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Review

Technological Insights on Glycerol Valorization into Propanediol through Thermocatalytic and Synthetic Biology Approaches

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Abstract: The adverse effects of climate change, predominantly propelled by greenhouse gas emissions from fossil fuels, underscore the urgency of seeking sustainable alternatives to fossil fuel use. Amid growing concerns about climate change caused by fossil fuels and petrochemicals, this review focuses on sustainable solutions through the conversion of glycerol into value-added biochemicals. Glycerol, as the main byproduct of biodiesel production, is a particularly attractive chemical due to its potential to be upgraded into value-added building blocks and biochemicals. This review provides a detailed analysis of different thermochemical (catalytic) and synthetic biology (fermentative) pathways for the conversion of glycerol into 1,2-propanediol and 1,3-propanediol, which have proven industrial and commercial applications globally. The synthesis of propanediol from glycerol hydrogenolysis and other catalytic processes using different active metals and acidic oxides is reviewed. The reaction mechanism involved in hydrogenolysis reactions concerning the surface reaction mechanism is systematically discussed. The metabolic activities of promising microorganisms in fermenting glycerol, as the carbon source used to produce propanediol, are illustrated and elaborated. Combining these insights, this review is a comprehensive resource that can foster a better understanding of glycerol transformation into propanediol and its implications for sustainable chemistry and industrial practices. This exploration of alternative methods emphasizes the potential of sustainable approaches to reshape production practices and contribute to climate change mitigation.

Keywords: 1,2-propanediol; 1,3-propanediol; catalysts; enzymes; fermentation; glucose; glycerol; hydrogenolysis; microorganisms; pyruvate

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1. Introduction

The negative effects of climate change on the world are becoming increasingly distinct and experiential. One of the primary contributors to climate change is the continued emission of greenhouse gases into the atmosphere through anthropogenic activities such as industrialization, deforestation, prescribed wildfires, waste mismanagement, resource mining, and fracking to exploit fossil fuels [1,2]. CO_2 accounted for 74% of the total global greenhouse gas emissions in 2020. They were followed by CH_4 and N_2O, attributing 17% and 6%, respectively [3]. The atmospheric concentration of CO_2 has dramatically increased from 336 ppm in 1979 to 420 ppm in 2023. The lifetime of greenhouse gases in the atmosphere is an important issue to consider. For example, recent studies have reported that CH_4, N_2O and CO_2 could remain in the atmosphere for an average of 11.8, 121 and 300–1000 years, respectively [3–5].

The emission of CO_2 is mostly related to the extraction, upgrading and usage of fossil fuels and petrochemicals. Coal, natural gas and petroleum account for 93% of the total CO_2 emissions in 2020 [3]. Greenhouse gas emissions and persistence in the atmosphere lead to the greenhouse effect, which causes depletion of the ozone layer, global warming, extreme heat waves, precipitation anomalies, the melting of glaciers, changes in ocean levels, more tropical storms, wildfires, ecological changes, changes in seasonal migration pattern of birds, and health effects in humans, among other effects [6,7]. Reducing the emissions of CO_2 is essential to preventing these harmful events from occurring more frequently.

Finding viable alternatives in order to reduce the usage of fossil fuels and petrochemicals is one of the main ways of reducing emissions. Many industries are beginning to use technologies and resources that are more sustainable, releasing less greenhouse gases compared to fossil fuels and sequestering CO_2. Biofuels and biochemicals derived from bioresources and renewable organic wastes have shown the potential to replace fossil fuels and petrochemicals while addressing waste management, energy security and climate change mitigation strategies [8,9]. The global biochemical market was reported to be worth $66 billion in 2022, with a forecast to grow annually by 11% and reach $180 billion by 2032 (Figure 1) [10]. This market growth is driven by the increasing demand for both chemicals and fuels, especially those created using sustainable and environmentally friendly technologies [11]. Despite this high market potential, the usage of biochemicals has been adopted slowly by industry leaders [12]. The chemical industry produced a total of 2.3 billion tons of consumer products in 2017, but only 2% of this was made from bio-based products [13]. Biochemicals not only offer a sustainable alternative that can be used to replace petrochemicals but also act as precursors to the synthesis of biodegradable plastics in order to prevent the further deterioration of the environment and ecosystems [14,15].

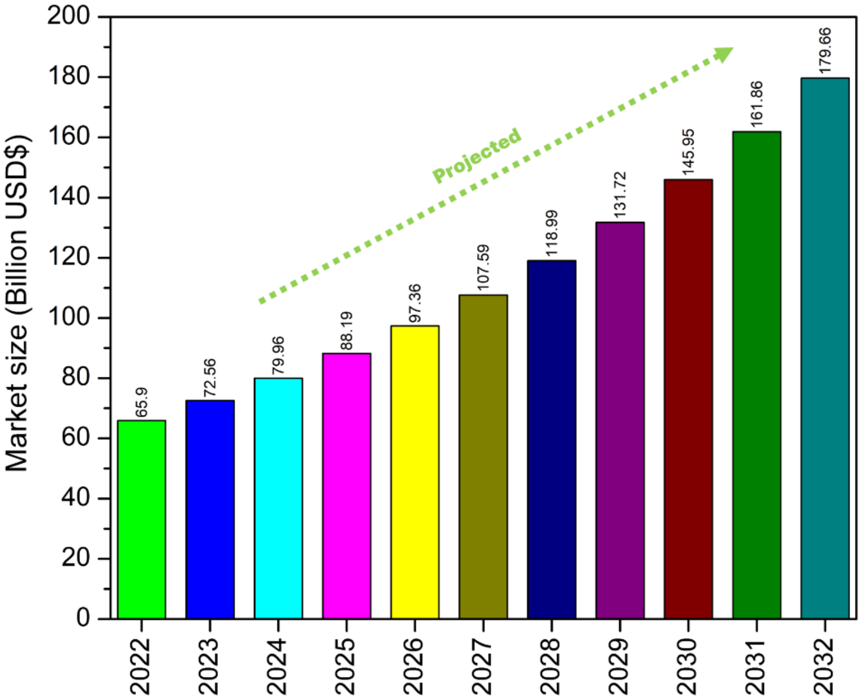

Figure 1. Predicted market value of biochemicals from 2021 to 2030. (Data source: Precedence Research [10]).

There have been many different routes developed in order to produce biochemicals. Thermochemical conversion technologies such as pyrolysis, liquefaction, torrefaction, gasification, transesterification and catalytic reforming are sustainable approaches to transforming biomass into valuable biofuels and biochemicals [16–19]. Biological conversion methods such as fermentation are other ecofriendly routes for biochemical synthesis. Fermentation utilizes microorganisms to facilitate the metabolic reaction, whereas thermochemical conversion relies on degrading the feedstocks under the action of heat, pressure, and/or catalysts for transformation. Value-added applications must be found for these byproducts to allow for more sustainable processes and further increase the economic viability of the biochemical production industry. Table 1 highlights the main advantages and disadvantages of the thermocatalytic and biocatalytic conversion of waste biomass into value-added products. Table 2 summarizes a few studies on the thermocatalytic conversion of waste feedstocks into biofuels and biochemicals for several value-added applications.

Table 1. Comparison of thermocatalytic and biocatalytic valorization of waste biomass.

Methods	**Advantages**	**Disadvantages**
Thermocatalytic conversion	• Time-efficient process. • Adaptable for industrial scale-up. • Flexibility for optimizing a wide range of process conditions (e.g., temperature, pressure, feedstock concentration, reaction time and catalyst loading). • Offers diverse pathways and reactions using homogenous and heterogenous catalysts. • Reuse of catalyst is possible.	• Designing a high-performance reactor for the accelerated commercialization of biomass into bioproducts is required. • Energy-intensive process. • May release wastes that require effective containment and disposal. • Reuse of catalyst can be difficult and expensive. • Catalysts can be prone to deactivation and poisoning compromising process efficiency.
Biocatalytic conversion	• Environmentally friendly. • Requires mild reaction conditions and fewer resources. • Relatively less expensive. • Requires less intensive infrastructure. • Easy separation of the product from the reaction mixture. • Metabolic pathways of microorganisms can be altered through genetic engineering. • No toxic byproducts are generated.	• Slower process. • Less preferred for industrial-scale processing, except in the case of particular products. • Prone to contamination, leading to undesired reactions and products. • Impurities in raw materials can prevent microbial growth and the fermentation process. • Raw biomass often requires pretreatment, adding to the cost of the process. • Enzymes and genetically engineered microorganisms can be expensive. • Recycling enzymes is possible but expensive.

References: Robles-Medina et al. [20], Ayodele et al. [21], Kaur et al. [22], Pattnaik et al. [23], Jha et al. [24], Jha et al. [25], Okoye et al. [26], and Nanda et al. [27].

Table 2. Thermocatalytic conversion of different waste biomass into value-added products.

Feedstock	**Reaction Conditions**	**Main Observations**	**Reference**
Glycerol	• Mechanism: Steam reforming • Temperature: 600 °C • Reaction time: 20 h • Catalyst: Rh/$MgAl_2O$	• Rh nanocatalyst prepared over promoted Al_2O_3 with MgO was found to have a 98% conversion of glycerol, which was the best performance among the precious metals tested (e.g., Rh, Ru, Pt and Ir). • Glycerol conversion from the Rh catalyst is the most stable compared to conversion from other (e.g., Ru, Pt and Ir) catalysts when under a long-term stability test of 20 h.	Senseni et al. [28]
Kraft lignin	• Mechanism: Pyrolysis–gas chromatography/mass spectrophotometer (Py-GC/MS) • Temperature: 500 °C • Reaction time: 40 min • Catalyst: Hierarchical HZSM-5 and Hβ zeolites	• Hβ zeolite was more effective at removing oxygenates from condensable volatiles than HZSM-5. • Optimizing the hierarchal HZSM-5 zeolite allowed for a decrease in the oxygenate selectivity from 27.2% to 3.3%.	Bi et al. [29]

Table 2. *Cont.*

Feedstock	Reaction Conditions	Main Observations	Reference
Metal soap	• Mechanism: Pyrolysis • Temperature: 500–550 °C • Heating rate: 200 °C/min • N_2 flux: 120 mL/min • Reaction time: 1–2 h	• Pyrolysis of the metal soaps in this study yielded 35–54% (wt/wt) bio-oil mainly comprising hydrocarbons from C_6 to C_{17}. • The types of hydrocarbons formed were found to depend on which metal soap was used in pyrolysis, as magnesium soaps gave a larger fraction of diesel while sodium soaps gave a larger fraction of gasoline.	Melchor and Fortes [30]
Volatile fatty acids	• Mechanism: Microbial digestion • Temperature: 21 °C • pH: 8 • Reaction time: 53 h	• Some 43.5% (wt/wt) polyhydroxyalkanoates were produced using an anaerobically digested municipal waste stream with volatile fatty acids rich in acetic acid. • Reduced cost by performing the experiments without pH or temperature controls (i.e., only monitoring the operating conditions).	Perez-Zabaleta et al. [31]
Waste cooking oil	• Mechanism: Transesterification • Temperature: 30–60 °C • Catalyst: KOH • Catalyst loading: 0.5–2% • Methanol/oil ratio: 1:12–1:1	• A 94% yield of fatty acid methyl esters was achieved using KOH at optimal reaction conditions (1:3 methanol/oil ratio, 1% catalyst loading and 60 °C). • Acid pretreatment of waste cooking oil using H_2SO_4 was found to have an 88% efficiency for the esterification of free fatty acids.	Sadaf et al. [32]
Waste effluent	• Mechanism: Pyrolysis • Temperature: 400–600 °C • Heating rate: 5–30 °C/min • Catalyst: Fe_2O_3 • Catalyst loading: 0–10%	• The addition of 5% Fe_2O_3 increased the gas and bio-oil yields from 8.7 wt% to 11.6 wt% and 32.5 wt% to 38.7 wt, respectively, but reduced the biochar yield from 58.8 wt% to 49.6 wt%. • The catalyst was found to promote the production of CO and H_2 while inhibiting the formation of CH_4.	Huang et al. [33]

Waste lignocellulosic biomass and starch-based feedstocks have been the main interest internationally as raw materials to produce biofuels and biochemicals [34]. Municipal solid wastes, industrial effluents and sewage sludge are other potential feedstocks that have not received wide attention for conversion into biochemicals, mainly due to the complexity and heterogeneity in their composition and physicochemical properties. Crude glycerol is one such feedstock that remains underutilized despite the continued research and development of biochemicals and bio-based commodities.

Crude glycerol is obtained in significant amounts as part of the waste liquid effluents from biodiesel refineries along with methanol and alkali catalysts [35]. The fraction of crude glycerol as a waste product from biodiesel industries is more than 10%. For example, for every gallon of biodiesel, nearly one pound of glycerol is produced [36]. Glycerol or glycerin can be produced using petroleum-based sources such as propene and propylene. Furthermore, yeast fermentation is considered a superseded method for glycerol production, with low conversion due to difficulties in recovery. Furthermore, high-pressure splitting at 220–260 °C under 2–6 MPa pressure leads to a 15% glycerol solution in water. The saponification process of triglycerides is another method for glycerol and fatty acid production. For large-scale production of glycerol, the direct catalytic hydrolysis of triglycerides at 250 °C under 6 MPa pressure is a promising technique. Glycerol can be obtained using other processes such as the hydrogenation of carbohydrates and starch [37].

The direct valorization of crude glycerol is intricate and requires cost-intensive separation of wastewater, inorganic elements, methanol and other impurities, which may impact its potential thermocatalytic and biocatalytic conversion. The main focus of this review article is to explore promising technologies involving thermochemical (catalysis) and synthetic biology (fermentation) for the conversion of glycerol to produce propanediol, a lucrative biochemical and precursor of several value-added industries. The chemistry of glycerol and an overview of its applications are thoroughly discussed. A detailed discussion on the properties, uses and production of 1,2-propanediol and 1,3-propanediol through thermochemical and biological processes, which remains a significant knowledge gap in the existing literature, is provided in this article.

2. Chemistry and Value-Addition of Glycerol

Glycerol or glycerin is a valuable byproduct in biodiesel production. Biodiesel can generate about 10 wt% glycerol as the main byproduct using hydrolysis and transesterification reactions. Crude waste effluents produced from biodiesel refineries contain glycerol, water, methanol and free fatty acids as well as organic and inorganic salts [38]. Glycerol and its derivatives have found diverse value-added applications in many industrial sectors such as pharmaceuticals, personal care, food processing, resins, explosives, cellophane, detergents, fabrics and others, as shown in Figure 2 [39].

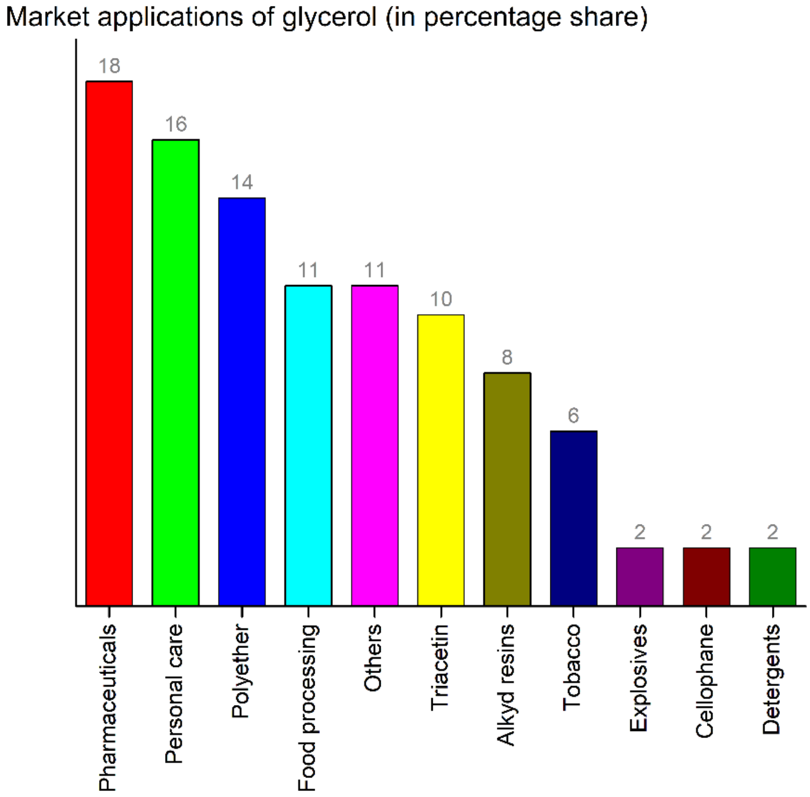

Figure 2. Industrial applications of glycerol. (Data source: Tan et al. [39]).

Pure glycerol is a sugary, colorless, odorless, viscous, non-toxic, biodegradable and hygroscopic liquid at room temperature. It is completely soluble in water due to the presence of three hydroxyl groups. Although it is chemically stable, glycerol is a reactive molecule owing to the formation of primary and secondary aromatic compounds. The glycerol backbone is central to all lipids known as triglycerides. The thermophysical properties of glycerol and polyethylene glycol have been investigated based on the deep eutectic solvent [40]. It was found that the use of deep eutectic solvent increased the thermal conductivity of glycerol with increasing temperature. In another study conducted by Hu et al. [41], the density of crude glycerol samples changed due to the presence of fatty acids methyl esters and water. Furthermore, the viscosity of five crude glycerol samples varied between 15 and 1213 mPa.s owing to their different compositions.

2.1. Transesterification and Saponification

The mechanism of biodiesel production through the transesterification of vegetable oil with methanol is shown in Figure 3. Glycerol from the transesterification process is obtained as a byproduct in batch or continuous reactors, resulting in environmental concerns around its effective disposal. Vávra et al. [42] demonstrated the production of glycerol via the transesterification of various edible and non-edible oil sources, followed by its purification. It was reported that, during transesterification, glycerol is obtained due to the dissociation of soaps. The characteristics of the glycerol phase after the transesterification of vegetable oil depend on the type of alcohol and reaction rates in the gas phase. Several researchers have studied the transesterification reaction of vegetable oils, which produces glycerol as a byproduct. Figure 4 illustrates the production of 1,2-propanediol and 1,3-propanediol via the hydrogenolysis of glycerol [43].

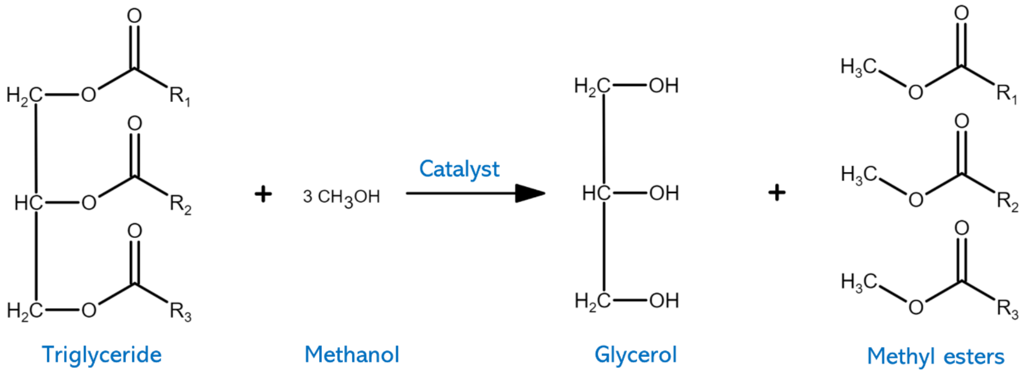

Figure 3. Schematic representation of transesterification reaction.

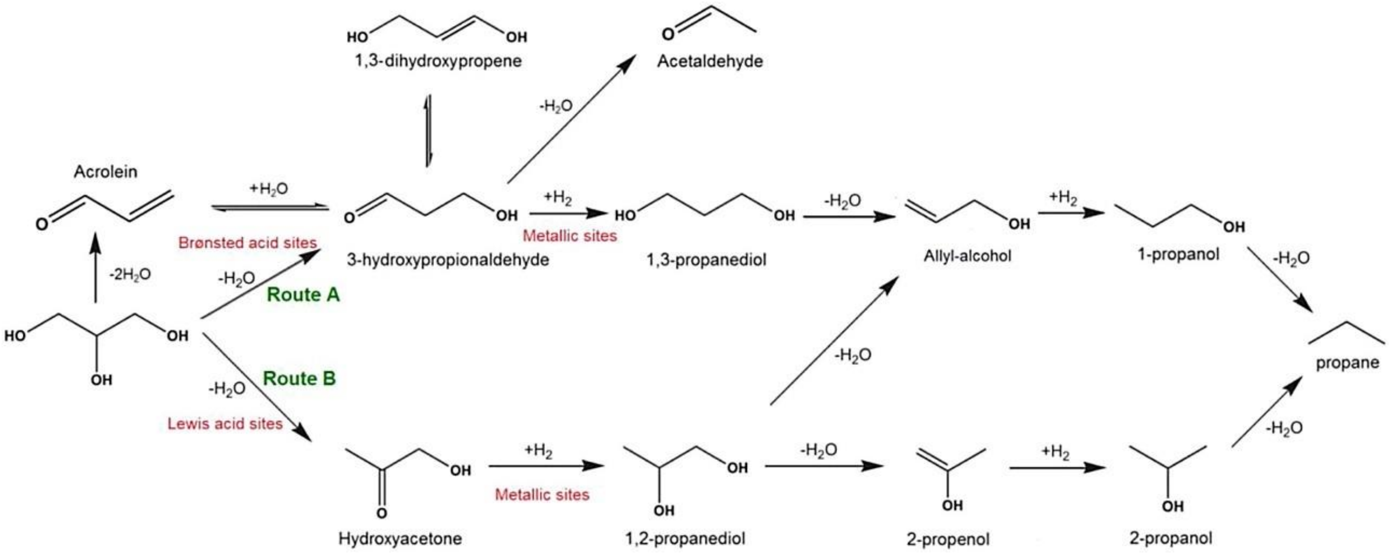

Figure 4. Mechanism for catalytic hydrogenolysis of glycerol to 1,2-propanediol and 1,3-propanediol. (Reproduced with permission from da Silva Ruy et al. [43]).

Teng et al. [44] investigated the transesterification reaction of glycerol into glycerol carbonate under microwave irradiation, using calcium oxide (CaO) as a catalyst. According to the effects of reaction time, it was concluded that the transesterification rate can be increased via microwave heating. Additionally, the influence of the catalytic activity of CaO on the yield of glycerol carbonate using microwave-assisted transesterification supported the idea that further increasing catalyst loading beyond 1 wt% can lead to a gradual decrease in the product yield.

Rodrigues et al. [45] reported on the use of crude glycerol as a carbon source during the transesterification of used cooking oils for hydrogen production. It was found that, in most of the bioconversion of glycerol pathways, biohydrogen is also produced during oxidative metabolism. It can be concluded that better results of biohydrogen and biomethane production are obtained at low concentrations of crude glycerol in batch fermentation processes.

As shown in Figure 5, glycerol and fatty acids are produced because of acidic saponification [46]. Furthermore, a chemical reaction between a strong base and some fatty acid results in metal soap production. Dhabhai et al. [47] reported a sequential procedure for crude glycerol purification including saponification, membrane filtration, and solvent extraction, that can be used to increase glycerol content. It was concluded that chemical purification at a low pH can increase glycerol content to further produce glycerol carbonate.

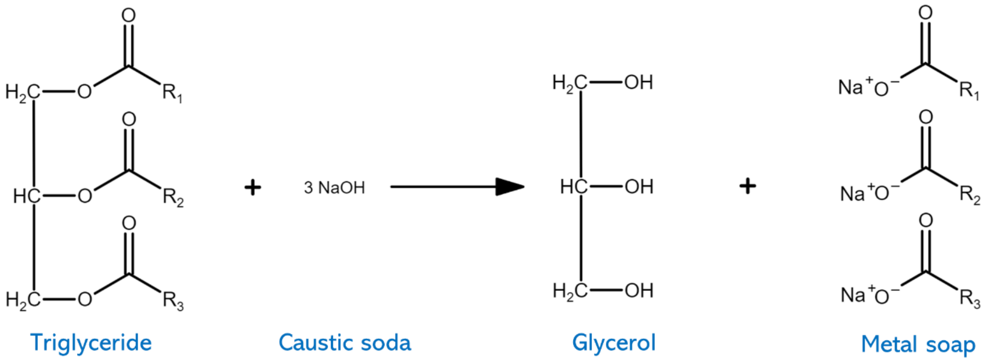

Figure 5. Schematic representation of saponification of triglycerides.

Another study by Chanakaewsomboon et al. [48] investigated saponification mechanisms in biodiesel production. It was found that the soap content in crude biodiesel influences washing losses and the amount of alkaline catalyst. The saponification of triglyceride was accelerated by an alkaline catalyst due to the diffusing rate of the alkaline methanol solution. It was concluded that the produced glycerol from transesterification reacts with an alkaline catalyst to form soap.

2.2. *Hydrolysis*

Glycerol and free fatty acids are produced via the hydrolysis of triacylglycerols. Melani et al. [49] reviewed lipase applications for biodiesel production in the presence of a high water content. It has been found that specific lipases can be used to produce biodiesel via enzymatic catalysis in the presence of glycerol. The authors concluded that improvements to fermentation conditions are key to increasing lipase production.

Díaz et al. [50] utilized Ni or Pd on Al_2O_3 or SiO_2 for the catalytic hydrolysis of soybean oil and tallow in the preparation of fatty acids. The results showed that glycerol reforming can be converted into byproducts such as hydrogen and syngas. The authors observed the reaction products after conducting hydrolysis of soybean oil and assessing the effect of reaction temperature on the overall yield. It was concluded that glycerol is not effectively converted into hydrogen and volatile fatty acids, leading to the formation of hydrocarbons.

Aguieiras et al. [51] studied biodiesel production in biphasic aqueous oil systems via hydroesterification. In the hydrolysis step, the Macauba oil was used as an alternative feedstock for biodiesel. This was followed by esterification, producing free fatty acids, glycerol and esters. Enzymatic hydrolysis of triglycerides using lipases from seeds and microorganisms resulted in an ester yield of 89.7 wt%, with an acidity of 6.5%.

Dmitriev et al. [52] presented promising results, using the synthesis of solketal and its hydrolysis to obtain high-purity glycerol. According to their observations, fatty acids were removed from crude glycerol by adding mineral acid. It was found that weak fatty acids cannot catalyze the reaction and the concentrated glycerol formed after cleavable hydrotrope hydrolysis. Soares et al. [53] carried out the hydrolysis of low-value feedstocks under pressurized hot water conditions followed by lipase-catalyzed esterification. The glycerol was absorbed into the catalyst in a packed-bed reactor, thus avoiding the costs of recovery and immobilization of the lipase.

3. Chemistry and Applications of Propanediol

Glycerol has many applications, but one route of its use is in the synthesis of other chemicals. One of the possible chemicals that can be produced is 1,2-propanediol, commonly referred to as ethylene glycol. 1,2-propanediol has applications as a solvent, antifreeze agent and additive for food and cosmetic products [54]. The market for 1,2-propanediol was globally valued at $4.35 billion in 2022 and is expected to grow at a compound annual growth rate of 6.1% until 2030 due to increasing demand [55]. Like its counterpart, 1,3-propanediol can be synthesized from glycerol and has applications as a monomer to produce chemicals such as polyurethanes, polyethers and polytrimethylene terephthalate [56]. Both 1,2-propanediol and 1,3-propanediol are used for many applications such as pharmaceuticals, artificial flavors, paints, urethane foams, cosmetics, fragrances and synthetic resins [57].

The market for 1,3-propanediol was reported as being $433 million in 2021 and is projected to grow with a compound annual growth rate of 11.5% until 2030 [58]. Figure 6 highlights significant industrial applications for 1,2-propanediol and 1,3-propanediol, such as in polymer production, as an additive in the food and medicinal drug industry, and as a solvent. The production of these two chemicals provides another value-added use for glycerol.

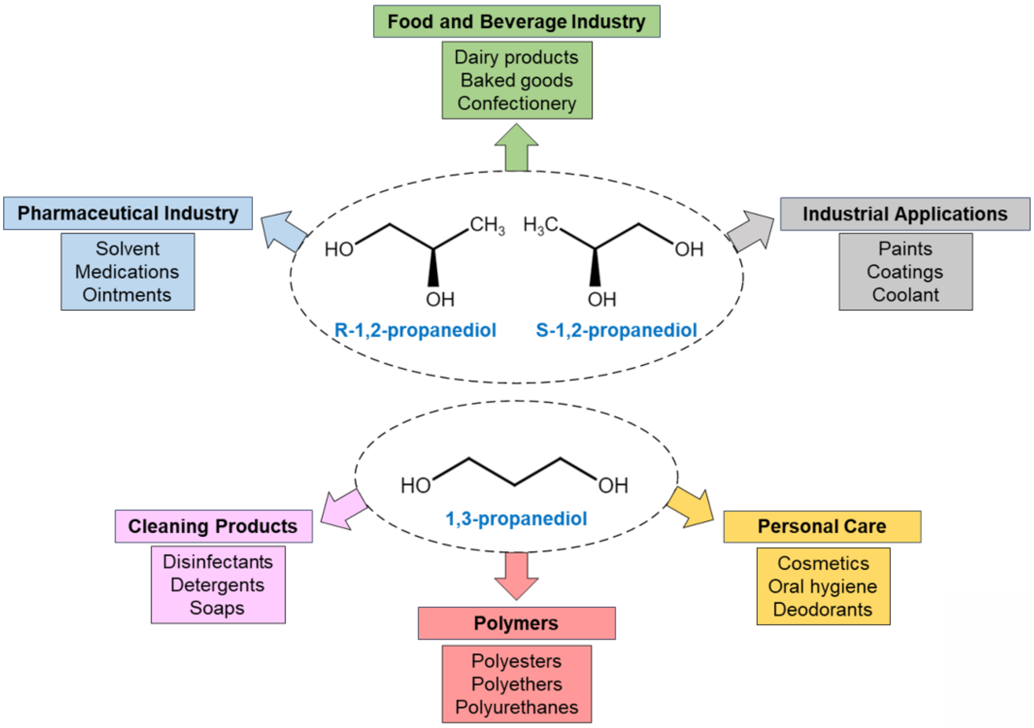

Figure 6. Chemical structure and applications of 1,2-propanediol and 1,3-propanediol.

Alternative sustainable routes for the production of 1,2-propanediol and 1,3-propanediol have been widely researched, especially through thermocatalytic and biocatalytic techniques, in order to aid the conversion of glycerol. A common catalytic method is hydrogenolysis [59]. Different catalytic systems are also utilized, examples of which are Pt/W/β, the Pt/deAl-β core and $Mg(OH)_2$ shell catalyst and the Pt-In alloy catalyst [60–62].

Several microorganisms have also been investigated in order to ferment glycerol and sugar substrates into 1,2-propanediol and 1,3-propanediol, examples of which include *Citrobacter freundii*, *Clostridium beijerinckii*, *Clostridium butyricum*, *Clostridium diolis*, *Clostridium pasteurianum*, *Escherichia coli*, *Klebsiella pneumoniae*, *Lactobacillus panis* and *Lactobacillus reuteri* [63–71]. *Lactobacillus* spp. involved in the fermentative production of propanediol are generally regarded as safe (GRAS) to handle compared to *Klebsiella* spp. and *Escherichia* spp., which are considered pathogenic unless specific containment measures are ensured.

3.1. 1,2-propanediol

While it is important to realize the value and applications of 1,2-propanediol and 1,3-propanediol, it is also key to understand the chemistry behind these biochemicals. 1,2-propanediol or propylene glycol has the chemical formula $C_3H_8O_2$ and is considered an organic chemical that physically appears as a clear, colorless and viscous liquid at room temperature. It has two possible spatial configurations, S-1,2-propanediol and R-1,2-propanediol, depending on the orientation of the second hydroxyl group. Figure 6 provides a visual of the chemical structure of each of these enantiomers. The freezing and boiling points for 1,2-propanediol are -60 °C and 188.6 °C, respectively, which demonstrates its applications as a component in both coolants and antifreeze applications [72,73].

1,2-propanediol is conventionally synthesized through the hydrolysis of propylene oxide, a chemical that is generated by the processing of crude oil [74,75]. There are multiple approaches to producing propylene oxide, but one regularly used method is the chlorohydrin route, which produces a large amount of calcium chloride waste [74,76]. New production facilities do not utilize this method as modern alternatives can greatly reduce the amount of waste produced when synthesizing propylene oxide. However, legacy facilities that use this method still account for 40% of the propylene oxide produced globally. There are also additional environmental drawbacks to using this chemical as part of the 1,2-propanediol hydrolysis process. To synthesize 1,2-propanediol, propylene oxide is mixed with water in ratios of 1:15 propylene oxide/water ratio or greater and is reacted at a pressure of 1.8 MPa and a temperature of 190 °C [74]. The cost associated with high energy requirements and significant water usage for this process makes it unsustainable, which is why utilizing new alternative green methods to produce 1,2-propanediol is key in reducing the environmental impacts.

3.2. 1,3-propanediol

With the same chemical formula as $C_3H_8O_2$, 1,3-propanediol has similar characteristics to its constitutional isomer 1,2-propanediol. Figure 6 provides a visual of the chemical structure of this compound. 1,3-propanediol is an organic compound and appears as a clear, colorless and viscous liquid at room temperature. The melting and boiling points of 1,3-propanediol are -26 °C and 214 °C, respectively. Analogous to 1,2-propanediol, these properties enable 1,3-propanediol to be utilized in coolants and antifreeze. 1,3-propanediol is also added to thermoplastic polyurethanes as it contributes to improving the stability of the polymer [77].

In order to produce 1,3-propanediol, multiple approaches can be taken. The two original methods of producing this chemical require the usage of the petrochemicals acrolein or ethylene oxide in the process. One route, developed by Shell, treats ethylene oxide through hydroformylation to produce 3-hydroxypropanal, which is further processed using hydrogenation into 1,3-propanediol [78]. The other approach is through the DuPont route, which relies on the hydration of acrolein into 3-hydroxypropionaldehyde and its further hydrogenation into 1,3-propanediol [79]. Not only do both these routes require petrochemicals, but they also have high pressure requirements (i.e., 9 MPa for the DuPont method and 15 MPa for the Shell method), increasing the energy demand and cost for specialized reactors resistant to high pressures during both of these processes [80]. The Shell approach obtains an 80% yield of 1,3-propanediol, while the DuPont approach results in a maximum yield of 65%. This has led DuPont, in collaboration with Genencor and Tate & Lyle, to pursue a biological process, using genetically modified microorganisms in order to produce 1,3-propanediol from glucose that can compete with Shell [81].

4. Thermocatalytic Conversion of Glycerol to Propanediol

Significant research efforts have been focused on the catalytic transformation of glycerol for the synthesis of value-added chemicals owing to the rising prices of petroleum resources. Glycerol is an important byproduct due to its application to produce acrolein, glyceric acid, glycerol carbonate, and propanediol. As shown in Figure 7, Cu-based catalysts require the selective cleavage of the secondary C–O bond against the cleavage of the C–C bond in the hydrogenolysis of glycerol in order to produce 1,2-propanediol [82]. Acid-catalyzed glycerol dehydration and metal-catalyzed intermediate hydrogenation are the two steps in glycerol hydrogenolysis [83]. Glycerol hydrogenolysis has been primarily attempted in the liquid phase over different metal catalysts synthesized via the impregnation, co-precipitation, solid combustion and decomposition of metal–organic frameworks. Some recent achievements in the selective hydrogenolysis of glycerol over bifunctional-supported catalysts for propanediol synthesis are summarized in Table 3.

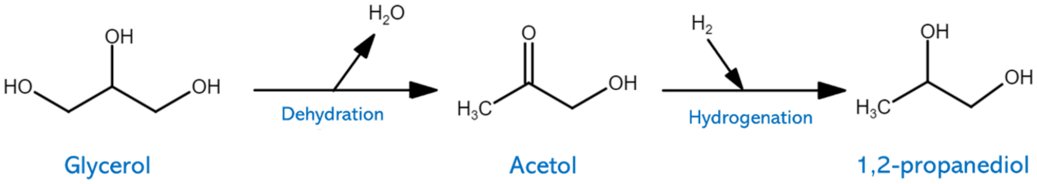

Figure 7. Schematic representation of hydrogenolysis of glycerol into 1,2-propanediol.

Table 3. Performance of various monometallic and bimetallic catalysts for hydrogenolysis of glycerol.

Catalyst	Preparation Method	Process Conditions	Main Observations	Reference
10Nb/Pd-Zr-Al	Impregnation	• Temperature: 200 °C • Pressure: 3.5 MPa • Reaction time: 8 h • Glycerol concentration: 10 wt% • Catalyst weight (g or wt%): 0.2	• Glycerol conversion: 66.4% • 1,2-propanediol selectivity: 81.3% • 1,2-propanediol yield: 53.9%	Cai et al. [84]
15Co0.5Cu/TiO_2	Co-impregnation	• Temperature: 230 °C • Pressure: 4 MPa • Reaction time: 8 h • Glycerol concentration: 50 wt% • Catalyst weight (g or wt%): 0.5	• Glycerol conversion: 60.2% • 1,2-propanediol selectivity: 86% • 1,2-propanediol yield: 51.7%	Mondach et al. [85]
Copper carbide composite	Co-precipitation	• Temperature: 240 °C • Pressure: 0.5 MPa • Reaction time: 8 h • Glycerol concentration: 10 wt% • Catalyst weight (g or wt%): 0.2	• Glycerol conversion: 79.3% • 1,2-propanediol selectivity: 60.5% • 1,2-propanediol yield: 47.9%	Liu et al. [83]
Cu/Al_2O_3	Wet impregnation	• Temperature: 200 °C • Pressure: 4 MPa • Reaction time: 10 h • Glycerol concentration: 20 wt% • Catalyst weight (g or wt%): 1	• Glycerol conversion: 28% • 1,2-propanediol selectivity: 66.8% • 1,2-propanediol yield: 18.7%	Azri et al. [86]
Cu/Mg-supported SiO_2	Chemisorption-hydrolysis	• Temperature: 210 °C • Pressure: 4.5 MPa • Reaction time: 24 h • Glycerol concentration: 20 wt% • Catalyst weight (g or wt%): 3.2	• Glycerol conversion: 73.1% • 1,2-propanediol selectivity: 88.2% • 1,2-propanediol yield: 63.4%	Kumar et al. [87]

Table 3. *Cont.*

Catalyst	Preparation Method	Process Conditions	Main Observations	Reference
Cu-Al-Zn	Co-precipitation	• Temperature: 200 °C • Pressure: 3 MPa • Reaction time: 16 h • Glycerol concentration: 20 wt% • Catalyst weight (g or wt%): 1	• Glycerol conversion: 43% • 1,2-propanediol selectivity: 69% • 1,2-propanediol yield: 29.6%	Mishra et al. [88]
CuNi30MgAl	Wet impregnation	• Temperature: 250 °C • Pressure: 4 MPa • Reaction time: 30 h • Glycerol concentration: 10 wt% • Catalyst weight (g or wt%): 1.25	• Glycerol conversion: 65% • 1,2-propanediol selectivity: 38.4% • 1,2-propanediol yield: 25%	Mendonça et al. [89]
Ni/Dolomite	Impregnation	• Temperature: 200 °C • Pressure: 4 MPa • Reaction time: 10 h • Glycerol concentration: 20 wt% • Catalyst weight (g or wt%): 1	• Glycerol conversion: 69.5% • 1,2-propanediol selectivity: 52.7% • 1,2-propanediol yield: 36.6%	Azri et al. [90]
Pt/WO_3/zirconium phosphate	Sequential wet impregnation	• Temperature: 200 °C • Pressure: 4 MPa • Reaction time: 12 h • Glycerol concentration: 3.2 wt% • Catalyst weight (g or wt%): 0.1	• Glycerol conversion: 68.4% • 1,2-propanediol selectivity: 38.5% • 1,2-propanediol yield: 26.2%	Bhowmik et al. [91]
Pt-In	Successive impregnation method	• Temperature: 200 °C • Pressure: 2 MPa • Reaction time: 12 h • Glycerol concentration: 16.6 wt% • Catalyst weight (g or wt%): 0.2	• Glycerol conversion: 88% • 1,2-propanediol selectivity: 82% • 1,2-propanediol yield: 72%	Zhang et al. [62]
Ru-Cu/CaO-ZrO_2	Successive incipient wetness impregnation	• Temperature: 180 °C • Pressure: 2.5 MPa • Reaction time: 12 h • Glycerol concentration: 10 wt% • Catalyst weight (g or wt%): 1.2	• Glycerol conversion: 8% • 1,2-propanediol selectivity: 87% • 1,2-propanediol yield: 69.6%	Salgado et al. [92]

Bellè et al. [59] found that carbon-supported bimetallic Ru-WO_x catalysts act effectively for the low-pressure hydrogenolysis of aqueous glycerol into propylene glycol. It was reported that WO_x clusters on the carbon surface resulted in chiral Brønsted acid sites, improving selectivity towards 1,2-propanediol (88%). Kunthakudee et al. [93] observed the synergistic effects of $CuAl_2O_4$-CuO-Al_2O_3 nanocatalysts with various mole ratios of Cu/Al for glycerol hydrogenolysis. It was found that nanoparticle agglomeration was induced by Cu species during the flame process. Higher Cu content led to improved catalytic activity due to the high dispersion of Cu nanoparticles on a high surface area of Al_2O_3. On the other hand, alumina and Cu species acted as active sites and contributed to the hydrogenation of methyl lactate into 1,2-propanediol. Wei et al. [94] evaluated a series of catalysts intercalated using Cu-Zn-Fe hydrotalcite-like compounds for glycerol hydrogenolysis. The catalytic performance for 1,3-propanediol production was greatly improved, with changes corresponding to the surface structure and physicochemical properties of the catalytic materials.

Sharma et al. [95] performed catalytic hydrogenolysis of glycerol using mixed-oxide catalysts and reported a high propylene glycol yield. The used metal oxide catalysts were separated and regenerated up to four runs. However, hydrogenolysis of glycerol in the liquid phase required high operating pressures of 4–8 MPa. Kinetic parameters such as apparent activation energy can also help with the commercialization of hydrogenation reaction for the formation of acetol and propanediol [96]. Recently, Khandelwal et al. [35]

demonstrated supercritical water gasification as a sustainable process for the conversion of crude glycerol into hydrogen-rich syngas at optimal temperature, pressure, reaction time and feed concentration conditions. Lastly, techno-economic assessment studies can determine the scalability of different thermocatalytic, biocatalytic or integrated processes for the commercial valorization of crude glycerol into biofuels and biochemicals [97].

Other thermocatalytic conversion techniques such as single-atom catalysts, metal-organic frameworks and graphene matrices are gaining popularity for the valorization of waste feedstocks [98–103]. Recently, the selective transformation of biomass-derived feedstocks into value-added materials using single-atom catalysts has become one of the interesting topics in this field. The selective hydrogenolysis of glycerol into 1,2-propanediol using PtCu/MgAl-mixed metal oxides has been investigated [100]. The authors suggested that 1,3-propanediol is selectively produced due to rising Brønsted acidity and the stabilization of secondary carbocation. Similarly, Xiong et al. [103] reported the selective C–C cleavage of glycerol into value-added products using single-atom photocatalyst Ni/TiO_2. The nickel single-atom catalyst showed a high selectivity of 60% to glycolaldehyde under ambient conditions driven by light irradiation.

Metal–organic frameworks (MOFs), due to their adjustable topological structures and high surface area, can be used for catalytic oxidation of glycerol under nanoalkaline conditions. Ke et al. [102] employed Pt-supported on an MOF-derived carbon nanosheet (Pt/Zr@NPCN) catalyst for the selective oxidation of glycerol into glyceric acid showing high catalytic activity and selectivity. It was suggested that a possible conversion of glycerol into glyceric acid and dihydroxyacetone can occur due to the side reaction of oxidation decarboxylation.

Due to its outstanding electrical conductivity, thermally expanded graphene oxide (TEGO) can be employed as a catalyst for the selective oxidation of glycerol. Yang et al. [98] used Pt-Au alloy nanoparticles based on TEGO with various compositions for the aerobic oxidation of glycerol in a base-free aqueous solution. It was found that by increasing the Pt/Au ratio in TEGO-supported Pt-Au bimetallic catalysts, the selectivity of glyceric acid was reduced significantly due to the agglomeration of Pt particles.

Glycerol conversion into chemicals and the presence of fuel additives integrating routes within a biorefinery can lead to biodiesel production efficiency, sustainability and profitability using vegetable oils and waste fats. To compare novel glycerol conversion methods with conventional glycerol biorefinery techniques, energy and waste streams together with lifecycle metrics should be considered. Furthermore, efficient catalyst design by altering the Brønsted-to-Lewis acid site ratio of the oxide can change propanediol yield. The lifecycle and economic aspects of glycerol hydrogenation are determined based on the use of a catalyst for at least ten reaction cycles before its replacement [104]. To maximize profitability and environmental benefits, the integration of glycerol conversion processes with other waste recovery processes should be considered. However, glycerol resources such as biodiesel production and the food industry supply chain are dependent on other processes. To consider an integrated biorefinery plant, glycerol needs to be an abundant and cheap waste raw material. The second step is minimizing the potential ecological risks associated with glycerol biorefinery systems to ensure sustainability [105].

5. Biocatalytic Conversion of Glycerol into Propanediol

The conversion of glycerol into 1,2-propanediol and 1,3-propanediol using biocatalytic methods provides another synthesis route aside from thermocatalytic methods. The typical biocatalytic technique utilized to generate 1,2-propanediol and 1,3-propanediol is fermentation. As these newer and more improved technologies become available, more applications for fermentation are developed as well. Much of this research into fermentation in recent years is directed toward developing sustainable and environmentally friendly processes that can provide alternatives for industries that traditionally rely on petrochemicals [106–108]. Two of the crucial aspects of fermentation are the identification of the substrate and a suitable microorganism that will be used to produce the desired product under optimal and time-efficient conditions [109].

Several researchers have found that some microorganisms require a dual-substrate mixture of glycerol and glucose to perform the conversion [110]. Since glycerol or a glycerol and glucose mixture is the intended substrate that must be converted into 1,2-propanediol or 1,3-propanediol, selecting microorganisms that can do this in a cost-effective and timely manner is essential. Previous research on the bioconversion of glycerol into 1,2-propanediol and 1,3-propanediol utilized multiple different microorganisms, both native and genetically modified strains, in order to find economically viable routes of production. Some of these recent studies can be summarized below in Table 4.

Table 4. Recent studies on the biocatalytic conversion of glycerol to propanediol.

Microorganisms	Process Conditions	Main Observations	Reference
Clostridium butyricum DL07	• Fermentation: Fed-batch • Temperature: 37 °C • Agitation: 250 rpm • pH: 7 • N_2 aeration: 0.15 vvm	• Achieved a 1,3-propanediol yield of 104.8 g/L and 94.2 g/L using pure and crude glycerol substrates, respectively. • The average 1,3-propanediol concentration in eight cycles was 85 g/L with a productivity of 3.1 g/L/h.	Wang et al. [67]
Escherichia coli Rosetta-*dhaB1-dhaB2* and *Escherichia coli* BL_{21}-*dhat* co-culture	• Fermentation: Batch • Temperature: 37 °C • Reaction time: 60 h • Agitation: 200 rpm • pH: 6.8 • Airflow: 0.25 vvm	• Produced 41.7 g/L of 1,3-propanediol after 60 h of co-fermentation. • Co-culture fermentation with these strains did not require vitamin B_{12} addition.	Yun et al. [111]
Klebsiella pneumoniae DSMZ 2026	• Fermentation: Batch • Temperature: 37 °C • Reaction time: 24 h • Agitation: 200 rpm • pH: 7	• Obtained 18.8 g/L of 1,3-propanediol after 12 h of fermentation using pure glycerol. • Crude glycerol was found to have little to no effect on the cell growth, but negatively impacted the 1,3-propanediol production resulting in 9.7 g/L yield in 12 h.	Laura et al. [112]
Klebsiella pneumoniae GEM167 Δ*adhE*/pBR-1,2-propanediol	• Fermentation: Fed-batch • Temperature: 37 °C • Reaction time: 48 h • Agitation: 200–400 rpm • pH: 7	• Achieved a yield of 1016.5 ± 37.3 mg/L after 48 h of fermentation.	Jo et al. [113]
Klebsiella pneumoniae Δ*tpiA*	• Fermentation: Fed-batch • Temperature: 37 °C • Reaction time: 144 h • Agitation: 350 rpm • pH: 7 • Air flow rate: 2 L/min	• Produced 9.3 g/L of 1,2-propanediol after 144 h of fermentation at optimal conditions.	Sun et al. [114]
Lactobacillus reuteri CH53	• Fermentation: Fed-batch • Temperature: 37 °C • Reaction time: 54 h • Agitation: 50–300 rpm • pH: 5.5	• Utilizing corn steep liquor in place of the beef extract, we produced 68.3 g/L of 1,3-propanediol at optimal conditions (unaerated and 100 rpm), which was 1.24-fold times higher compared to that from the MRS agar (deMan, Rogosa, Sharpe) media.	Ju et al. [115]
Saccharomyces cerevisiae	• Fermentation: Batch • Temperature: 30 °C • Reaction time: 120–160 h • Agitation: 800 rpm • pH: 5 • Airflow: 1 vvm	• Fermentation using the best-performing strain resulted in a yield of 4 g/L of 1,2-propanediol.	Islam et al. [116]

Note: Volume of air per volume (vvm).

1,2-propanediol production through biological methods is becoming an increasingly researched topic. To produce 1,2-propanediol from glycerol, the latter is first transformed into dihydroxyacetone via the use of the glycerol dehydrogenase enzyme [117]. This is further reacted into dihydroxyacetone phosphate, requiring the usage of the dihydroxyacetone kinase enzyme. Two pathways then lead to the potential fate of dihydroxyacetone phosphate. One leads to the production of pyruvate, which further connects to the glycolysis or Embden–Meyerhof–Parnas (EMP) pathway. The other route leads to 1,2-propanediol and uses methylglyoxal synthase enzyme to catalyze the reaction. There are two routes from methylglyoxal that the reaction may take, but they both lead to 1,2-propanediol formation. The overall reaction to produce 1,2-propanediol requires one mol of nicotinamide adenine dinucleotide (NAD^+) to be converted into $NADH_2$. Figure 8 depicts the basic pathway for the transformation of glycerol into 1,2-propanediol.

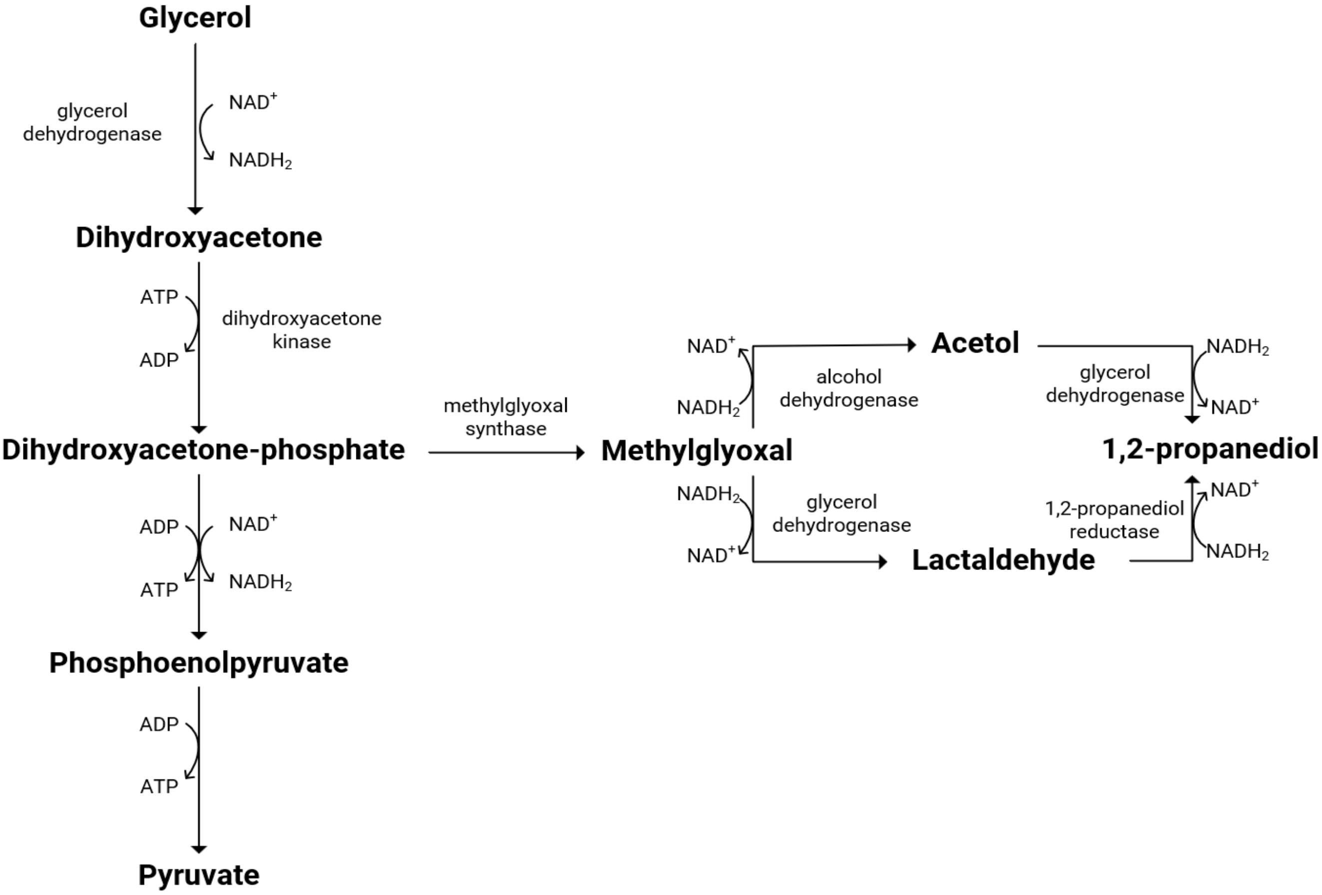

Figure 8. Simplified microbial metabolic pathway showing the route to produce 1,2-propanediol using glycerol. (Adapted from Chen and Liu [117]).

Sun et al. [114] reported that *K. pneumoniae* possesses the capability to synthesize 1,2-propanediol through the methylglyoxal pathway, as shown in Figure 8. However, the bacterium typically lacks the natural activity for this pathway unless metabolically modified. The route taken by these researchers was to block the pyruvate and 1,3-propanediol pathways in order to allow for the methylglyoxal pathway to function. This route produced 9.3 g/L of 1,2-propanediol after 144 h of fed-batch fermentation.

Jo et al. [113] undertook another recombinant approach, genetically modifying *K. pneumoniae* to synthesize 1,2-propanediol via a pyruvate route. Typically, this route converts pyruvate into lactic acid for further catalysis via enzymes into 1,2-propanediol. Additionally, the researchers genetically modified *K. pneumoniae* to prevent the formation of ethanol and enable the synthesis of 1,2-propanediol. A yield of 1016.5 mg/L of 1,2-propanediol was obtained through this pathway.

Islam et al. [116] investigated the common baker's yeast *S. cerevisiae*, which is a model microorganism used in fermentation. As *S. cerevisiae* does not produce 1,2-propanediol naturally, it was genetically modified to enable the methylglyoxal pathway shown in Figure 8. This required the addition of several *E. coli* genes to allow the expression of the various enzymes used in the methylglyoxal pathway, including methylglyoxal synthase, glycerol dehydrogenase and aldehyde reductase. The usage of this modified fungus allowed the production of 4 g/L of 1,2-propanediol.

As mentioned earlier, DuPont has commercialized a fermentation process to produce 1,3-propanediol using glucose as the carbon source. This method uses a recombinant strain of *E. coli* to facilitate this bioconversion [118]. In more recent years, increases in biodiesel production have resulted in higher glycerol availability [119]. Glycerol is a desired substrate for this process because it can be more readily converted into 1,3-propanediol than glucose [118].

Figure 9 shows the basic metabolic pathway utilized by bacteria to naturally produce 1,3-propanediol from glycerol. These two pathways are regulated through the *dha* regulon [56]. The pathway to produce 1,3-propanediol is known as the reductive branch, where glycerol is converted into 3-hydroxypropionaldehyde by the glycerol dehydratase enzyme, releasing water as a byproduct. It is further reduced into 1,3-propanediol by the 1,3-propanediol dehydrogenase enzyme. This metabolic reaction requires 1 mol of NAD^+ to be converted into $NADH_2$. The other pathway is the oxidative pathway, where glycerol is transformed by the glycerol dehydrogenase enzyme into dihydroxyacetone. This is further converted into dihydroxyacetone phosphate by the dihydroxyacetone kinase enzyme and eventually transformed into pyruvate. Pyruvate can be connected to the glycolysis pathway for further conversion into lactate, acetate, 2,3-butanediol, butyrate and other similar byproducts [64].

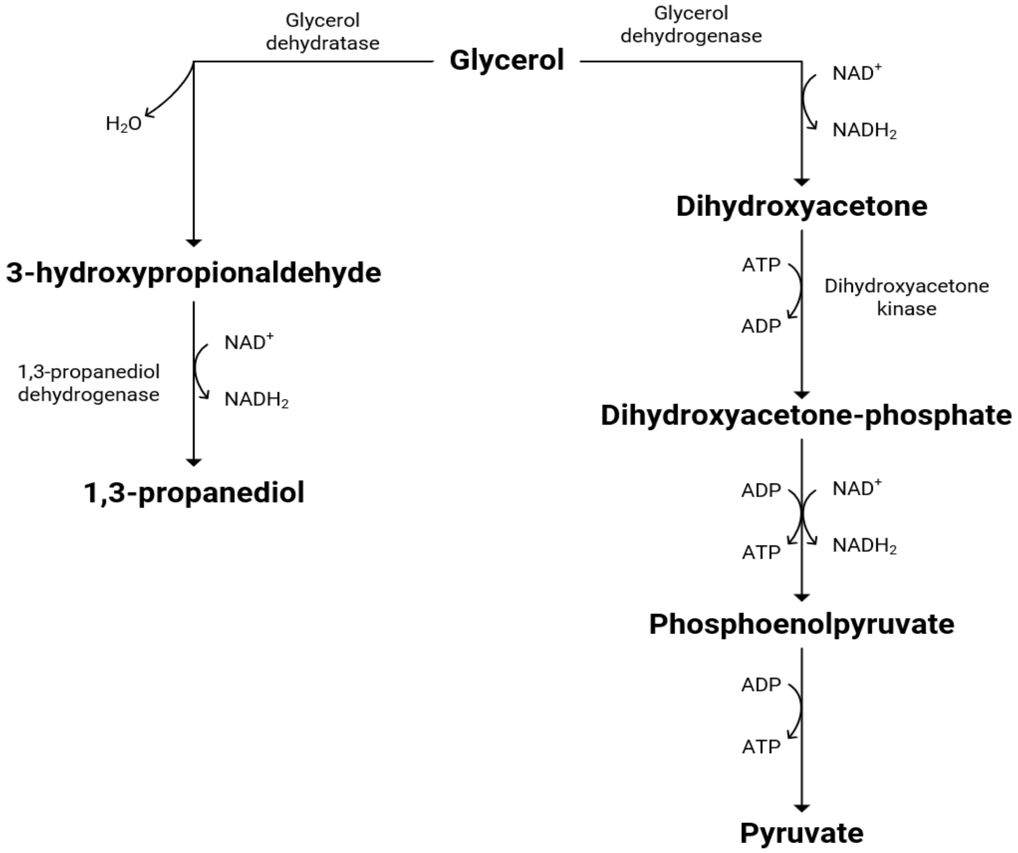

Figure 9. Simplified microbial metabolic pathway showing the route to produce 1,3-propanediol using glycerol. (Adapted from Przystałowska et al. [120]).

C. butyricum has been reported to utilize glycerol as the sole carbon substrate in producing 1,3-propanediol, with a yield and productivity of 85 g/L and 3.1 g/L/h, respectively [67]. *K. pneumoniae* also uses glycerol as the sole substrate to produce 1,3-propanediol. Laura et al. [112] used *K. pneumoniae* to biosynthesize 1,3-propanediol, with a productivity and yield of 1.6 g/L/h and 18.8 g/L, respectively.

Utilizing glycerol as the sole source of carbon and fermentation substrate is highly desired as it offers possibilities for its valorization. Recently, several studies have reported that having co-substrate mixtures such as glycerol–glucose, glycerol–corn steep liquor, glycerol–molasses and glycerol–lignocellulosic hydrolysates allow for more effective production of propanediol through an enhanced fermentation process [56,63,69,111,113,121–124]. The usage of this co-substrate mixture links the oxidative pathway of glycerol with the glycolysis pathway of glucose. In such a cascaded fermentation process, once metabolized, glucose provides the reduction equivalents needed to perform the reductive glycerol reactions that produce 1,3-propanediol.

E. coli has demonstrated the ability to convert a glucose–glycerol substrate into 1,3-propanediol, with a yield of 41.7 g/L [93]. *L. panis* PM1 resulted in a 1,3-propanediol yield of 23.4 g/L from a co-substrate fermentation media containing glucose and glycerol. These chemicals were in the presence of potassium ferricyanide as an oxidant to control the redox potential levels [69]. *L. reuteri* has also shown potential through the utilization of a co-substrate using glucose and glycerol, achieving 68.3 g/L of 1,3-propanediol [115]. Continued research into these areas will enable these processes to continue to become more sustainable and environmentally friendly while advancing the biotechnological knowledge base [125–128].

6. Conclusions and Perspectives

In summary, this review sheds light on thermocatalytic and biocatalytic pathways as sustainable routes for the valorization of waste glycerol into essential platform biochemicals such as 1,2-propanediol and 1,3-propanediol. This review navigated through the complexities and opportunities of both these environmentally friendly processes in developing suitable metal catalysts and microbial or enzymatic biocatalysts in order to transform glycerol into these value-added biochemicals. Thermocatalytic conversion, facilitated through hydrogenolysis, emerges as a time-efficient and industrially preferred technique. It uses diverse metal catalysts such as Pt-In, Ni/dolomite, Cu/Al_2O_3 and Ru-Cu/CaO-ZrO, among many other promising catalysts, for the efficient conversion of glycerol into propanediol. In order to obtain high propanediol yields, the metal and acid/base properties of the catalysts should be controlled.

The challenges associated with the thermocatalytic valorization of crude glycerol can be multifaceted. The catalytic hydrogenolysis of glycerol on a commercial scale depends on the purity of glycerol, meaning that various impurities derived from biodiesel production affect the reaction. Water, alkali hydroxides and free fatty acids can also impact the performance of the process, including catalyst deactivation, catalyst sintering and reactor blockage due to byproduct deposition. Secondly, high hydrogen pressure is required to reach an acceptable propanediol yield, resulting in a high capital cost. Catalyst stability in the hydrogenolysis of glycerol over time can be affected by poisoning, coking, fouling, and sintering, increasing the industrial operation costs.

On the contrary, the fermentative route offers further prospects through the utilization of microorganisms like *K. pneumoniae*, *E. coli*, *C. pasteurianum*, *C. butyricum*, *L. panis* and *L. reuteri*, each of which has its benefits and limitations based on pathogenesis, conversion efficiency, substrate metabolism, productivity, tolerance to inhibitors, and growth conditions. Nonetheless, sustainable 1,2-propanediol and 1,3-propanediol production using glycerol via catalytic and synthetic biology approaches must be further analyzed in order to understand the underlying mechanisms used for these processes.

Finally, this comprehensive analysis underscores the potential use of value-added biochemical production to mitigate climate change impacts as well as offer sustainable management and valorization possibilities for glycerol-rich effluents from biodiesel refineries. As industries and research communities continue to explore alternative avenues, the synthesis of sustainable chemistry principles and pragmatic applications becomes paramount. This review encourages further investigations into the promising realm of glycerol conversion in order paving the way for more ecologically conscious approaches and a sustainable future.

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