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 is derived 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 or 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 to man. In the modern era, it was identified in 1779, by Swedish chemist Carl W Scheele, who discovered a new transparent, syrupy liquid by heating olive oil with litharge (PbO, used in lead glazes on ceramics). It is completely soluble in water and alcohols, is 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 g mL⁻¹, 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. Indeed, glycerol has over 1500 known end uses, including applications as an ingredient or processing aid in cosmetics,
toiletries, personal care products, pharmaceutical formulations and foodstuffs. 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 negative 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 recent study using density functional theory (DFT) methods. In particular, a systematic series of \textit{ab initio} molecular 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 \textit{gG}, 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.

![Figure 1.1] Structure of glycerol.

\begin{table}[h!]
\centering
\begin{tabular}{ll}
\hline
Chemical formula & C\textsubscript{3}H\textsubscript{6}(OH)\textsubscript{3} \\
Molecular mass & 92.09382 g mol\textsuperscript{-1} \\
Density & 1.261 g cm\textsuperscript{-3} \\
Viscosity & 1.5 Pa.s \\
Melting point & 18.2 °C \\
Boiling point & 290 °C \\
Food energy & 4.32 kcal g\textsuperscript{-1} \\
Flash Point & 160 °C (closed cup) \\
Surface tension & 64.00 mN m\textsuperscript{-1} \\
Temperature coefficient & –0.0598 mN (mK)\textsuperscript{-1} \\
\hline
\end{tabular}
\caption{Physicochemical properties of glycerol at 20 °C.}
\end{table}

(Reproduced from Ref. 2, with permission)
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 conformation 1 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 to structures without intramolecular hydrogen bonding.

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. This network is very stable and very 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\(^{-1}\) 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 at about 187 K transition to a glassy state whose nature has been the subject 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) comprising pockets of fluid.
isolated from one another by glass-like regions, which retain their distinct dynamics over surprisingly long timescales.\textsuperscript{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 in the range 300–400 K glycerol in practice exhibits only three backbone conformations, namely $\alpha \alpha$, $\alpha \gamma$ and $\gamma \gamma$ (Figure 1.3).

Intermolecular interactions stabilize slightly the $\alpha \alpha$-conformation and destabilize the $\gamma \gamma$-conformation as the temperature decreases (Table 1.2). As the liquid approaches the freezing point about half of the molecules are present in the $\alpha \alpha$-conformation.

![Figure 1.3](image)

**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.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Conformer</th>
<th>400 K Liquid</th>
<th>400 K Gas</th>
<th>300 K Liquid</th>
<th>300 K Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \alpha$</td>
<td>44 (3)</td>
<td>39.9 (5)</td>
<td>48 (1)</td>
<td>43.0 (8)</td>
</tr>
<tr>
<td>$\alpha \gamma + \gamma \alpha$</td>
<td>45 (2)</td>
<td>47.0 (3)</td>
<td>46.0 (6)</td>
<td>46.9 (5)</td>
</tr>
<tr>
<td>$\gamma \gamma$</td>
<td>6 (1)</td>
<td>11.0 (2)</td>
<td>4.4 (6)</td>
<td>9.8 (4)</td>
</tr>
<tr>
<td>$\alpha \beta + \beta \alpha$</td>
<td>3.8 (9)</td>
<td>1.40 (1)</td>
<td>1.4 (4)</td>
<td>0.22 (1)</td>
</tr>
<tr>
<td>$\beta \gamma + \gamma \beta$</td>
<td>1.2 (5)</td>
<td>0.67 (1)</td>
<td>0.2 (1)</td>
<td>0.11 (1)</td>
</tr>
<tr>
<td>$\beta \beta$</td>
<td>0.01 (1)</td>
<td>0.03 (1)</td>
<td>0 (1)</td>
<td>0.002 (1)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Errors in the last digit are given in parenthesis. (Reproduced from Ref. 5, with permission.)
The activation energy for a conformational transition is around 20 kJ mol\(^{-1}\), in other words 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 \(\alpha\)-\(\alpha\)-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 time scales, 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 action of polyhydric alcohol functions,\(^7\) 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 formulated the implicate order theory,\(^11\) inspired by a simple experiment in which a drop of ink was squeezed on to a cylinder of glycerol. When the cylinder rotated (Figure 1.4), the ink diffused through the glycerol in an

Figure 1.4  Glycerol with a high concentration of dye is inserted into the space between two concentric transparent plastic cylinders, the space between them filled with clear glycerol. The inner cylinder is then slowly and steadily rotated. As the cylinder rotates, the dye smears and appears to be diffused. Since the flow of the viscous glycerol is laminar, however, 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.)
apparently irreversible fashion; its order seemed to have disintegrated. When the inner cylinder was rotated in the opposite direction, the ink recovered its initial profile.

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).\textsuperscript{13}

Currently, the amount of glycerol that goes annually into technical applications is around 160 000 tonnes and is expected to grow at an annual rate of 2.8%.\textsuperscript{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 is added. Glycerol is widely used in alkyd resins and regenerated cellulose as a

![Figure 1.5](image-url)  

**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). However, technical grades of glycerol that are not certified as USP or FCC quality are also found. Also available is Food Grade Kosher glycerol, which has been prepared and maintained in compliance with the customs of the Jewish religion.\textsuperscript{14}

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 a variety of materials such as sheeting 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 a significant 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, pharmaceutical, and industrial applications. Some characteristics of polyols are reduced 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, providing lubrication and as a humectant, that is as a hygroscopic substance which keeps the preparation moist. Glycerol helps to maintain texture and adds humectancy, 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 on 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 not able to significantly reduce 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

Figure 1.6  Glycerin soap.  
(Photo courtesy of A K A Saunders, Inc.)
with DEG. The revamped 1938 law provided food standards, addressed 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). As late as 2007 the Food and Drug Administration blocked all shipments of toothpaste from China to the USA after 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 occurrence of 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. Eventually, a large batch of toothpaste contaminated with DEG also reached the EU market, with a number of poisoning cases being reported in Italy and southern Europe.

The glycerol market is currently undergoing radical changes, driven by very large supplies of glycerol arising from biodiesel production. Researchers and industry have been looking at new uses for glycerin to replace petrochemicals as a source of chemical raw materials, and in a relatively few years there have been an impressive series of achievements. These topics are discussed in the following chapters. After the sustained period of increasing oil prices starting in the early 2000s, glycerol is now becoming established as a major platform for the production of chemicals and fuels.
1.3 Production of Bioglycerol

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 fat stores as a source of energy, glycerol and fatty acids are released into the bloodstream. The glycerol component is converted to glucose in the liver and provides energy for cellular metabolism. Natural glycerol is obtained hydrolytically from fats and oils during soap and fatty acid manufacture, and by transesterification (an interchange of fatty acid groups with another alcohol) during the production of biodiesel fuel (Figure 1.8). It therefore comes as no surprise that in these energy intensive days glycerol has become a hot topic in industry at large.

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 making was largely insufficient to meet the wartime demand for nitroglycerine, \textit{i.e.}, for dynamite, the smokeless gunpowder.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cover.png}
\caption{Cover of the September 2006 issue of \textit{Biodiesel Magazine}. (Photo courtesy of the publisher.)}
\end{figure}
used in 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 detonator for igniting nitroglycerine by means of a strong shock rather than by heat combustion. Nitroglycerine, invented by Italian chemist Ascanio Sobrero in 1846, is very volatile in its natural liquid state. In 1866 Nobel discovered that mixing nitroglycerine with silica (kieselguhr) would convert the liquid into a malleable paste, called 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. Soon after World War I the US Government therefore decided to make its production independent of soap manufacture in order to meet wartime demand, 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 closing and being replaced by other plants which use glycerol as a raw material, even for the production of epichlorohydrin itself (see Chapter 4). This is the result of the large surplus of glycerol created as a by-product in the manufacture of biodiesel fuel by transesterification of seed oils with methanol using KOH as a base catalyst, or batch esterification of fatty acids catalyzed by sulfuric acid (Figure 1.9).

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

\[
100 \text{ kg of oil} + 10.5 \text{ kg MeOH} = 100 \text{ kg methyl esters (biodiesel)} + 10.5 \text{ kg glycerol}
\]

Colza, soybean and palmitic oils have the most suitable physico-chemical characteristics 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 fatty acids comprise some 2% of the original product, and after distillation 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 the 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 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 glycerol 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). The recovered glycerol, after polishing if necessary using ion exchange and removal of water–methanol solution by evaporation, easily meets USP glycerol standards. This membrane-based technique avoids expensive evaporation and distillation, and also such problems as foaming, carry-over of contaminants, and limited recovery.

In general, the traditional biodiesel manufacturing processes have several disadvantages, including soap formation (from the KOH catalyst); use of an excess of alcohol (for shifting the equilibrium to fatty esters), which must be separated and recycled; homogeneous catalysts which require neutralization, causing salt 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

![Figure 1.11 Glycerol purified by membranes combining electrodialysis and nanofiltration. (Photo courtesy of EET Corporation.)](image-url)
triglycerides, the transesterification step was performed using a solid catalyst, a mixed Zn–Al oxide. 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 of methanol is removed by partial evaporation and the esters and glycerol are separated in a settler.

A second alternative, developed by the Dutch company Yellowdiesel in 2006, is especially suited to mixed feedstocks with high free fatty acid (FFA) content, such as those used for cooking oil and low-grade greases. The process combines the reaction and the separation in a single step, using reactive distillation (also known as catalytic distillation, Figure 1.13). This intensifies mass transfer, allows in situ energy integration, reduces equipment costs, and simplifies process flow and operation.

Furthermore, the thermodynamic equilibrium of the reaction can be shifted by controlling the vapour–liquid equilibrium in the column. The first pilot biodiesel plant based on this process (2500 tonnes/year), built by Fertibom, will come on stream in Rio de Janeiro in 2008.
References


---

**Figure 1.13** Simplified schematic of the Yellowdiesel 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.)


11. D. Bohm: Wholeness and the Implicate Order, Oxford: Routledge, 1996. Underlying the apparently chaotic realm of physical appearances – the explicate order – there is always a deeper, implicate order that is often hidden.

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/lecture demonstrations.


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 accordingly, including glycerol for cough syrups. To be Kashrut endorsed, glycerol must be from vegetable sources instead of from animal tallow.

15. F. Case, 100 years of the FDA. Chemistry World (July 2006). Similar pictures are available at the URL: http://www.rsc.org/chemistryworld/restricted/2006/july/100yearsfdad.asp.


18. In two years DuPont sales increased from $25 million to $318 million and profits soared from $5.6 million to $82 million. DuPont used these profits to diversify into dyestuffs, plastics and paints.


21. This efficient electro-pressure membrane (HEEPM) technology for desalinating liquids is available from the EET Corporation: http://www.eetcorp.com/heemp/glycerine.htm.


Future of Glycerol
New Usages for a Versatile Raw Material
Rossi, M.
2008, 104p., Hardcover
ISBN: 978-0-85404-124-4
A product of Royal Society of Chemistry