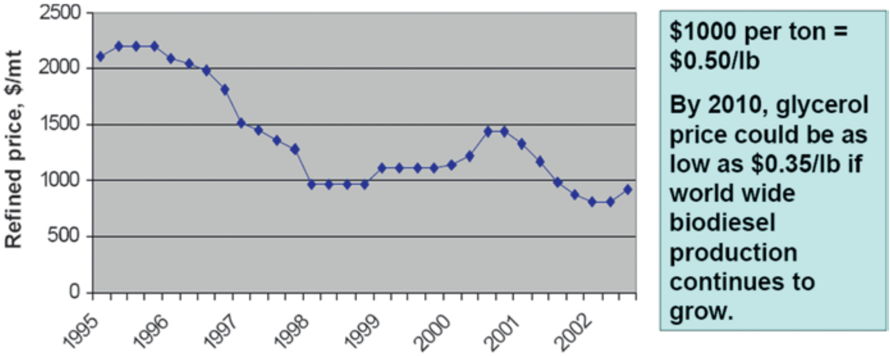

Figure 10.8 Price trend of industrial glycerol (reproduced from Ref. 11, with permission).

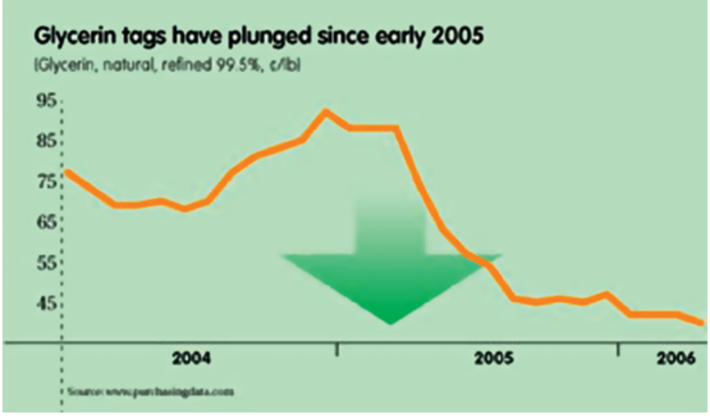

Figure 10.9 Price trend of refined glycerol (reproduced from Ref. 11, with permission).

glycol, whose price since the US hurricanes of September 2005 had risen by a factor of six. This has in fact proved to be the case. Already in 2006 purchasers of vegetable-based refined glycerol were obtaining contracts in the range US$0.38–0.42 per lb, and by mid-2007 were paying "in the high 40s".[18] One of today's most up to date and reliable sources of information is the "Glycerine report",[19] issued online once or twice a month by Petrosil Group, a privately owned company in India.

In 2008, the demand for glycerol was badly hit by the global recession, but following an unprecedented collapse glycerol prices began to recover in the final quarter of 2009 as the result of stronger demand and tighter supplies. In the first half of 2009, average monthly consumption of glycerol in the USA was nearly 12% lower than over the same period a year earlier, and 17% below historical monthly consumption.[20] Contract glycerol prices at the end of 2009 were in the range 40–50¢/lb for buyers demanding guarantees, and spot prices are in "the low-to-mid 30s" (without supply guarantees).

10.3 Glycerol: A Platform Chemical for the Biorefinery

Glycerol can be expected to evolve into an even more commonly used chemical than at present. It will become a substitute for many of the common petrochemicals on the market or, in the words of one practitioner, "Glycerol may become the next biodiesel". Globally, glycerol arising from biodiesel production has increased from 200 000 tonnes in 2004 to 800 000 tonnes in 2007. Well-regarded experts in the industry consider that production of biodiesel could by 2010 rise to 9 million tonnes in Europe alone, translating into 900 000 tonnes of glycerol.[13] This gives a clear indication of the potential status of glycerol as a key raw material. In three to five years it will be seen as an environmentally friendly way of replacing competing petroleum products, and it will be one of the next chemical platforms to become widely available. As an example, in the USA Dow, Senergy Chemical, ADM, Cargill and Ashland are all set to produce glycerol-derived industrial products such as propylene and ethylene glycols. In Europe, Solvay is already making epichlorohydrin from biodiesel glycerol and will start large-scale production in Asia within two years. Along with Dow, Grace in its turn will commercialize large quantities of concrete with crude glycerol as additive.

Experts realistically predict the end of cheap oil by 2040 at the latest, since increased consumption will irrevocably diminish fossil sources and build up environmental pressure.[21] It follows that a trend on the part of the chemical industry towards renewable feedstocks is unavoidable. We can already witness this development as chemical manufacturers come to terms with the rising cost of oil and natural gas, and the transition to more bio-based production is underway. In the near future biorefineries in which biomass is catalytically converted to pharmaceuticals, agricultural chemicals, plastics and transportation fuels will take the place of petrochemical plants based on chemicals derived from fossil resources (Figure 10.10).[22]

A biorefinery is a facility which uses biomass conversion to produce fuel, power and chemicals. In concept it is analogous to today's petroleum refineries, which produce a range of fuels and other products from

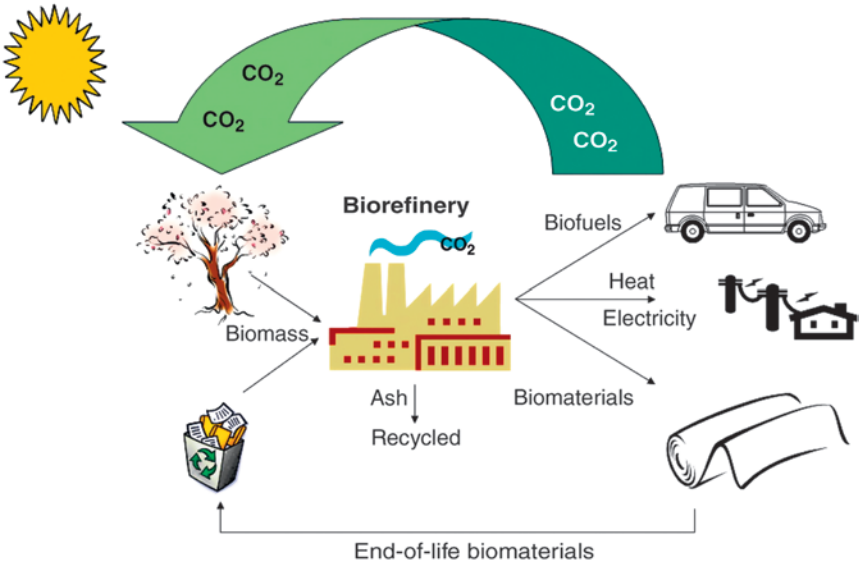

Figure 10.10 The fully integrated agro–biofuel–biomaterial–biopower cycle for sustainable technologies (reproduced from Ref. 16, with permission).

petroleum. Conversion of renewable materials to hydrogen assists in the utilization of renewable energy sources, and their conversion to commodity chemicals enables the replacement of petroleum by renewable sources. Glycerol will become a key renewable feedstock for future biorefineries, in which a number of commodity chemicals (Figure 10.11) will be produced from it, especially now that an energy- and atom-efficient conversion of glycerol to syngas has been developed.[23]

Focusing on recent developments in new applications and conversion of glycerol into value-added chemicals (Figure 10.11), we have shown in this book how glycerol is developing into a key raw material for future biorefineries. Human chemical ingenuity has rapidly created a route to glycerol derivatives that find application in fields as diverse as chemicals and fuels, and the automotive, pharmaceutical, detergent and building industries.

As China and Islamic finance rapidly become central features of the global economy, the value of intellectual property will be progressively weakened.[24] It is now markets, rather than ideas, which generate products. This means that successful products are increasingly copied or further developed, and the original product loses its unique status. This will have a major impact on the chemical production of biofuels, which will increasingly be produced in developing countries.

The technology to make biodiesel is simple and, bearing in mind the new heterogeneous processes, it has reached a high degree of efficiency.

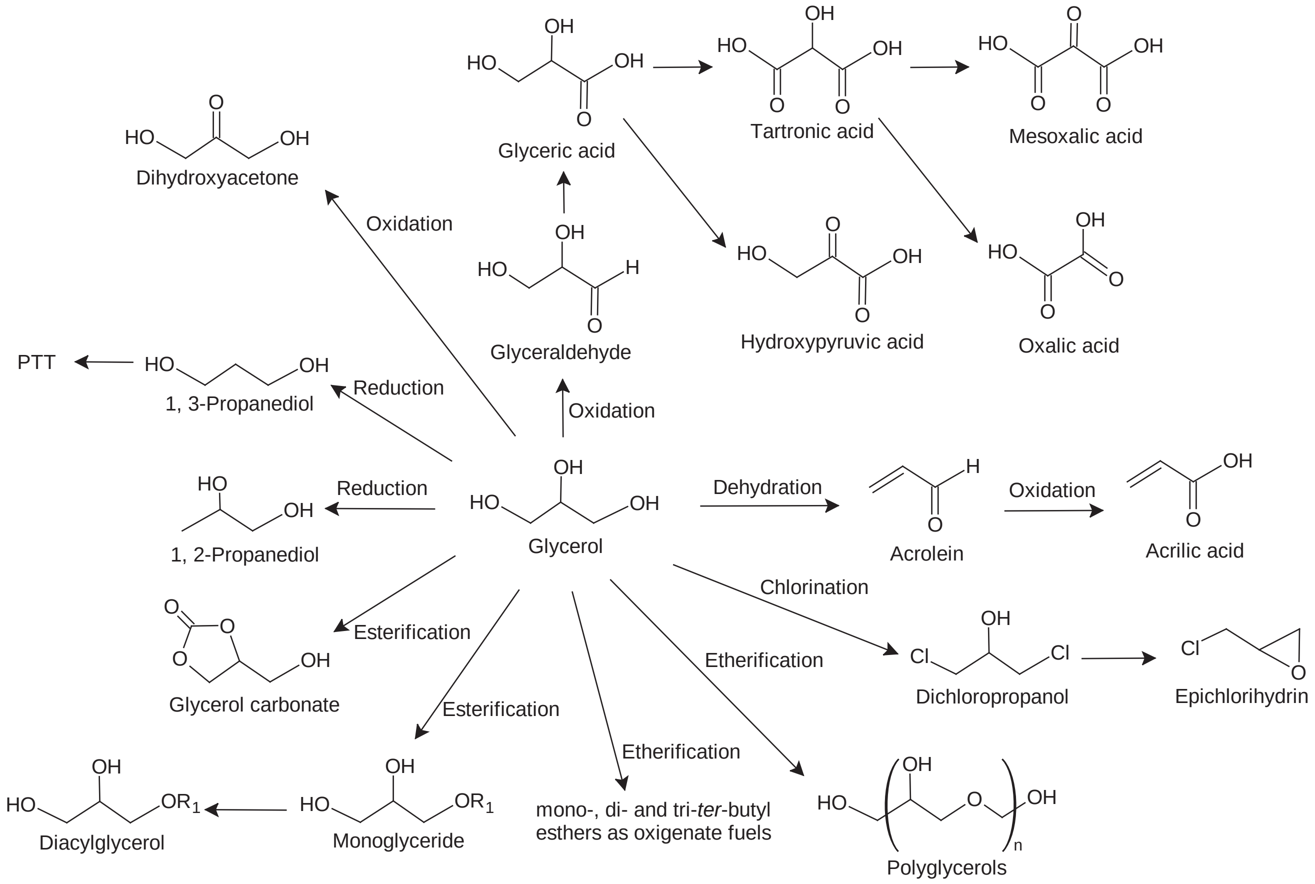

Figure 10.11 Commodity chemicals from glycerol.

The pure glycerol generated as a by-product will further lower the price, including that of USP-grade glycerol, and this is before taking account of the surplus crude glycerol currently being given away free. The raw materials are not localized in only a few countries, but instead their production is increasingly determined by the availability of land. In the US, the production of oleochemicals, yielding glycerol as a by-product, was 20% lower during 2009 than in the same period of 2008, and biodiesel production was down by 50% over this period. Despite this, global production of biodiesel climbed to 39.8 million tonnes by 2010 (9% above 2009), even though many plants worldwide were running at extremely low rates following the global economic downturn.[25] Increases were most notable in Asia and South America, with the entrance of large manufacturing countries such as Argentina, in which a national biofuel law was enacted in 2006 and the production capacity of biodiesel grew from 150 000 tonnes in 2006 to 1.4 million tonnes by the end of 2008, all the additional production being for export.[26]

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