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Glycerol Transformation to Value-Added 1,3-Propanediol Production: A Paradigm for a Sustainable Biorefinery Process

Shanthi Priya Samudrala

Abstract

The impact of diminishing fossil fuel resources, rising environmental issues as well as the global demand for energy, fuels and chemicals has significantly directed to the use of renewable biomass for sustainable production of fuels and chemicals. Glycerol, a three carbon feedstock, is one of the most promising biomass resources which at present is obtained as a by-product in large quantities during the biodiesel production. This stimulated a lot of interest in developing new valorization technologies to produce high-value tonnage chemicals from glycerol by sustainable processes such as oxidation, dehydration, hydrogenolysis, steam reforming, carboxylation, acetalization, esterification and chlorination. In this chapter, we intend to focus on the hydrogenolysis of glycerol which produces important commodity chemicals such as propanediols, propanols and ethylene glycol. In particular, the selective hydrogenolysis of glycerol to 1,3-propanediol performed in both liquid phase and vapor phase reaction processes is described. Furthermore, the most significant progress in the development of the catalytic materials for glycerol hydrogenolysis including the reaction pathways is herein summarized.

Keywords: glycerol, hydrogenolysis, biomass, biodiesel, 1,3-propanediol, metal-acid catalyst

1. Introduction

The consideration of renewable energy resources and sustainable processes for energy, fuel and chemical production is the most important research targeted areas of this century. Currently around 90% of all chemicals are synthesized from fossil fuels or petrochemicals. However, to combat the issues of climate change, depletion of oil resources as well as its escalating prices, the investigation of the potential renewable sources to meet the future energy requirements has been a perpetual study driving researcher's attention. Consequently, there is a pressing need to develop alternative processes for the sustainable ways of producing fuels and chemicals. In this regard, utilizing "biomass as feedstock" is well thought out as an outstanding sustainable renewable energy source for fuel and chemical production, as a substitute to fossil fuel energy.

1.1 Biomass

In the recent past, biomass has been recognized as the most widespread renewable energy source and a potential substitute to fossil fuels that could be regenerated faster. It is extensively used as a building block for fuels, fuel additives and fine chemicals. Biomass refers to plant- and animal-derived biological material. By using different processes such as thermal, chemical, biological and electrochemical methods, biomass resources can be converted to valuable fuels and chemicals [1]. Biomass can be chemically converted to other usable forms of energy like methane gas or transportation fuels like ethanol and biodiesel. Vegetable oils and animal fats are used to produce 'biodiesel', whereas the fermentation of corn and sugarcane produces 'ethanol'. Unlike fossil fuels, carbon dioxide released into the atmosphere by biomass combustion is absorbed by the plants as the regrowth of the biomass crops takes shorter time and hence results in a closed carbon cycle with net zero carbon emission. Therefore, biomass is regarded as the naturally occurring clean and efficient renewable energy carbon resource used as a substitute for fossil fuels.

1.2 Biodiesel

Biodiesel is a renewable, potentially viable environmentally friendly diesel fuel, which directly replaces conventional petroleum diesel. Given its non-toxic and biodegradable nature, biodiesel offers several benefits including better combustion emission profile, with low greenhouse gas emissions. The enhanced lubricating properties that can extend the engine life, high flash point (150°C) and material compatibility made biodiesel a benign transportation fuel and a better substitute to petroleum-based fuel. It can either be blended with petroleum in different proportions or can be used directly in its pure form in the diesel engines. Base-catalyzed transesterification process of canola oil/soya bean oil, animal fats or cooking oil (triglycerides) with alcohol produces biodiesel (fatty acid methyl esters) and glycerol (valuable by-product) (**Figure 1**).

Biodiesel production has shown a steady growth from 2000 to 2010 rising from less than 1 million tons to 10 million tons, respectively. For every 1 tonne of biodiesel synthesized, 100 kg of glycerol is cogenerated, approximately 10 wt% of total product which is fairly greater than that produced from soap manufacturing process. Due to the rapid growth in biodiesel production, a glut of glycerol has been created, and subsequently the market value of glycerol is dropped abruptly. One of the key problems challenged by biodiesel companies is the disposal of glycerol, which is quite expensive. Now the major question arises! How the glycerol

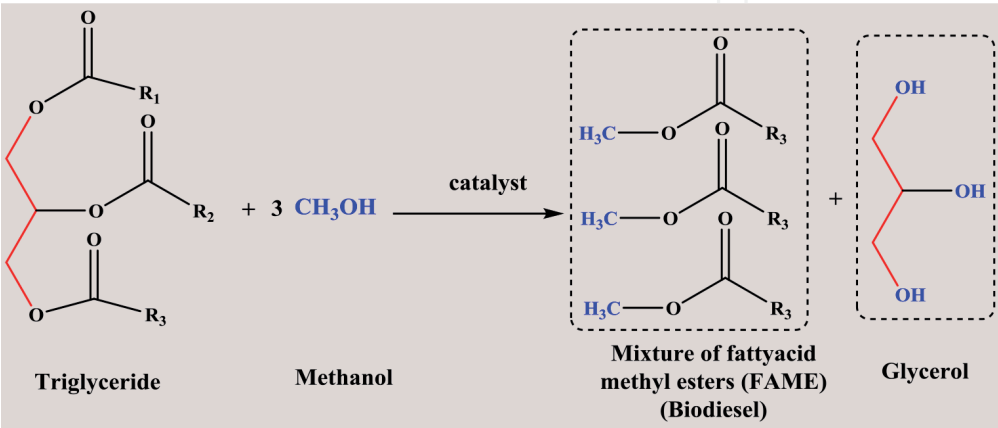


Figure 1.
Biodiesel production through transesterification of triglyceride.

is separated and valorized from biodiesel production? Therefore, to contribute to the cost affordability of biodiesel processes and for sustainable development, it is imperious to develop methods of producing value-added chemicals from glycerol. In this context, the excess glycerol derived from biodiesel process could be utilized as a renewable feedstock for substituting fossil-derived chemicals, and research is being directed worldwide to utilize glycerol as a chemical building block [2].

1.3 Bio-glycerol

Glycerol or glycerine also known as propane-1, 2, 3-triol is a simple trihydroxy sugar alcohol primarily used as a sweetening agent, solvent, pharmaceutical agent and emollient. It is a colorless, odorless, viscous liquid miscible in water. Glycerol is non-toxic and hygroscopic in nature. Purified glycerin is used in the production of various foods, beverages, pharmaceuticals, cosmetics and other personal care products. Glycerol is produced by saponification process (traditional soap manufacture) and obtained as a major by-product in biodiesel process (fatty acid ester production) (**Figure 2**). The convenient method for the production of glycerol is biological fermentation and hydrogenolysis of glucose. Synthetic glycerol is prepared from propylene, but this method is at present economically unappealing because of rising crude oil prices [4].

It is projected that by 2020, glycerol production will rise six times more than request. The crude glycerol from biodiesel process is of variable quality comprising a mixture of methanol, unreacted mono-, di- and triglycerides, fatty acids, water, inorganic salts, methyl esters and a range of organic constituents with an estimated 50% purity and has a low market value. The purification processes of glycerol are expensive, and it is being disposed as a waste by small biodiesel plants. This remains problematic because the methanol content of glycerol is considered as harmful waste. Currently, energy production by incineration is one method to remove surplus glycerol. In terms of both environmental protection and economic benefit, the value addition of glycerol is of great importance to further enhance the cost efficacy of biodiesel processes.

1.4 Valorization of bio-glycerol

With glycerol offered as a low cost, large-volume bio-feedstock, consumption of surplus glycerol is a prerequisite for the commercial sustainability of biodiesel processes. Glycerol is one among the top 12 platform chemicals from biomass, compelled by its non-toxic, edible, biodegradable properties as well as multifunctional structure. Glycerol is a highly attractive molecule used to produce variety of valuable chemical intermediates. In order to provide new applications for glycerol valorization, chemical

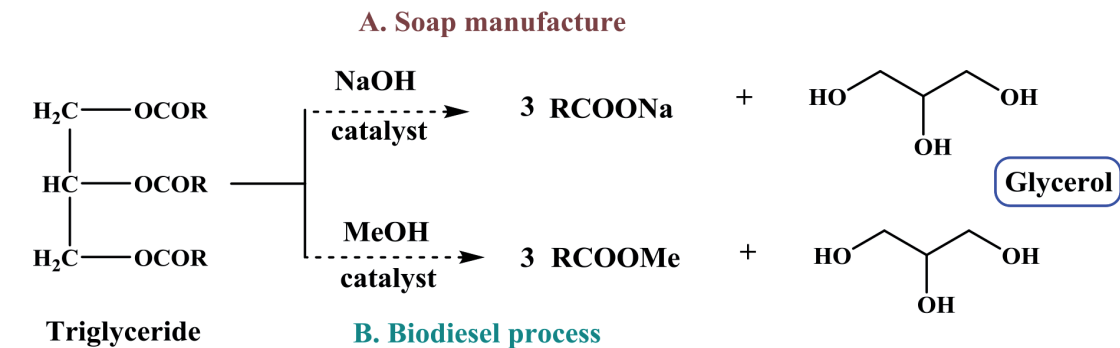


Figure 2.
Glycerol production by saponification and biodiesel processes [3].

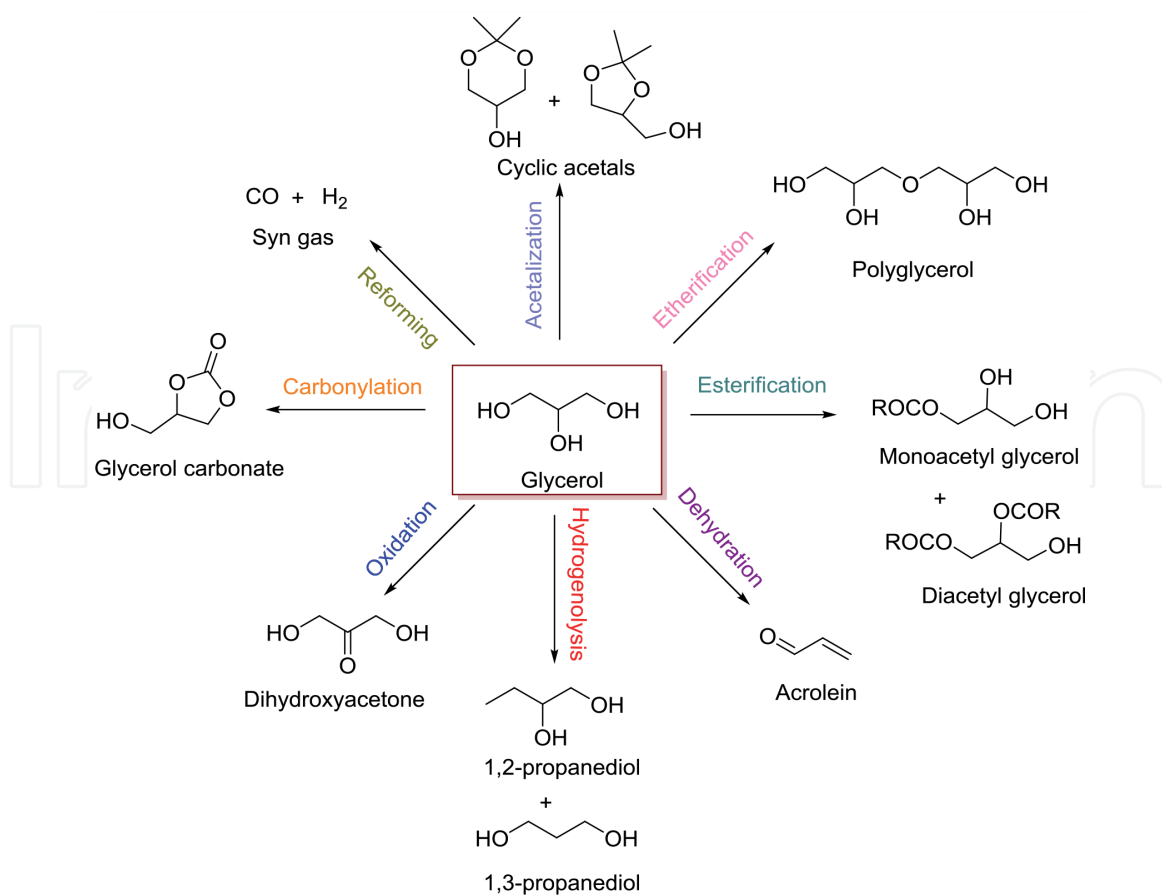


Figure 3.
Different chemical transformations of glycerol to value-added chemicals.

catalysis is an important approach to green chemical processes. In this regard, significant research on the chemical transformation of glycerol into high value-added specialty chemicals has been developed during the past decade [5].

Glycerol is a highly functionalized molecule used as a precursor for the production of wide range of commodity chemicals such as 1,2-propanediol, 1,3-propanediol, ethylene glycol, propanols, hydrocarbons, acrolein, dihydroxyacetone, glyceric acid, syngas, hydrogen, glyceryl ethers, glyceryl esters, glycerol carbonate, 1,3-dichloro propanol, polyglycerols as well as acetals and ketals of glycerol by means of several different methods such as fermentation, hydrogenolysis, pyrolysis, oxidation, etherification, dehydration, esterification, carboxylation, halogenation, polymerization and glycerol acetalization [6, 7] (**Figure 3**). Furthermore, glycerol has received a great attention as a 'green solvent' in synthetic organic chemistry because of its exceptional physical and chemical properties. Its compatibility with most organic/inorganic compounds, high boiling point, negligible vapor pressure, easy dissolution and nonhazardous nature, simple handling and storage provides an innovative way to revalorize glycerol and to be used as sustainable reaction medium [8].

2. Hydrogenolysis of glycerol

Hydrogenolysis reaction is a class of reduction which involves dissociation of chemical bonds ($\text{C}-\text{C}$ or $\text{C}-\text{O}$) in an organic compound and subsequent addition of hydrogen to the resultant molecular fragments. $\text{C}-\text{C}$ hydrogenolysis reactions have gained commercial importance in petroleum refineries, a method to produce lower hydrocarbons. On the other hand, $\text{C}-\text{O}$ hydrogenolysis reduces the oxygen content and is an important area of research for biomass conversion to fuels and

chemicals (**Figure 4**). C—O hydrogenolysis is highly favorable industrial relevant route of glycerol conversion processes as glycerol is rich in oxygen functionality.

Glycerol hydrogenolysis is a complex reaction involving many reaction pathways giving rise to valuable products. At first, C—O hydrogenolysis of glycerol yields propanediols (1,2-propanediol and 1,3-propanediol). Subsequent C—O hydrogenolysis gives rise to propanols (1-propanol and 2-propanol) and finally propane, whereas C—C hydrogenolysis of glycerol or the C—C hydrogenolysis of the products derived from C—O hydrogenolysis gives degradation products such as ethylene glycol, ethanol, methanol, ethane and methane. The reaction routes and products from glycerol hydrogenolysis are shown in **Figure 5**. 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), ethylene glycol (EG), 1-propanol (1-PrOH) and 2-propanol (2-PrOH) are industrially important products of glycerol hydrogenolysis. Therefore, to increase the cost-effectiveness of biodiesel industry, the catalytic hydrogenolysis of glycerol appears to be an attractive option. Furthermore, the products obtained from glycerol hydrogenolysis can certainly replace the chemical compounds produced from non-renewable sources.

2.1 Propanediols (1,2-propanediol and 1,3-propanediol)

Propanediols are the most important value-added chemicals obtained from glycerol hydrogenolysis. 1,2-propanediol (1,2-PDO) is a medium-value commodity

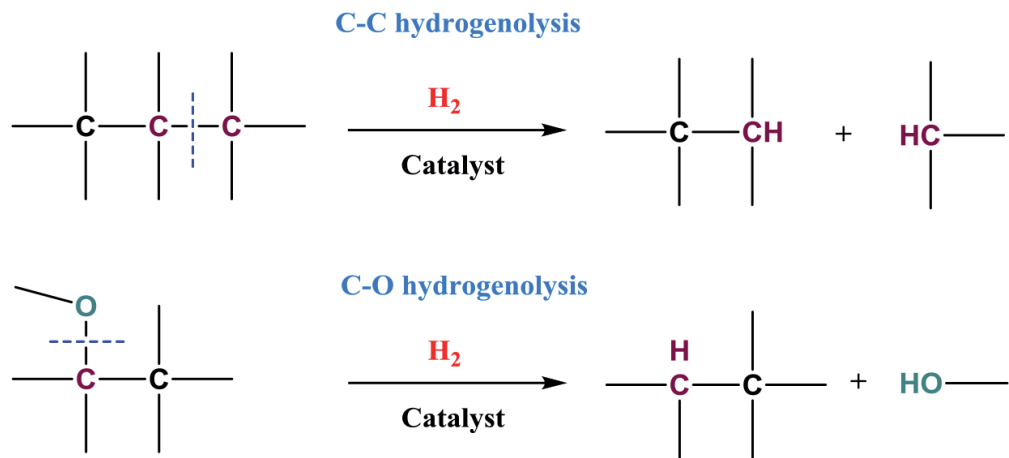


Figure 4.
Reaction pathways of hydrogenolysis.

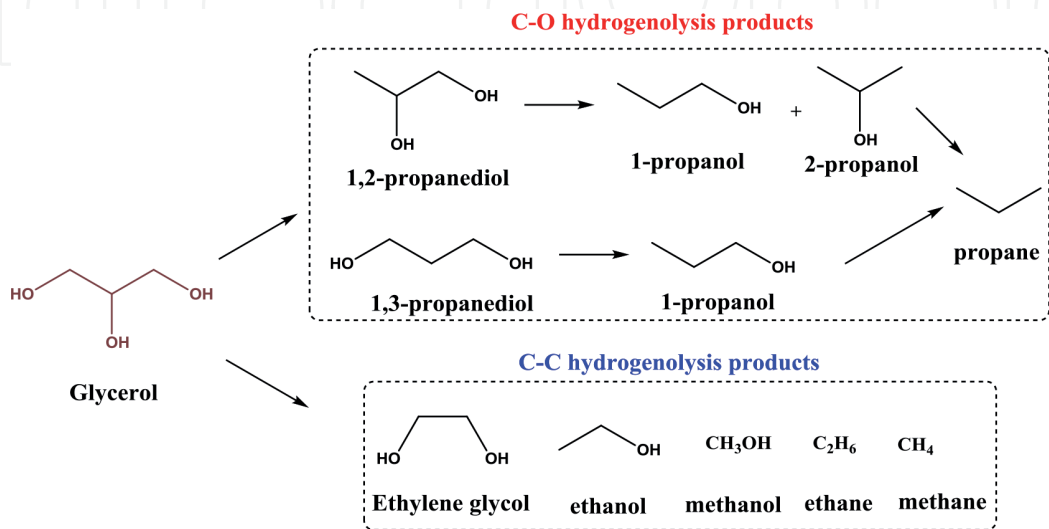


Figure 5.
Products obtained from glycerol hydrogenolysis.

chemical used as a component in paints, liquid detergents, cosmetics, food, animal feed, personal care products, tobacco humectants, flavors and fragrances. Besides being an antifreeze coolant and a de-icing agent [9], it is used as raw material for the synthesis of polyester resins, in the fiber manufacture and in pharmaceutical production. Conventionally, 1,2-propanediol is produced by hydroperoxide process or the chlorohydrin process from propylene oxide. 1,3-propanediol (1,3-PDO) is other valuable product of glycerol hydrogenolysis used as an important monomer in the manufacture of polymethylene terephthalate (PTT) or polypropylene terephthalate (PPT), a biodegradable polyester used in textile and carpet manufacturing. It finds applications in the manufacture of cosmetics, personal care, cleaning, lubricants, medicines, and in the synthesis of heterocyclic compounds in addition to engine coolants, food and beverages, de-icing fluids, water-based inks, heat transfer fluids and unsaturated polyester resins [10]. The global 1,3-PDO production is estimated to reach \$621.2 million by 2021 growing at an annual growth rate of 10.4%.

2.2 Reaction pathways and mechanistic studies of glycerol hydrogenolysis

Glycerol is a trihydroxy compound with two primary hydroxyl groups and a secondary hydroxyl group. The hydrogenolysis reaction of glycerol involves C—O or C—C chemical bond cleavage in the presence of catalysts and hydrogen. 1,2-PDO is produced by the hydrogenolysis of primary (1°) hydroxyl groups of glycerol, whereas the hydrogenolysis of secondary (2°) hydroxyl group gives 1,3-PDO. Successive hydrogenolysis of 1,2-PDO produces monohydroxy 1-PrOH and 2-PrOH and eventually propane. The consecutive removal of the remaining —OH from 1,3-PDO could yield 1-PrOH first and then propane. The reaction mechanisms of glycerol hydrogenolysis and the products obtained mostly depend on the operating conditions of the reaction systems, nature of catalytic materials like metal properties and acidity or basicity of catalysts [11]. The generally accepted reaction mechanisms of glycerol hydrogenolysis are illustrated below.

2.2.1 Two-step mechanism

The two-step mechanism of glycerol hydrogenolysis is the dehydration-hydrogenation route that involves acid-catalyzed dehydration of glycerol first and subsequent hydrogenation of intermediate in the presence of metallic sites to yield the final product (**Figure 6**). This mechanism is highly favorable under acidic conditions. Acid-catalyzed dehydration of 1° hydroxyl groups of glycerol

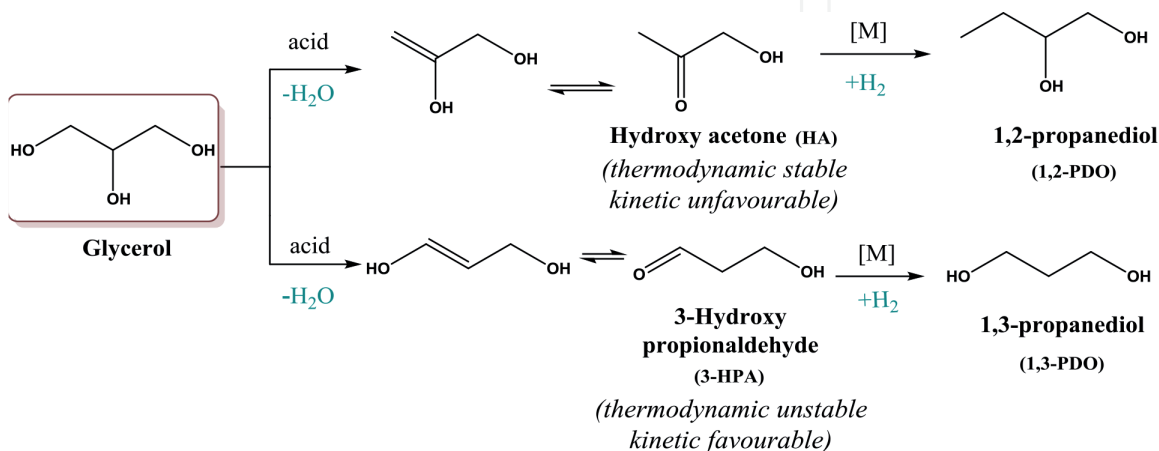


Figure 6. Dehydration-hydrogenation (two-step) mechanism of glycerol hydrogenolysis [11].

generates hydroxyacetone (acetol) followed by hydrogenation over metal to 1,2-PDO. Similarly, 1,3-PDO is formed by the acid-catalyzed dehydration of 2° hydroxyl group of glycerol to form 3-hydroxy propionaldehyde (3-HPA) and subsequent hydrogenation over metal. However, 3-hydroxy propionaldehyde, though kinetically favorable, is thermodynamically less stable than hydroxyacetone. Furthermore, double dehydration of glycerol will produce acrolein, whereas double dehydration followed by hydrogenation gives rise to the formation of 1-PrOH and 2-PrOH [11].

2.2.2 Three-step mechanism

Another route of glycerol hydrogenolysis is dehydrogenation-dehydration-hydrogenation which is a three-step mechanism, more prevalent under basic conditions [11]. It involves initial dehydrogenation of glycerol to form glyceraldehyde and 2-hydroxy acrolein by glyceraldehyde dehydration followed by hydrogenation of 2-hydroxy acrolein into 1,2-PDO (**Figure 7**). On the other hand, 1,2-PDO could also be generated by the keto-enol tautomerization of 2-hydroxy acrolein into pyruvaldehyde which hydrogenates to acetol and further hydrogenation to 1,2-PDO. Pyruvaldehyde also undergoes oxidation to yield lactic acid, and on the other hand, ethylene glycol (EG) formation can be explained through the retro-aldol reaction of glyceraldehyde to produce glycolaldehyde followed by its hydrogenation.

2.2.3 Direct route

A direct glycerol hydrogenolysis reaction mechanism (**Figure 8**) was demonstrated over specific catalysts such as Ir-ReOx/SiO₂. In this mechanism, the glycerol adsorbed on the interface of metal species generates 2,3-dihydroxypropoxide and 1,3-dihydroxypropoxide. The hydride attack facilitates the dissociation of C—O bonds in the alkoxides, and final hydrolysis yields respective products [12].

2.3 Role of acidic sites in the selective hydrogenolysis of glycerol to propanediols

The properties of catalyst systems and reaction conditions effect the selective cleavage of primary or secondary hydroxyl group from glycerol. It is evident from previous research that 1,2-propanediol (1,2-PDO) and 1,3 -propanediol (1,3-PDO) are produced

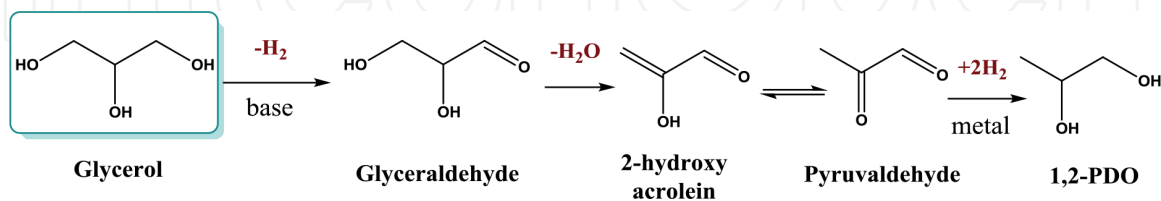


Figure 7.
 Dehydrogenation-dehydration-hydrogenation (three-step) mechanism of glycerol hydrogenolysis [11].

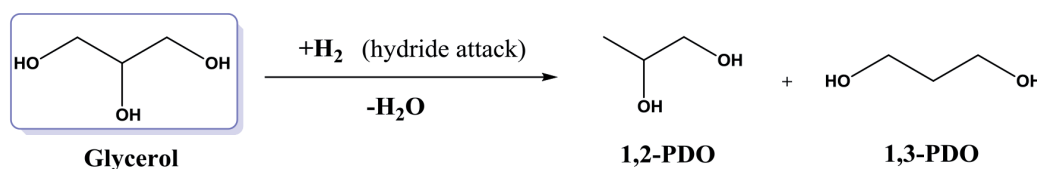


Figure 8.
 Direct hydrogenolysis mechanism of glycerol hydrogenolysis [3].

from glycerol hydrogenolysis by acid-catalysed dehydration of glycerol to form acetol and 3-hydroxypropaldehyde (3-HPA) intermediates and successive hydrogenation on metal sites. Acrolein is produced by the double dehydration of glycerol over strong acid sites. Hence, surface acidity or acid strength of the catalyst is an important parameter in directing the product distribution. Indeed, the nature of acid sites also plays a vital role in determining the selective formation of propanediols from glycerol. Brønsted acid site favors the abstraction of 2° hydroxyl group of glycerol to generate 1,3-PDO via 3-HPA, while Lewis acid sites assist in the dehydration of 1° hydroxyl group of glycerol to form 1,2-PDO through the acetol intermediate (**Figure 9**) [13].

The nature of acidic sites governs the reaction mechanism of selective glycerol conversion to propanediols which is quite interesting and important in designing the appropriate catalytic materials (**Figure 10**). The primary or secondary —OH group of glycerol is attacked by the proton from a Brønsted acidic site (**Figure 10A**) without any steric hindrance. However, protonation at secondary —OH group of glycerol generates secondary carbocation which is more stable than primary carbocation resulted from protonation of primary —OH group. It should be noted that 3-HPA is thermodynamically unstable; however, its formation is kinetically more favorable over the formation of acetol or hydroxyacetone. Hence, reaction proceeds via secondary —OH group protonation followed by dehydration to form highly unstable 3-HPA intermediate that quickly hydrogenates on metallic sites to produce 1,3-PDO. The immediate hydrogenation of 3-HPA is essential to stop further dehydration of 3-HPA to yield acrolein as final product. The Lewis acid sites of the catalysts possess empty orbital to accommodate the lone pair of electrons either from primary or secondary —OH groups of glycerol by coordinate covalent bond (CCB). This CCB seems to appear like a complex due to the direct interaction of the metal empty orbital (from the catalyst surface) with —OH groups of glycerol. However, the complex is preferentially formed with less steric hindered primary —OH group of glycerol than that of secondary —OH group. Therefore, the interaction of Lewis acid site with primary —OH group followed by dehydration results in a thermodynamically stable hydroxyacetone intermediate which is further hydrogenated to produce 1,2-PDO (**Figure 10B**). The mechanism of glycerol hydrogenolysis based on the nature of acidic sites is well in accordance with the reaction mechanism proposed by Alhanash et al. [14].

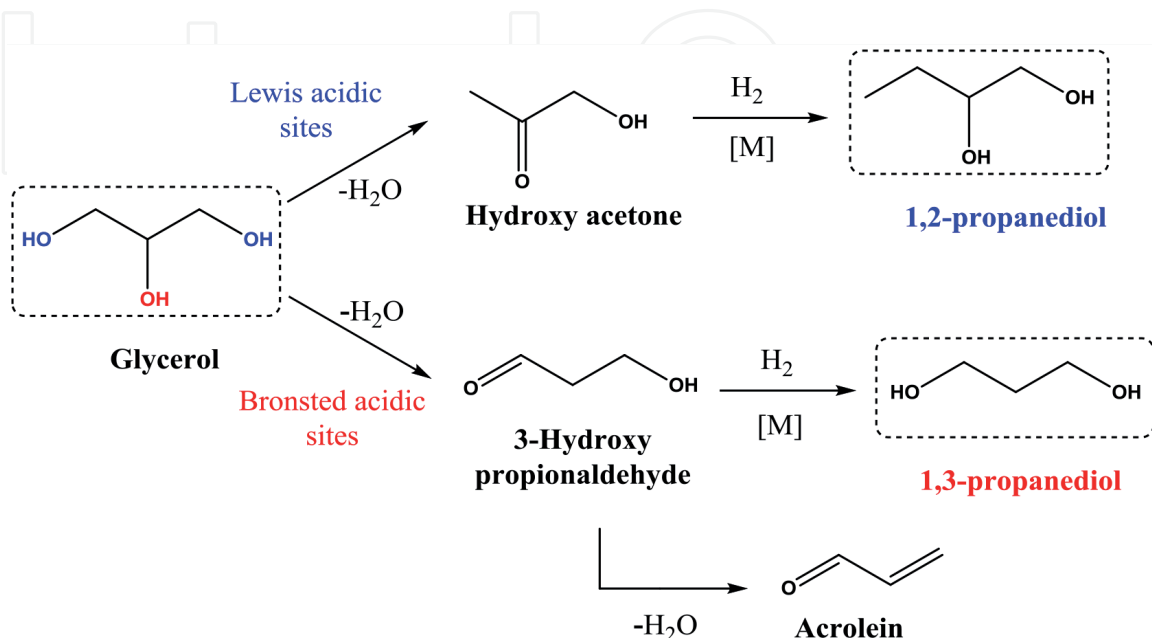


Figure 9.
Selective production of propanediols from glycerol.

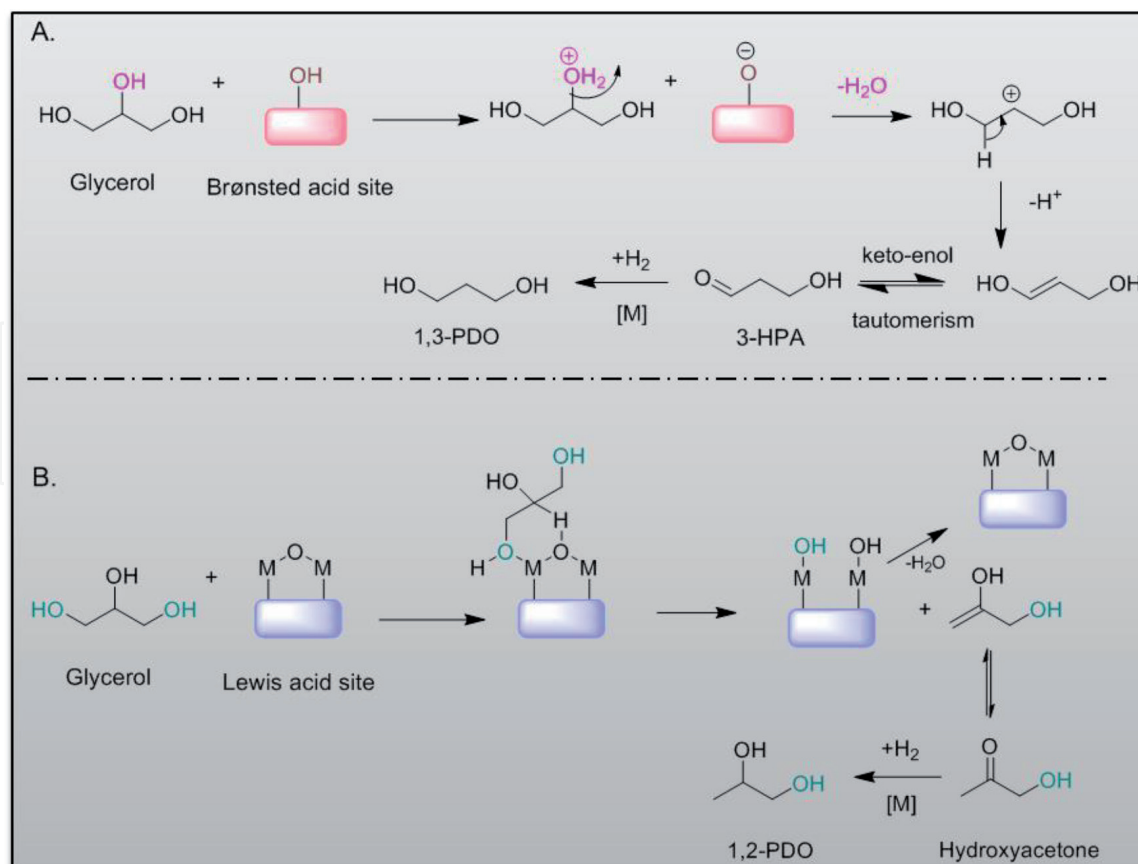


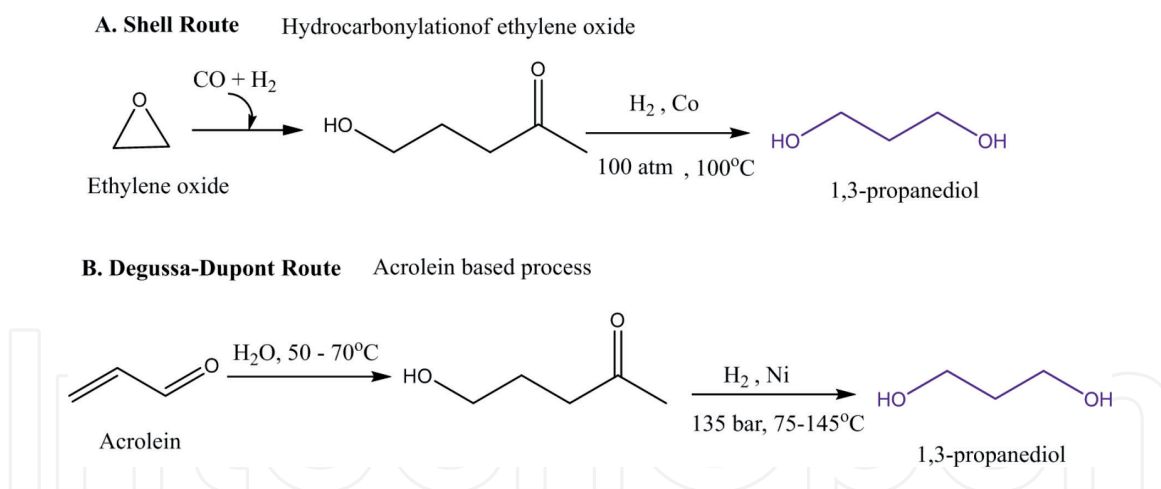
Figure 10.
 Selective production of propanediols directed by the nature of acidic sites [14].

3. Selective conversion of glycerol to 1,3-propanediol

In glycerol hydrogenolysis, the selective cleavage of one of the C—O (primary or secondary) bonds over C—C cleavage is highly challenging and depends on the operating reaction conditions as well as the nature of catalytic material in particular acidic properties of the catalyst [11]. The type of acidic sites (Lewis acid sites or Brønsted acid sites) plays an important role in directing towards the desired product formation. 1,3-propanediol is an industrially important commodity chemical and is a component of industrial polyesters such as Dupont's Sorona®, Shell Chemical's Corterra™ and CDP Natureworks®. Three different methods including chemical, microbial and catalytic methods have so far been the commonly employed methodologies for the production of 1,3-PDO.

3.1 Chemical method (conventional routes) for 1,3-PDO production

There are two well-known chemical methods for the synthesis of 1,3-PDO (**Figure 11**). The first method employs 'ethylene oxide' as the feedstock and commonly known as 'Shell' route of 1,3-PDO synthesis. It is a two-step process involving hydroformylation of ethylene oxide to 3-hydroxypropionaldehyde (3-HPA) and subsequent hydrogenation of 3-HPA to 1,3-PDO. The second method of 1,3-PDO synthesis is 'Degussa-DuPont' route and uses acrolein as the feedstock [15]. The hydration of acrolein gives 3-HPA which is further hydrogenated to 1,3-PDO. However, the chemical methods of 1,3-PDO synthesis are petroleum-based methods and have many disadvantages such as high pressure, high temperature and catalysts. Consequently, the costs of 1,3-PDO production becomes very high.

**Figure 11.**

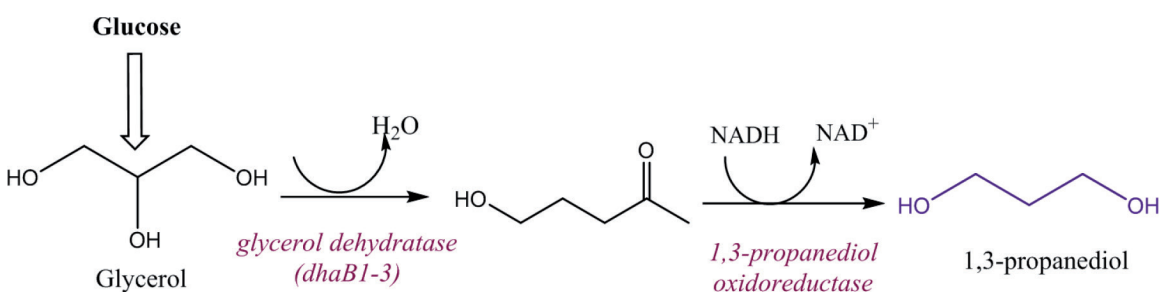
Traditional synthetic methods for the production of 1,3-propanediol [15].

3.2 Microbial method (fermentation process) for 1,3-PDO production

An attractive alternative for chemical synthesis is a microbial conversion of raw materials to 1,3-PDO. This method is easy and does not generate toxic by-products. The biological conversion of glycerol into 1,3-PDO is mainly achieved by the fermentation process using anaerobic or aerobic bacteria [12, 16, 17]. The commonly used microbes in the fermentation process include *Clostridium*, *Enterobacter* and *Lactobacillus* [18]. The biological conversion of glycerol in a bacterial cell is carried out at functional temperature (37°C) and normal atmospheric pressure. In this process (**Figure 12**), glycerol is first dehydrated to 3-HPA in the presence of B12-dependent enzyme, and then 1,3-PDO is produced by the reduction of 3-HPA in the presence of NADH-oxido reductase. However, the energy consumption and cost of the equipment in the fermentation process are relatively high.

3.3 Catalytic method (homogeneous and heterogeneous catalysis) for 1,3-PDO production

In view of shortcomings of chemical and biological methods, the most economically attractive approach would be the development of new, cost-competitive process that utilizes renewable resources as feedstocks for green and sustainable chemical technologies. Catalytic method is one such process which not only represents milestones towards the goal of reducing fossil fuel dependency and greenhouse gas emissions but also has the potential to provide substantial energy savings. As glycerol hydrogenolysis to propanediols proceeds via a dehydration-hydrogenation mechanism, typically the reaction requires a bifunctional catalyst where metals (transition or noble metals) are used for hydrogenation and acidic or basic support materials can

**Figure 12.**

Microbial production of 1,3-propanediol.

be used for dehydration. The literature reviews suggests that 1,2-PDO formation can be achieved by a simple acidic or basic catalyst; however, the formation of 1,3-PDO is challenging and definitely requires a cocatalyst that acts as a Brønsted acid additive [11]. The hydrogenolysis of glycerol has been investigated by quite a few researchers in the recent past for glycerol hydrogenolysis both in batch and continuous flow reactors using homogeneous as well as heterogeneous catalytic systems. Catalysts based on various transition and noble metals such as Cu, Ni, Co, Pd, Ru, Rh, Ir, Re, Ag, Au and Pt have been tested in glycerol hydrogenolysis [19, 20]. This chapter highlights the catalytic materials employed for the selective hydrogenolysis of glycerol to 1,3-PDO till date and summarizes all different catalyst systems used.

3.3.1 Homogeneous catalytic processes

The homogeneous catalytic hydrogenolysis of glycerol has been demonstrated by Celanese and Shell corporations using Rh and Pd metal complexes in the late 1980s and 1990s [21, 22]. Later, Bullock et al. described the dehydroxylation of glycerol in sulfolane at 110°C and 52 bar pressure over a ruthenium catalyst, but 1,2-PDO and 1,3-PDO were produced in very low yields (<5%) [23]. The results of homogeneous catalytic systems have been represented in **Table 1**. Nonetheless, the major drawback of these homogeneous catalytic processes is the separation/recovery of catalyst from product and corrosion of the reactor due to reaction medium. Furthermore, glycerol hydrogenolysis using homogeneous catalysts leads to a range of by-products. Apparently, homogeneous catalytic processes end up with hazardous environmental problems, and in efforts to address these problems, researchers paid significant attention on heterogeneous catalysts.

3.3.2 Heterogeneous catalytic systems

The problematic separation of homogeneous catalysts from their products and rather their instability led to the development of successful, industrially applicable heterogeneous catalysts with high levels of activity, selectivity and catalyst stability. Different classical heterogeneous metal catalysts Cu, Ru, Rh, Ir, Pt and Pd supported on a wide range of qualitatively different carriers and in presence of Brønsted acids as cocatalysts were, so far, widely employed for direct hydrogenolysis of glycerol to obtain 1,3-propanediol. Wide-ranging reaction parameters including temperature (around 180–350°C) and hydrogen pressure (1–9 MPa) are typically applied. As shown in the mechanism of glycerol hydrogenolysis via dehydration-hydrogenation and dehydrogenation-dehydration-hydrogenation

| Author (year) | Catalyst | Solvent/additive | Temp (°C) | P (MPa) | Yield of 1,3-PDO (%) | Ref. |
|----------------|----------------------------|--|-----------|--------------------|----------------------|------|
| Che (1985) | Rh(CO) ₂ (acac) | MPI ^a /H ₂ WO ₄ | 200 | 32 syngas | 21 | [21] |
| Shell (1998) | Pd complex ^b | Sulfolane-water/MSA ^c | 140 | 6 syngas | 30.8 ^d | [22] |
| Bullock (2001) | Ru-complex ^e | Sulfolane | 110 | 5.2 H ₂ | <5 | [23] |

^aMPI, 1-methyl-2-pyrrolidinone.
^bPd-BCPE (BCPE, 1,2-bis(1,5-dicyclohexylphosphino)ethane).
^cMethane sulfonic acid.
^dSelectivity.
^e[{Cp*₂Ru(CO)₂}]₂Cu-HJ⁺ OTf⁻ (Cp* = η⁵-C₅Me₅; OTf = OSO₂CF₃).

Table 1.
Glycerol hydrogenolysis to 1,3-propanediol over homogeneous catalytic systems.

routes, for selective production of 1,3-PDO from glycerol, addition of a suitable cocatalyst that can act as a Brønsted acid is highly essential. From the earlier reports, it is clearly evident that Brønsted acid catalysts have been successfully employed and found to be highly active for 1,3-PDO production. The Brønsted acidity in the catalyst could be generated either from addition of a cocatalyst/additive to the catalyst or directly from the support material chosen. Supported noble metal (Pt, Ir, Rh) catalysts with a cocatalyst or a Brønsted acid additive have been proven to be more efficient catalytic materials for the selective production of 1,3-PDO from glycerol hydrogenolysis. The catalytic materials so far investigated for the selective hydrogenolysis of glycerol to 1,3-propanediol can be categorized into four different types based on the Brønsted acid additive used. These include supported metal catalysts containing tungsten oxide or heteropolyacid or Rhenium as a cocatalyst/Brønsted acid additive. All the supported metal catalysts with different types of additives used for 1,3-PDO are herein summarized systematically.

3.3.2.1 Metal-tungsten-based catalytic materials

A number of supported metal catalysts comprising WO_x as a cocatalyst were actively investigated in both liquid phase and vapor phase reaction processes of glycerol hydrogenolysis of glycerol and showed that platinum-tungsten-based catalysts were the most efficient catalytic materials for the selective production of 1,3-PDO. A tungstate consists of an oxoanion of tungsten, and the simplest tungstate ion is WO₄²⁻. Tungsten in the presence of hydrogen undergoes reduction (W⁶⁺ to W⁵⁺) and produces acidic protons (H⁺). Various examples of Pt-tungsten catalysts used in glycerol hydrogenolysis for selective 1,3-PDO formation are summarized in **Table 2**. The use of tungsten in glycerol hydrogenolysis started in 1980s by the innovative work led by Celanese Corporation using a homogeneous rhodium complex (Rh(CO)₂(acac)) + tungstic acid catalyst [21]. In comparison to a simple protic acid, the addition of H₂WO₄ to the catalyst enhanced the catalytic performance to propanediols. Later extensive research work was carried out based on noble metal- and tungsten-based catalysts (Pt-WO_x) [24–42]. While Pt/WO_x catalysts stand out to be the most outstanding high-performance catalysts for selective hydrogenolysis of glycerol to 1,3-PDO compared to other noble metals, Cu-based WO_x supported on titania catalyst has also been investigated and was found to be efficient in the production of 1,3-PDO [42]. Though the mechanism is still uncertain, it is obvious from previous research that the addition of tungsten as a cocatalyst has very well enhanced the acid strength especially the number of Brønsted acid sites which favors the formation of 1,3-PDO [11]. Therefore, the major conclusions from all the previous studies indicate that the Brønsted acid sites generated from tungstate species are responsible for dehydration of glycerol and the loaded platinum acts as active centre for the hydrogenation of the intermediate to 1,3-PDO.

3.3.2.2 Metal-heteropolyacid-based catalytic materials

Heteropolyacid-based metal-supported catalysts have also been investigated for selective hydrogenolysis of glycerol to 1,3-propanediol. In general, catalysis by heteropolyacids (HPAs) is a field of prominence, appealing growing attention throughout the world, in which many new and exciting developments are taking place in both research and technology. HPAs are polyoxometalates having metal-oxygen octahedra as the basic structural units. Among a wide variety of HPAs, those belonging to the so-called Keggin series such as silicotungstic acid and phosphotungstic acid are potential catalysts and can replace corrosive liquid acids to afford green chemical processes. HPAs possess strong Brønsted acidity as compared to other solid acid

| Author | Catalyst | Temp (°C) | H ₂ (MPa) | Solvent | Process | C (%) | S (%) | Ref. |
|-----------------------|--|-----------|----------------------|------------------|--------------|-------|-------|------|
| Kurosaka et al. 2008 | Pt/WO ₃ /ZrO ₂ | 170 | 8 | DMI ^a | Liquid phase | 85.8 | 28.2 | [24] |
| Gong et al. 2010 | Pt/WO ₃ /TiO ₂ /SiO ₂ | 180 | 5.5 | H ₂ O | Liquid phase | 15.3 | 50.5 | [25] |
| Qin et al. 2010 | Pt/WO ₃ /ZrO ₂ | 130 | 4 | — | Vapor phase | 70.2 | 45.6 | [26] |
| Liu et al. 2012 | Pt/m-WO ₃ | 180 | 5.5 | — | Vapor phase | 18 | 39.2 | [27] |
| Dam et al. 2013 | Pt/WOx/Al ₂ O ₃ | 200 | 4 | H ₂ O | Liquid phase | 49 | 28 | [28] |
| Arundathi et al. 2013 | Pt/WOx/AlOOH | 180 | 5 | H ₂ O | Liquid phase | 100 | 66 | [29] |
| Zhu et al. 2014 | Pt/WO ₃ /ZrO ₂ /SiO ₂ | 180 | 5 | — | Vapor phase | 54.3 | 52.0 | [30] |
| Fernandez et al. 2015 | Pt/WOx/Al ₂ O ₃ | 200 | 4.5 | H ₂ O | Liquid phase | 53.1 | 51.9 | [31] |
| Zhu et al. 2015 | Pt-WOx/Al ₂ O ₃ | 160 | 5 | — | Vapor phase | 64.2 | 66.1 | [32] |
| Priya et al. 2015 | Pt-WO ₃ /SBA-15 | 210 | 0.1 | — | Vapor phase | 86 | 42 | [33] |
| Wang et al. 2016 | Pt/WOx | 140 | 1 | H ₂ O | Liquid phase | 2.2 | 45.7 | [34] |
| Ma et al. 2016 | Pt/ZrW | 180 | 8 | H ₂ O | Liquid phase | 53.4 | 36 | [35] |
| Edake et al. 2017 | Pt/WO ₃ /Al ₂ O ₃ | 260 | 0.1 | — | Vapor phase | 99 | 14 | [36] |
| Zhang et al. 2017 | AuPt/WOx | 140 | 1 | H ₂ O | Liquid phase | 81.4 | 51.6 | [37] |
| Liu et al. 2017 | Pt-WO ₃ -Al ₂ O ₃ -SiO ₂ | 160 | 6 | H ₂ O | Liquid phase | 48 | 56 | [38] |
| Shi et al. 2018 | Pt-WOx/SAPO-34 | 210 | 6 | H ₂ O | Liquid phase | 44.3 | 19.2 | [39] |
| Wang et al. 2018 | Pt/Au/WO ₃ | 155 | 5 | H ₂ O | Liquid phase | 30.7 | 54.3 | [40] |
| Chen et al. 2018 | Pt-Li ₂ B ₄ O ₇ /WOx/ZrO ₂ | 150 | 4 | H ₂ O | Liquid phase | 90.7 | 36 | [41] |
| Wu et al. 2018 | Cu-WOx-TiO ₂ | 180 | 3.5 | H ₂ O | Liquid phase | 12.7 | 32.3 | [42] |

^aDMI, 1,3-dimethyl-2-imidazolidinone; C, conversion of glycerol; S, selectivity of 1,3-PDO.

Table 2.
Metal-tungsten-based catalysts for glycerol hydrogenolysis into 1,3-propanediol.

catalysts and have been widely employed in several homogeneous and heterogeneous catalytic reactions. Much research has been focussed on heterogeneous catalysts containing active metal and heteropolyacid as a cocatalyst supported on metal oxides for the glycerol hydrogenolysis to selectively produce 1,3-propanediol (**Table 3**). The results showed that the catalysts exhibited better activity in glycerol conversion and 1,3-PDO selectivity which is ascribed to the synergic interaction of Keggin structure of HPA with the active metal as well as stability of the catalyst. HPA-based catalysts

| Author | Catalyst | Temp (°C) | H ₂ (MPa) | Solvent | Process | C (%) | S (%) | Ref. |
|-------------------|---|-----------|----------------------|------------------|--------------|-------|-------------------|------|
| Huang et al. 2009 | Cu-H ₄ SiW ₁₂ O ₄₀ /SiO ₂ | 210 | 0.54 | — | Vapor phase | 83.4 | 32.1 | [43] |
| Zhu et al. 2012 | Pt-H ₄ SiW ₁₂ O ₄₀ /SiO ₂ | 200 | 6 | — | Vapor phase | 81.2 | 31.4 ^a | [3] |
| Zhu et al. 2013 | Pt-H ₄ SiW ₁₂ O ₄₀ /ZrO ₂ | 180 | 5 | — | Vapor phase | 26.7 | 38.9 | [44] |
| Zhu et al. 2013 | Pt-H ₄ SiW ₁₂ O ₄₀ /ZrO ₂ | 180 | 5 | — | Vapor phase | 24.1 | 48.1 | [45] |
| Shen et al. 2017 | PtNps-HSiW/mAl ₂ O ₃ | 200 | 4 | H ₂ O | Liquid phase | 60.5 | 33.3 | [46] |

^aC, conversion of glycerol; S, selectivity of 1,3-PDO; Yield.

Table 3.
Metal-heteropolyacid-based catalysts for glycerol hydrogenolysis into 1,3-PDO.

provided an approach to tune the acidic property in terms of Brønsted acid sites in the catalyst and assisted in enhancing the selectivity of 1,3-PDO. Furthermore, the so far reported heteropolyacid-based platinum catalysts exhibited superior long-term performance because of the robust catalyst structure and good thermal stability.

3.3.2.3 *Metal rhenium-based catalytic materials*

Furthermore, rhenium-oxide-modified supported metal catalysts are proven to offer new opportunities for achieving high selectivity to 1,3-PDO. Rhenium exhibits similar chemical properties as that of tungsten in terms of metal oxide formation and reduction. Rhenium was found to be an effective cocatalyst for noble metal-based catalysts. In the recent past, iridium- and rhodium-based catalysts have been widely explored for selective production of 1, 3-PDO by glycerol hydrogenolysis. Ir-ReOx/SiO₂ catalyst was found to be the most effective one for hydrogenolysis of glycerol into 1,3-PDO. The catalytic activity of various M1-ReOx/SiO₂ (M1 = Pt, Pd, Ru, Ir and Rh) and Ir-M₂Ox/SiO₂ (M2 = Mo, Re, W, Cr, Ag and Mn) catalysts has been investigated and screened to conclude that Ir-ReOx/SiO₂ catalyst achieved the highest 1,3-PDO yield (38%) at 81% glycerol conversion. It was also observed that the method of catalyst preparation and the metal precursors had an effect on the catalytic performance. A list of all different rhenium-based catalysts screened for glycerol hydrogenolysis to 1,3-PDO is included in **Table 4**. The mechanism of glycerol hydrogenolysis to selectively produce 1,3-propanediol over Ir-ReOx-based catalysts is presented in **Figure 13**. Ir-ReOx is a solid acid catalyst with two active centres, Ir being the hydrogen activation centre and Re-OH being the substrate activation centre. Glycerol adsorbs on Re-OH sites to form alkoxide species with hydroxyl groups of glycerol. The activation of hydrogen to form a hydride species takes place in the interface between Ir and Re. The hydride species attacks the neighboring C—O bond by a nucleophilic substitution reaction (S_N²-type), and subsequent hydrolysis of the alkoxide produces 1,3-propanediol. The combined synergic interaction between positively charged Re, acting as a Brønsted acid site, and noble metal Ir with high hydrogenating capacity has strengthened the hydrogenolysis reaction and favored the formation of 1,3-propanediol.

3.3.2.4 *Other supported metal catalysts*

Several other supported metal catalysts have been extensively tested for liquid phase and vapor phase glycerol hydrogenolysis which included various

| Author | Catalyst | Temp (°C) | H ₂ (MPa) | Solvent | Process | C (%) | S (%) | Ref. |
|-------------------------|---------------------------------------|--------------|-------------------------|--------------------|-----------------|----------|----------|------|
| Werpy et al. 2006 | Ni-Re/C | 230 | 9 | H ₂ O | Liquid phase | 47 | 4.6 | [47] |
| | Pd-Re/C | | | | | 26 | 5.2 | |
| Shimao et al. 2009 | Rh-ReOx/SiO ₂ | 160 | 8 | H ₂ O | Liquid phase | 86 | 10.4 | [48] |
| Ma et al. 2009 | Ru-Re/SiO ₂ | 160 | 8 | H ₂ O | Liquid phase | 51.7 | 4.2 | [49] |
| | Ru-Re/ZrO ₂ | | | | | 56.9 | 5.5 | |
| | Ru-Re/H β | | | | | 52.8 | 2.7 | |
| | Ru-Re/HZSM-5 | | | | | 54.2 | 2.9 | |
| | Ru-Re/TiO ₂ | | | | | 36.3 | 8.1 | |
| Nakagava et al. 2010 | Ir-ReOx/SiO ₂ | 120 | 8 | H ₂ O | Liquid phase | 81 | 46 | [50] |
| Shinmi et al. 2010 | Rh-ReOx/SiO ₂ | 120 | 8 | H ₂ O | Liquid phase | 79 | 14 | [51] |
| Ma et al. 2010 | Ru-Re/SiO ₂ | 160 | 8 | H ₂ O | Liquid phase | 23.8 | 13.6 | [52] |
| Daniel et al. 2010 | Pt-Re/C | 170 | 4 | | | 45 | 30 | [16] |
| Yamada et al. 2011 | Ir-ReOx/SiO ₂ | 120 | 8 | H ₂ O | Liquid phase | 57.6 | 45.1 | [12] |
| Nakagava et al. 2012 | Ir-ReOx/ SiO ₂ + HZSM-5 | 120 | 8 | H ₂ O | Liquid phase | 58.8 | 44.7 | [17] |
| Deng et al. 2015 | Ir-Re/KIT-6 ^a | 120 | 8 | H ₂ O | Liquid phase | 46.3 | 54.1 | [53] |
| Falcone et al. 2015 | Pt-Re/SiO ₂ | 120 | 4 | H ₂ O | Liquid phase | 8.3 | 24 | [54] |
| | Pt-Re/SiO ₂ -W | | | | | 9.1 | 29 | |
| | Pt-Re/C | | | | | 6.5 | 34 | |
| Luo et al. 2016 | Egg shell type Ir-ReOx | 130 | 8 | — | Vapor phase | 48.9 | 37.0 | [55] |
| Salagre et al. 2017 | Ni-CuRe/acid mesoporous saponite | 120 | 5 | Glycidol+sulfolane | Liquid phase | 98 | 35 | [56] |

^aKIT-6, mesoporous silica; C, conversion of glycerol; S, selectivity of 1,3-PDO.

Table 4.
Metal rhenium-based catalysts for glycerol hydrogenolysis into 1,3-PDO.

active support materials such as zeolites (HZSM-5, H β , Y-zeolite and mordenite), metal oxides (zirconia, titania, alumina and silica), activated carbon, aluminum phosphate, mordenite and montmorillonite. In these catalysts, the support itself provided Brønsted acid sites necessary for the dehydration of glycerol to 3-HPA. Besides metal oxides, zeolites are proven to be efficient catalysts for glycerol hydrogenolysis with a greater degree of product control as the reaction occurs within the pores of the zeolite. Zeolites are solid acid hydrated aluminosilicate catalysts with relatively large open pores and a regular three-dimensional crystal structure. Most of the researches focused on the use of zeolites in gas phase dehydration of glycerol to acrolein due to their versatility.

In our earlier research, we reported 2 wt% Pt supported on mordenite as a highly active and selective catalyst in the hydrogenolysis of glycerol with 48.6% 1,3-PDO selectivity at 94.9% glycerol conversion [57]. In our recent study, we have

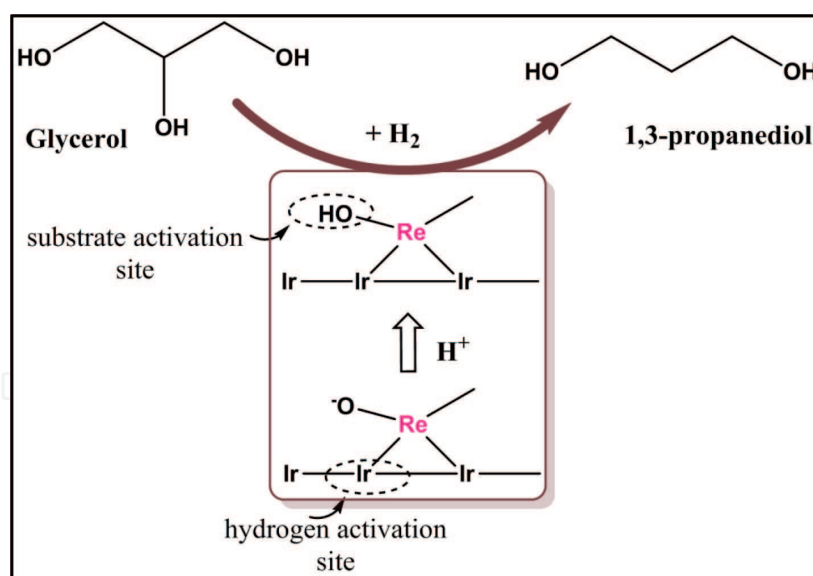


Figure 13.
Selective hydrogenolysis of glycerol to 1,3-PDO over Ir-Re-based catalysts.

| Author | Catalyst | Temp (°C) | H ₂ (MPa) | Solvent/Additive | Process | C (%) | S (%) | Ref. |
|-----------------------|---|-----------|----------------------|---|--------------|-------|-------|------|
| Chaminand et al. 2004 | 5% Rh/C | 180 | 8 | H ₂ O/H ₂ WO ₄ | Liquid phase | 32 | 12 | [60] |
| | 1% Rh/Nafion | | | | | 8 | 19 | |
| Kusunoki et al. 2005 | Rh/C | 140 | 8 | H ₂ O/Amberlyst | Liquid phase | 6.4 | 7.2 | [61] |
| Miyazawa et al. 2006 | Ru/C | 120 | 8 | H ₂ O/Amberlyst | Liquid phase | 6.4 | 5.6 | [62] |
| Furikado et al. 2007 | Rh/SiO ₂ | 120 | 8 | H ₂ O/Amberlyst | Liquid phase | 14 | 9.8 | [63] |
| Alhanash et al. 2008 | Rh/Cs _{2.5} H _{0.5} [PW ₁₂ O ₄₀] | 180 | 0.5 | H ₂ O | Liquid phase | 6.3 | 7.1 | [64] |
| Ma et al. 2009 | Ru/SiO ₂ | 160 | 8 | H ₂ O | Liquid phase | 16.8 | 6.4 | [49] |
| | Ru/ZrO ₂ | | | | | 25.4 | 1.8 | |
| | Ru/HZSM-5 | | | | | 20.5 | 6.0 | |
| | Ru/H β | | | | | 32.0 | 4.0 | |
| | Ru/TiO ₂ | | | | | 6.0 | 6.8 | |
| Zhou et al. 2010 | Cu-Cr/Al ₂ O ₃ | 200 | 1.5 | H ₂ O | Liquid phase | 1 | 2 | [65] |
| | Cu-Cr/HY | | | | | 2 | 2 | |
| | Cu-Cr/H β | | | | | 2 | 1 | |
| Oh et al. 2011 | Pt/sulfated zirconia | 170 | 7.3 | DMI ^a | Liquid phase | 66.5 | 83.6 | [59] |
| Priya et al. 2014 | Pt/ZrO ₂ | 230 | 0.1 | — | Vapor phase | 68 | 6.7 | [66] |
| | Pt/ γ -Al ₂ O ₃ | | | | | 55 | 2.8 | |
| | Pt/C | | | | | 86 | 5.8 | |
| | Pt/Y-zeolite | | | | | 100 | 4.9 | |
| Priya et al. 2014 | Pt/AlPO ₄ | 260 | 0.1 | — | Vapor phase | 100 | 35.4 | [67] |
| Priya et al. 2016 | Pt/mordenite | 225 | 0.1 | — | Vapor phase | 94.9 | 48.6 | [57] |

| Author | Catalyst | Temp (°C) | H ₂ (MPa) | Solvent/Additive | Process | C (%) | S (%) | Ref. |
|-------------------|-----------------|-----------|----------------------|------------------|-------------|-------|-------|------|
| Priya et al. 2016 | Pt-Cu/mordenite | 210 | 0.1 | — | Vapor phase | 90 | 58.5 | [58] |
| Priya et al. 2018 | Pt/S-MMT | 200 | 0.1 | — | Vapor phase | 94 | 62 | [68] |

^aDMI, 1,3-dimethyl-2-imidazolidinone; C, conversion of glycerol; S, selectivity of 1,3-PDO.

Table 5.
Other supported metal catalysts for glycerol hydrogenolysis into 1,3-propanediol.

successfully demonstrated that sulfuric acid-activated montmorillonite-supported platinum catalysts achieved highest selectivity (62%) to 1,3-PDO at 94% glycerol conversion under mild reaction conditions [58]. The modification of montmorillonite by acid treatment has significantly increased the acid catalytic performance of montmorillonite. Its combination with noble metal, platinum, which has been demonstrated to hold high hydrogenation activity and selectivity in C=O bond hydrogenolysis, was therefore a promising formulation to obtain high yields of 1,3-PDO possibly by two different mechanistic routes. Prior to this study, Oh et al. reported sulphated zirconia-supported platinum catalysts as super acid catalysts for selective formation of 1,3-PDO by glycerol hydrogenolysis [59] again based on the fact that Brønsted acid sites facilitated the selective production of 1,3-PDO. Furthermore, the mechanism of glycerol hydrogenolysis and the selective production of propanediols depending on the nature of acidic sites (Lewis or Brønsted) present in the catalyst have been clearly illustrated in another research based on platinum-copper bifunctional catalysts supported on mordenite [58]. Examples of other supported metal catalysts are summarized in **Table 5**.

4. Conclusions and future perspectives

Glycerol, one of the top 12 building block chemicals, can serve as a feedstock for the production of valuable fuel, fuel additives and chemical products. One of the most attractive route of upgrading glycerol is the formation of ‘1,3-propanediol’ (1,3-PDO), a valuable industrial chemical with wide applications from carpet and textile manufacturing to cosmetics, personal and home care industry. Glycerol can be selectively converted to 1,3-PDO over a metal catalyst and H₂ via hydrogenolysis reaction. In spite of many past studies on selective glycerol hydrogenolysis, knowledge in order to achieve sustainable and economically competitive processes is still lacking and needs to be addressed. This need necessitates focusing research on developing highly efficient, economic viable and environmental-friendly catalytic processes. It is concluded that the supported metal catalysts with appropriate metal/acid balance were highly desirable for selective glycerol hydrogenolysis. Surface acidic sites as well as their strength in the support were found to be the important factors in controlling the product selectivity in glycerol hydrogenolysis. In addition to the acidic strength, the nature of acidic sites (Brønsted and Lewis) also played a key role in the product formation. Irrespective of the presence of weak, moderate or strong acidic sites in the support, Brønsted acidic sites selectively led to the formation of 1,3-propanediol, whereas Lewis acid sites favored the formation of 1,2-propanediol. In this chapter, selective glycerol hydrogenolysis to 1,3-PDO through different methods focussing on the catalytic conversion of glycerol has been presented. The reaction mechanisms elucidating the selective formation of propanediols and the role of acidity in product formation have been clearly

illustrated. The importance of Brønsted acidity towards 1,3-PDO formation and the different classes of catalytic materials reported have been presented. Overall, the bifunctional metal-acid catalysts employed in the selective hydrogenolysis of glycerol to 1,3-PDO usually contained noble metals (Pt, Ir, Rh) in combination with Brønsted acid components (tungsten/heteropolyacid/rhenium).

The catalytic hydrogenolysis of glycerol is a promising route to transform glycerol into useful compounds; however, in order to achieve acceptable selectivities, additional important work should be carried out to gain further insights and it still remains a challenge. A systematic understanding of the principles behind converting glycerol into 1,3-propanediol paves the way for future work on developing novel catalytic systems and reaction processes. The selectivity to 1,3-PDO can be improved with the appropriate choice of the acidic support, and its interaction with the metal and further development of novel ways would be an important and challenging area of research. Vapor phase hydrogenolysis reactions carried out under solventless conditions and atmospheric pressure provide an economic viable and eco-friendly process. However, except for a few reactions, most of the research work in glycerol hydrogenolysis was performed in liquid phase using hazardous reaction conditions which makes the process incompatible. Therefore, much attention has to be focussed on the development of an economically viable commercial production of 1,3-propanediol from glycerol, with respect to both catalytic materials and the reaction processes.

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Conflict of interest

The author declares no conflict of interest.


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