

Conversion of Glycerol in to value added chemicals

Jayaram Molleti

Department of chemical technology

Institute of Chemical Technology, Mumbai

Abstract:

New opportunities for the conversion of glycerol into value-added chemicals have emerged in recent years as a result of glycerol's unique structure, properties, bioavailability, and renewability. Glycerol is currently produced in large amounts during the transesterification of fatty acids into biodiesel and as such represents a useful by-product. Research efforts to find new applications of glycerol as a low-cost feedstock for functional derivatives have led to the introduction of a number of selective processes for converting glycerol into commercially valued products. This review provides a comprehensive review and critical analysis on the different reaction pathways for catalytic conversion of glycerol into commodity chemicals, including selective oxidation, selective hydrogenolysis, selective dehydration, steam reforming, thermal reduction into syngas, selective transesterification, selective etherification and synthesis of epichlorohydrin.

Key Words: Glycerol; Oxidation; Hydrogenolysis; Etherification; Esterification.

1. Introduction:

The use of renewable feedstock is essential to the sustainable development of society. Much attention has been devoted to applying green catalytic processes to convert biorenewable feedstock to commodity chemicals and clean fuels. Glycerol can be obtained from biomass via

hydrolysis or methanolysis of triglycerides. The reactions for the direct transformation of vegetable oils and animal fats into methyl esters and glycerol have been known for over a century. However, it is only recently, following more than 10 years of research and development, that the transesterification of triglycerides, using rapeseed, soybean and sunflower oils, has gained significance for its role in the manufacture of high quality biodiesel fuel. Glycerol (1, 2, 3-propanetriol) is widely available and is rich in functionalities. Glycerol can be found naturally in the form of fatty acid esters and also as important intermediates in the metabolism of living organisms [1]. Traditionally, glycerol is obtained as a by-product in four different processes: soap manufacture, fatty acid production, fatty ester production [1], and microbial fermentation [2]. It can also be synthesized from propylene oxide. Glycerol is the main byproduct in this process and is normally generated at the rate of 1 mol of glycerol for every 3 mol of methyl esters, approximately equivalent to 10 wt % of the total product. With the increasing demand for biodiesel, the production of crude glycerol is excessive [3], which leads to the reduction of the current glycerol market price. To utilize the low-cost glycerol, many researchers have paid much attention to the catalytic conversion of glycerol into value-added chemicals, for example, through selective oxidation [4], hydrogenolysis to propylene glycol [5], dehydration to aldehydes [6], reforming to syngas [7], fermentation to 1,3-propanediol [8], trans-esterification to glycerol carbonate [9], and synthesis of epichlorohydrin [10], etherification of glycerol with an olefin such as isobutylene toward fuel oxygenates [11].

Today, glycerol has over 2000 different applications, in cosmetics, pharmaceuticals, foods and drinks, tobacco, paper, inks and printing colors, the production of phthalic and maleic alkyd resins and cross linked polyesters, and as a hydraulic agent. Polyglycerols have a wide range of applications as emulsifiers, and technical esters of glycerol

with fatty acids are used as synthetic lubricants [12]. The price of glycerol has already fallen by 50% over the past ten years [13, 14]. Thus, the application of glycerol, obtained from the biodiesel process, should be increased, and new applications must be invented to improve the economics of the biodiesel processes [12]. USP grade (United States Pharmaceutical grade) glycerol has substantial value and many uses, but the glycerol from the biodiesel processes is not suitable for these uses as such [15], because of many impurities, resulting in expensive and challenging purifying steps [16]. With a focus on recent developments in the conversion of glycerol into value-added chemicals, we describe in this review how the “new” chemistry of glycerol will play a crucial role in future biorefineries [17], as its derivatives find use in sectors as diverse as fuels, chemicals, automotive, pharmaceutical, detergent, and building industries.

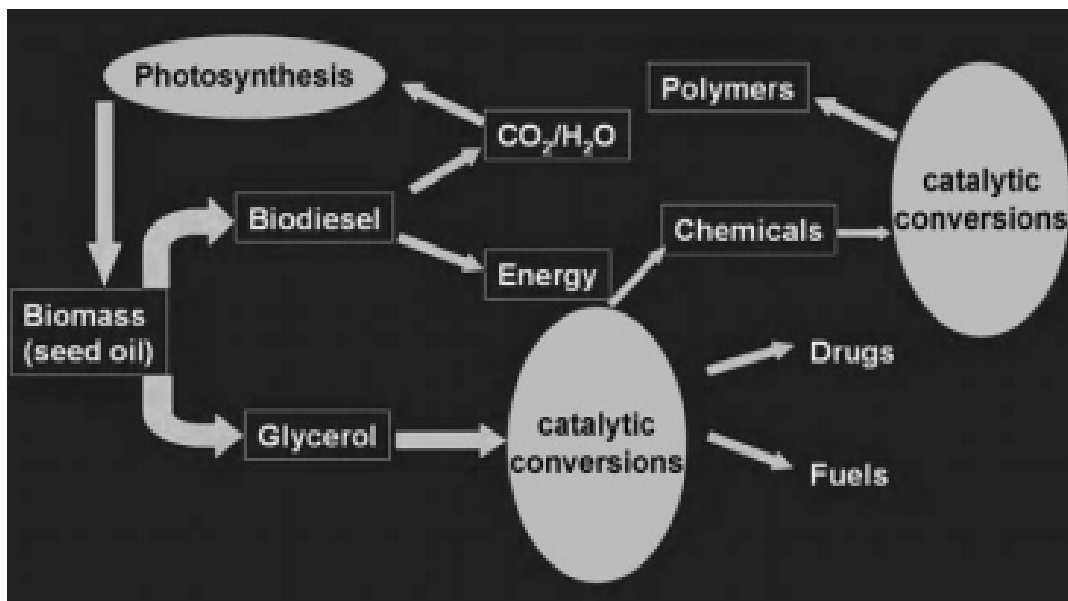


Figure1. The chemistry of glycerol will play a crucial role in future biorefineries.

2. Catalytic Conversion of Glycerol:

Recently, a series of novel catalytic conversion processes that transform glycerol into useful chemicals was reported in the literature. This review examines the most recent developments in chemo selectively catalytic conversion of glycerol to promising commodity chemicals and fuels. As a result, new opportunities and challenges exist for research and industry to improve both the catalytic materials and technologies needed for the efficient transformation of glycerol into valuable chemicals.

2.1 Oxidation of glycerol:

A large number of products can be obtained from glycerol oxidation processes. If the secondary hydroxy group of glycerol is oxidized selectively, dihydroxyacetone (DHA) is formed. DHA has been used for years as an active substance in sunless tanning lotions. The oxidation of the primary hydroxyl groups of glycerol leads to glyceraldehydes, an intermediate in the carbohydrate metabolism. Further oxidation of glyceraldehydes produces carboxylic acids, like glyceric acid, tartronic acid and mesoxalic acid. These acids are mainly converted into various market products, e.g. polymers or bio-degradable emulsifiers. In addition to these applications, glyceric acid can be used as anionic monomer of packaging material for exothermic and volatile agents [18]. In its ester form, glyceric acid can act together with a quaternary ammonium salt as an effective and biodegradable fabric softener [19]. Tartronic acid can be used as a potentiating agent or adjuvant to increase the blood absorption of a tetracycline antibiotic [20]. Platinum and Palladium are well known metal catalysts for the glycerol oxidation process. A process which is catalyzed by platinum metal supported on active charcoal can produce glyceric acid with 55 percent selectivity at 90 percent conversion. Beside platinum, gold, as a relatively new metal

catalyst for catalytic glycerol oxidation, has a better resistance to oxygen poisoning and higher selectivity towards glyceric acid (more than 90 percent selectivity at 90 percent conversion) [21] compared to platinum [22]. To improve the rate and selectivity of glycerol oxidation processes bimetallic catalysts were used. The comparisons between monometallic Au, Pd, or Pt and bimetallic Au-Pd [23] or Au-Pt [24, 25] catalysts proved that in many cases bimetallic catalysts have higher activity and resistance to deactivation [23, 26, 27].

2.2 Hydrogenolysis of glycerol:

Glycerol is a polyol and thus competes with other polyols on the market. A remarkable conversion of crude glycerol into propylene glycol (1,2-propanediol), however, was recently introduced which resulted in an antifreeze product (70 % propylene glycol and 30 % glycerol) that can be produced, refined, and marketed directly by existing biodiesel facilities[28]. The method is based on hydrogenolysis (i.e. dehydration followed by hydrogenation) of glycerol over a copper chromite catalyst at 200 °C and less than 10 bar coupled with a reactive distillation [29]. The reaction pathway proceeds via an acetol (hydroxyacetone) intermediate in a two-step process. The first step of forming acetol occurs at atmospheric pressure, while subsequent hydrogenation at 200 °C and 10 bar H₂ eventually affords propylene glycol in 73 % yield at significantly lower cost than propylene glycol made from petroleum. A main advantage of the process is that the copper chromite catalyst can be used to convert crude glycerol without further purification (whereas supported noble-metal catalysts are easily poisoned by contaminants such as chloride) [30]. Finally, the hydroxyacetone (acetol) formed as an intermediate is an important monomer used in industry to make polyols, thus the process opens up more potential applications and markets for products made from glycerol.

2.3 Dehydration of glycerol:

Acrolein is a versatile intermediate largely employed by the chemical industry for the production of acrylic acid esters, super absorber polymers, and detergents. It can be obtained from glycerol in excellent yield by using a method introduced in the mid-1990s which is based on glycerol dehydration on acidic solid catalysts. Hence, passing a glycerol water gas mixture at 250 to 340 °C over an acidic solid catalyst with a Hammett acidity function of less than 2 results in full conversion of glycerol into acrolein [31]. The process was not commercialized owing to its poor economics compared to a commercial production route based on the oxidation of propylene with a Bi/Mo mixed oxide catalyst. Most recently, the usage of sub and supercritical water as the reaction media has been investigated but, again, the conversion and acrolein selectivities achieved so far do not satisfy the criteria of an economical process [32].

2.4 Reforming to synthesis gas:

From both industrial and innovation viewpoints, the major achievement of the new chemistry of glycerol is the reforming process in which glycerol in the aqueous phase is converted into hydrogen and carbon monoxide under relatively mild conditions (225–300 °C) by using a platinum-based catalyst in a single reactor [33]. Such formation of synthetic gas is crucial for the future of biorefineries because syngas can be used as a source for fuels and chemicals by Fischer–Tropic or methanol syntheses. Moreover, glycerol (advantageously obtained by the fermentation of glucose) [34] offers an energy efficient alternative to ethanol based products because higher product concentrations can be formed. Careful selection of the Pt catalyst allows the ratio of the gases produced in the degradation of glycerol to be adjusted to the 2:1 value suitable for the Fischer–Tropic process by minimizing the extent of the water gas shift reaction.

The energy balance for these coupled reactions is also favorable. The 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 alkenes is highly exothermic (110 kcal mol), such that the overall conversion of glycerol into alkenes by the combination of reforming and Fischer–Tropsch synthesis is mildly exothermic, with an overall gain in energy of 30 kcal per mole of glycerol.

2.5 Fermentation of glycerol:

Glycerol can serve as a feedstock for the fermentative production of 1, 3-propanediol, one of the two primary components (the other is terephthalic acid) of Sonora and Corterra fibers, a polyester with excellent potential for use in textiles and carpeting that has been dubbed the “new nylon”. Fermentation uses bacterial strains in the groups Citrobacter, Enterobacter, Ilyobacter, Klebsiella, Lactobacillus, Pelobacter, and Clostridium [35]. In each case, glycerol is converted into 1, 3-propanediol in a two-step, enzyme-catalyzed reaction sequence. In the first step, a dehydratase catalyzes the conversion of glycerol into 3-hydroxypropionaldehyde (3-HPA) and water [Eq. (1)]. In the second step, 3-HPA is reduced to 1, 3-propanediol by a nicotinamide adenine dinucleotide (NAD⁺)linked oxidoreductase [Eq. (2)], whose oxidized form partly oxidizes glycerol to DHA [Eq. (3)]. The 1, 3-propanediol is not metabolized further and, as a result, accumulates in the media. The overall reaction consumes a reducing equivalent in the form of the cofactor, NADH, which is oxidized to NAD⁺.



As such, this biological process for the production of 1,3-propanediol has a low metabolic efficiency and uses relatively expensive glycerol, [36] but a less costly production of 1,3-propanediol can be achieved by using glucose as optimal substrate thus combining the pathway from glucose to [34] successfully with the bacterial route from glycerol to 1,3-propanediol.

2.6 Trans-esterification of glycerol:

The main application of glycerol esters is their use as emulsifiers. Two different ways of production exist. The first way is the conversion of glycerol with fatty acids or fatty acid methyl esters using appropriate catalysts. The second way is known as transesterification and means the conversion of fats with glycerol. Glycerol can be replaced by glycerol oligomers, which lead – under comparable conditions to polyglycerol esters. Such compounds are described as good anti fogging agents [37]. According to the oligomerization reaction of glycerol, the same catalysts have been investigated for the production of glycerol esters. The work of Perez-Pariente et al. [38] gives a good overview about Mesoporous catalysts for this reaction. The influence of the catalyst synthesis procedures is described in detail as well as the influence of the structure itself. Moreover, metal oxides have been investigated as potential catalysts for the synthesis of glycerol esters [39].

2.7 Etherification of glycerol:

Glycerol cannot be added directly to fuel because at high temperatures it polymerizes and thereby clogs the engine and it is partly oxidized to toxic acrolein. On the other hand, oxygenated molecules such as methyl tertiary butyl ether (MTBE) are used as valuable additives as a result of their antidetonant and octane-improving properties. In this respect, glycerol tertiary butyl ether (GTBE) is an excellent additive with a large potential for diesel and biodiesel reformulation. In

particular, a mixture of 1,3-di-, 1,2-di-, and 1,2,3-tri- tert -butyl glycerol, when incorporated in standard 30–40 % aromatic-containing diesel fuel, leads to significantly reduced emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes [40]. Glycerol alkyl ethers, especially the glycerol tertiary-butyl ethers (GTBE), should be mentioned here, too. The higher ethers, the h-GTBE can be used as octane booster in automotive fuels analogue to MTBE, but they do not exhibit their environmental problems. Glycerol can be converted with isobutene or with tert-butanol. The latter way, however, leads to water as by-product. The first way was investigated by Behr and Lohr [41], the second one by Klepacova et al. [42].

2.8 Synthesis of Epichlorohyrin:

Epichlorohyrin, a chemical employed in the production of epoxy resins, is now commercially synthesized from glycerol by a catalytic reaction with HCl followed by dehydrochlorination with NaOH. The glycerol-based process (named Epicerol) involves the direct synthesis of dichloropropanol, an intermediate product, from glycerine and hydrochloric acid. Thus, natural glycerol is used as a substitute for the propylene feedstock employed in the traditional epichlorohyrin production process, involving formation of allyl chloride by reaction of propylene with Cl₂. Overall, the Epicerol process uses a combination of undisclosed metal catalysts and requires a lower specific consumption of chlorine and water, thereby reducing chlorinated effluents [43].

Conclusion:

By highlighting the basic advances on which these processes are based, we hope to have shown how a number of practical limitations posed by glycerol chemistry, such as the low selectivity encountered when employing traditional stoichiometric and older catalytic conversions, were actually solved based on the understanding of the fundamental chemistry of glycerol.

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