Review

Production of Propanediols through In Situ Glycerol Hydrogenolysis via Aqueous Phase Reforming: A Review

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Abstract: Production of 1,2-propanediol and 1,3-propanediol are identified as methods to reduce glycerol oversupply. Hence, glycerol hydrogenolysis is identified as a thermochemical conversion substitute; however, it requires an expensive, high-pressure pure hydrogen supply. Studies have been performed on other potential thermochemical conversion processes whereby aqueous phase reforming has been identified as an excellent substitute for the conversion process due to its low temperature requirement and high H_2 yields, factors which permit the process of in-situ glycerol hydrogenolysis which requires no external H_2 supply. Hence, this manuscript emphasizes delving into the possibilities of this concept to produce 1,2-propanediol and 1,3-propanediol without "breaking the bank" with expenses. Various heterogenous catalysts of aqueous phase reforming (APR) and glycerol hydrogenolysis were identified, whereby the combination of a noble metal, support, and dopant with a good amount of Brønsted acid sites are identified as the key factors to ensure a high yield of 1,3-propanediol. However, for 1,2-propanediol, a Cu-based catalyst with decent basic support is observed to be the key for good yield and selectivity of product. The findings have shown that it is possible to produce high yields of both 1,2-propanediol and 1,3-propanediol via aqueous phase reforming, specifically 1,2-propanediol, for which some of the findings achieve better selectivity compared to direct glycerol hydrogenolysis to 1,2-propanediol. This is not the case for 1,3-propanediol, for which further studies need to be conducted to evaluate its feasibility.

Keywords: aqueous phase reforming; glycerol; 1,2-propanediol; 1,3-propanediol; glycerol hydrogenolysis

1. Introduction

Biodiesel is a renewable alternative for diesel fuel. It is generally synthesized from various biological sources such as vegetable oils and animal fats. In addition to being biodegradable and nontoxic in nature, it has low emission profiles and is beneficial for reducing impact towards the environment [1]. The discovery of biodiesel started around the 1890s, when Rudolf Diesel, the original inventor of diesel, began experiments about biodiesel using vegetable oil, specifically peanut oil, as fuel for his diesel engine. As time advanced to the 1930s and 1940s, biodiesel was slowly incorporated as the emergency diesel fuel for various technologies [2]. However, during the 1970s, the abundance and lower market prices for fossil fuels caused biodiesel and biofuel to be considered uncompetitive in the global market [3]. Due to the sudden oil crisis caused by geopolitical changes, in the 1980s, biodiesel observed a sudden rise, during which sugarcane ethanol was the first biofuel to be formally introduced to domestic fuel markets, considered as the first

generation of biofuel. However, the implementation of sugarcane as feedstock for biofuel production sparked intense debate with respect to "fuel vs. food" trade-off, as sugarcane is one of the main sources for the sugar-processing industry, and raising concerns about the "real" carbon dioxide reduction (CO_2) potential of biofuels, as the process of producing biofuels itself is claimed to have a larger carbon footprint than the utilization of fossil fuel [4]. Hence, second-generation biofuels were produced from biomass waste and energy crops to counter and mitigate the "food vs. fuel" issue. Through years of research and development, biodiesel was then produced from easy-growing, low-maintenance algae, which marked the beginning of third-generation biofuel, which has been recognized as very energy-efficient, with higher yield by 10 to 100 times compared to a normal oil crop such as soybeans or peanuts. These algae grow 20 to 30 times faster than normal crops [5]. Lastly, in the fourth generation, these micro- and macroalgae were then genetically modified to further enhance biofuel production, while some other technologies, such as direct usage of solar energy as fuel, were also implemented [6].

Figure 1 summarizes the advancement of biodiesel, from edible biomass to the current breakthrough.
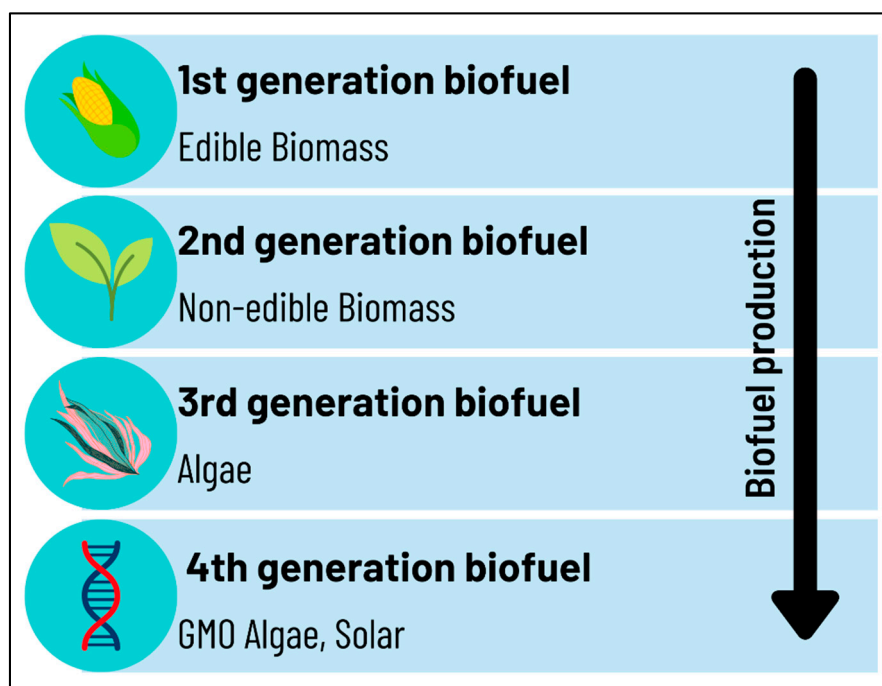

Figure 1. Generations of biodiesel advancement. Reprinted/adapted with permission from Abdullah, et al. [6], Elsevier 2019.

The biodiesel market has shown some remarkable growth since its boom in 2002; by 2008, the United States (US) itself produced 2.3 million tons of biodiesel compared to few thousand tons in the year 2002, while the European Union (EU) produced 7.8 million tons compared to fewer than 1 million tons in the year 2002 [7]. Another market analysis made in the year 2017 showed the growth of the global biodiesel market, estimated at around USD 28.04 billion in 2016 due to the increasing demand for biodiesel to replace traditional fossil fuels in automotive and power generation applications [8]. Based on the statistics provided by Inkwood Research for the U.S. [9] and EU [10] regions, the biodiesel and biofuel market has shown some tremendous progress; in the case of the United States, the overall market has increased from around USD 50 billion up to a predicted value of around USD 70 billion in the year 2026. The EU region has similarly seen a tremendous increase from a cumulative value of USD 50 billion in the year 2016 to an expected USD 80 billion in the year 2026. The market value is projected to increase as the years progress.

The boom of biodiesel productions has led to an oversupply of large amounts of glycerol. It is estimated that about 1 kg of glycerol is generated per production of 10 kg of biodiesel [11,12]. Due to the rise of biodiesel production, generation of glycerol has significantly increased from 200,000 tons in 2003 to 600,000 tons in 2006; as reported by the European Biodiesel Board, in 2015, production of glycerol in the EU was recorded at an astounding value of 1.16 million tons, and it showed a significant increase to more than 2 million tons in the year 2017 [13,14]. Data analysis from the Organization for Economic Cooperation and Development (OECD) observes that production of glycerol has significantly increased since the year 2000, from less than 10 million litres of glycerol to more than 4000 million litres in the year 2020. In 2024, glycerol production is expected to reach a level 29% more than the largest commercialized volume in 2018, which was 3.6 million tons [15]. The prices of pure glycerol and crude glycerol have plummeted significantly since the year 2007, from USD 1.50 per kg to USD 0.66 per kg and from USD 0.55 per kg to USD 0.11 per kg, respectively; the price dropped as low as 0.04 to 0.09 USD per lb in the year 2014 and is predicted to drop further [16–18]. This is due to oversaturation of the glycerol market; according to glycerol market analysis, biodiesel industry became the highest contributor to the glycerol market at around 67% in comparison to other contributing industries such as fatty acid (21%), fatty alcohol (8%), soap, and others (4%). The glycerol market is dominated by biodiesel companies, who took over 55% of the market, due to the implementation of anti-dumping duties for biodiesel in the United States and Europe, forcing them to sell the excess glycerol [19,20]. The production of large amounts glycerol and its low price have forced biodiesel enterprises to pay extra for storing and handling the excess glycerol, which consequently can hinder the development of the biodiesel industry [21].

This oversupply of glycerol generally comes from the first and second generation of biofuel production, as crude glycerol by-products are difficult to incorporate back into the biodiesel production processes due to their alkalinity and high impurity; they contain chemicals such as methanol, inorganic salts, free fatty acids, unreacted mono-, di-, and triglycerides, methyl esters, and a variety of other organic materials [22]. Consequently, they are commonly stored, converted into other beneficial products, or thrown away as waste. From the third generation of biodiesel onwards, produced crude glycerol from biofuel production from bioalgaes and microbioalgaes is commonly consumed as a substrate to generate more docosahexanoic acid (DHA)-rich bioalgaes with higher biodiesel production compared to non-glycerol-grown microalgae, generating less crude glycerol by-products [23]. However, careful consideration must be taken, as impurities such as methanol and soap from saponification will reduce the growth rate of algae [24,25]. However, in 2021, most of countries, such as China, Malaysia, India, Indonesia, Thailand, and the Philippines, are still making glycerol from biomass (edible and non-edible) such as Jatropha oil, palm oil, and even waste cooking oil [26]. The aim of this review paper is to assist these first- and second-generation biodiesel-producing countries in making use of their waste glycerol before their transition to the third generation of biofuel production.

2. Glycerol as the Feedstock for Production of 1,2-Propanediol and 1,3-Propanediol

Excess glycerol is normally considered as waste; however, the management and disposal of large volumes of waste glycerol have become a severe financial burden and environmental liability for the biodiesel industry [27]. Glycerol was then proposed to be utilized by a variety of industries, including the paint, tobacco, food, and pharmaceutical industries; however, glycerol obtained from biodiesel production is mostly crude due to the excess methanol or ethanol from the transesterification of triglycerides, and it is consequently rejected from these industries due to its low grade [28]. Due to this, another method of glycerol utilization must be identified, where the glycerol is converted into various lucrative products to mitigate the problem. However, its potential for producing various value-added products must be reviewed in terms of the final potential product, abundance, price, and product pathway. Among the identified products suitable for conversion of glycerol are 1,2-propanediol and 1,3-propanediol.

2.1. Glycerol

According to Zhou et al. [29] in Figure 2, glycerol is a versatile feedstock with the potential to be converted into various products via various conversion technologies ranging from C_2 to C_6 chemicals. As observed, it has the potential to produce various acids and ketones via oxidations, such as dihydroxyacetone, which is commonly used for the production of tanning cream [30], glyceraldehyde for the preparation of polyesters and adhesives, as a cellulose modifier, and in the tanning of leather [31]; tartronic acid [32] and glyceric acid [33] can also be produced. Glycerol can also be converted into polyols via hydrogenolysis, such as 1,3-propanediol for the production of polytrimethylene terephtahalate (PTT) and other food and pharmaceutical usages [34]; 1,2-propanediol for making polyester compounds, serving as a base for deicing solutions, and being used in antifreeze [35]; and acetol [36]. Acrolein [37] can also be produced from glycerol via dehydration. Various combinations of alkanes, alcohols, syngas, carbon, and hydrogen (H_2) can be produced via pyrolysis [38] and gasification [39]. Monoesters can also be obtained from glycerol via polymerization. Esters and ethers can also be obtained from esterification and etherification of glycerol, respectively [40,41]. Carbonation of glycerol will yield glycerol carbonate. Based on the findings by Bezerra et al. [42], most of these products are still being actively researched using pure and crude glycerol, showing the vast potential of glycerol as a feedstock due to its low price and abundancy. The number of possible products obtained is also lower as compared to other polyols due to glycerol's small carbon chain, making a specific conversion to a targeted product easier compared to other, larger-sized sugars and polyols such as sorbitol and glucose. As reported by Crosse et al. [43], in the year 2019, 1,3-propanediol was the product with by far the most research conducted on its production, with nearly 20% of all journal articles mentioning 1,3-propanediol as a very lucrative product, followed by 1,2-propanediol, which is easier to produce compared to the former, as it is a major product of hydrogenolysis.

2.2. 1,2-Propanediol and 1,3-Propanediol

1,2-propanediol, also known as propylene glycol or methyl ethyl glycol, with the molecular formula $C_3H_8O_2$ is colourless with a hint of a faint, sweet smell; it is a viscous liquid that is miscible in water, acetone, and chloroform. It has low toxicity and is safe for food, drug, and cosmetic applications. 1,2-propanediol has various uses, such as being a precursor for the synthesis of unsaturated polyester resins, biodegradable functional fluids such as antifreeze, de-icing, coolants, and heat transfer fluids. 1,2-propanediol-based antifreeze and de-icing liquid are currently on the rise, which can be attributed to concern over the toxicity of ethylene glycol to humans and animals [44]. Other industries that can make use of 1,2-propanediol include foods, pharmaceutical, and cosmetics, and it can be used in the production of products such as tobacco humectants, flavours, and fragrances, personal care products, liquid detergents, paints and animal feed [45].

1,3-propanediol, also known as 1,3-dihydroxypropane or trimethylene glycol, with the molecular formula of $C_3H_8O_2$, is a colourless, viscous liquid that is soluble in water, alcohol, ether, and formamide but less soluble in benzene and chloroform. It also has low toxicity but is not permitted to be used the food and livestock industries. 1,3-propanediol is a linear aliphatic diol, which makes it a useful chemical building block. It is commonly used for a vast number of applications including the production of polymers, personal care products, solvents, adhesives, laminates, resins, detergents, antifreezes, medical products, cosmetics, and lubricants [46]. 1,3-propanediol is mostly used in the production of biopolymers, specifically polytrimethylene terephtahalate (PTT) and polyurethane (PU). Bio-based PTT serves as a green alternative for the petrochemical-based polyethylene terephthalate (PET) and polybutylene terephthalate due to its excellent physical and mechanical properties, having various applications in the manufacturing of carpet, textile polymers, and coating materials [47,48]. 1,3-propanediol is also utilized in various personal care industries such as cosmetics and pharmaceuticals, where it is generally used as an antibacterial and moisturizing agent for cosmetics due to it having no irritating effects on skin. 1,3-propanediol

also has antifreeze properties, making it a perfect engine coolant. 1,3-propanediol can also act as humectant, emollient, solvent, and in other roles; it is useful for household usage such as paints. Its antifreeze and coolant functions also lead to its use industrially as a heat transfer fluid.
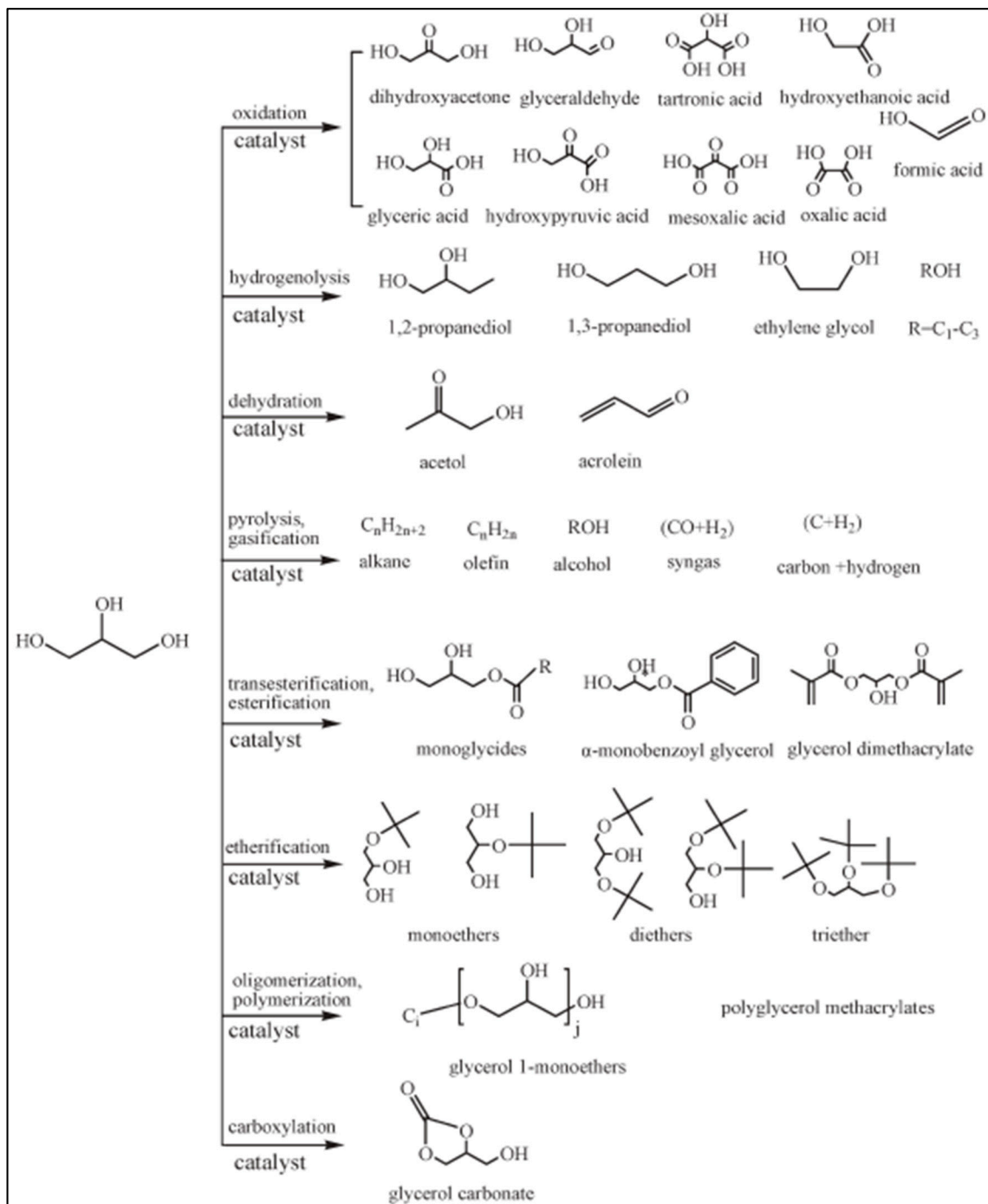
Figure 2. Potential products of conversion of glycerol. Reprinted/adapted with permission from Zhou, et al. [29], Royal Society of Chemistry, 2009.

Commercially, propylene glycol is produced via hydration of propylene oxide derived from propylene through the chlorohydrin process or the hydroperoxide process [49]. For glycerol feedstock, the commercial process of 1,2-propanediol production uses a copper chromite catalyst with mild parameters, specifically at approximately 200 °C and 10 bar hydrogen, in a two-step process involving the dehydration of glycerol to acetol and the

subsequent hydrogenation of the carbonyl intermediate to 1,2-propanediol, yielding 55% glycerol conversion and with a selectivity to 1,2-propanediol of 85% [50]. 1,3 propanediol is widely produced commercially via two methods, the Degussa–Du Pont process from acrolein and the Shell process from ethylene oxide. In the Degussa–Du Pont process, acrolein is first obtained by catalytic oxidation of propylene, which is then hydrated to 3-hydroxypropionaldehyde (3-HPA). The 3-HPA is then hydrogenated to 1,3-propanediol through a Ru catalyst and under high pressure. In the Shell process, on the other hand, ethylene oxide is obtained by the oxidation of ethylene, which is then transformed in a hydroformylation process into 3-HPA, and subsequently to 1,3-propanediol via hydrogenolysis using a Ni catalyst [51]. Industrial-scale biochemical conversion of glycerol to 1,3-propanediol has also been performed with promising results, though concern has arisen regarding the usage of toxic raw materials such as acrolein [47].

3. Aqueous Phase Reforming as the Technology of Choice for In Situ Glycerol Hydrogenolysis

Aqueous phase reforming is a technology where hydrocarbons or oxygenates such as ethanol, ethylene glycol, and polyols including glycerol and sorbitol are dissolved in water and react with water molecules at low temperature and high pressure. The process yields H_2 and various hydrocarbons; the selectivity is highly dependent on the activity of the metal catalyst, support, feed, pH of the solution, and other process conditions [52]. This technology was pioneered by Dumesic and his co-workers. It was initiated when Zartman and Atkins attempted to convert sugars and polyols dissolved in ethanol using a $CuCrO_x$ catalyst under the presence of H_2 gas, which resulted in the formation of water, diols, and triols [53]. In the 1980s and 1990s, two researchers, Montassier and Giroud, further expanded aqueous phase reforming by attempting to convert sorbitol and glycerol in an aqueous phase on a supported metal catalyst in the presence of H_2 gas [53]. In 2002, Dumesic and his research team formally introduced aqueous phase reforming (APR) for the first time. Using APR, the team managed to convert glucose into hydrogen and other alkanes over a platinum-based catalyst at 225 °C, with hydrogen being approximately 50% of the total product formed. They discovered that the selectivity of hydrogen increases when molecules that are more reduced than glucose, such as ethylene glycol and methanol, are used as a feedstock [54]. In 2004, Dumesic then proposed a novel process to produce liquid alkanes from sugar polyols through aqueous phase reforming. In his research, hydroxyl groups of sorbitol were hydrogenated over a bifunctional metal–acid catalyst to produce hydrogen and various chemicals [55].

APR requires lower operation temperature and energy compared to steam reforming and gasification, as the need to vaporize both water and oxygenated hydrocarbons is eliminated [56]. This low temperature requirement of aqueous phase reforming minimizes the production of undesirable products such as char and tars; these undesirable products reduce the performance of the reforming process [57,58]. Because APR takes place in the liquid phase, it is not necessary to remove water, thus reducing the production cost [59]. The effect of APR on greenhouse gases emission is zero due to the low energy requirement and low harmful gas emissions, making it an environmentally friendly technology. The products can also be generated in a single chemical reactor, due to the working conditions of APR being in the range that encourages the water–gas shift process, as compared to steam reforming, where multiple reactors are needed due to stark differences in working conditions with the water–gas shift (WGS) process [56]. APR generates 15 times more hydrogen per mass of catalyst compared to the steam reforming processes, and hydrogen can be used for hydrogenolysis for production of 1,2-propanediol and 1,3-propanediol through a process called catalytic transfer hydrogen (CTR) [60,61]. Martin, et al. [61] derived the equations below that explain general reforming, glycerol reforming, and WGS. The general stoichiometry in Equation (1) shows the conversion from polyols and sugars into H_2 and CO through APR [61–63], where m and n are the number of carbons. The values of m and n are then inserted to obtain the stoichiometry for glycerol reforming as shown in

Equation (2), which is an extremely endothermic process with an energy requirement of 349 kJ/mol at a reaction temperature of 250 °C. Equation (3) shows the stoichiometry of the WGS, where the carbon monoxide formed will react further with excess water through the water–gas shift reaction to produce more hydrogen and carbon dioxide [64], and the temperatures are withing the range of WGS reactions. WGS is exothermic, with an energy level of 41 kJ/mol at a temperature of 250 °C. Because the H_2 yield of APR is high, in situ glycerol hydrogenolysis is possible, which also happens within a temperature range of 190 to 245 °C [65].
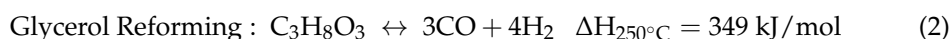
$$\text{General Reforming}: C_nH_{2m}O_n \leftrightarrow nCO + mH_2 \tag{1}$$

$$\text{Glycerol Reforming}: C_3H_8O_3 \leftrightarrow 3CO + 4H_2 \quad \Delta H_{250°C} = 349 \text{ kJ/mol} \tag{2}$$

$$\text{WGS}: CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{250°C} = -41 \text{ kJ/mol} \tag{3}$$

Table 1 shows previous research on APR of glycerol, which shows that the popular catalyst for APR is doped Pt/Al_2O_3 due to its high H_2 selectivity. Platinum (Pt)-based catalysts are very efficient for producing H_2 from oxygenated hydrocarbons by APR, even when using polluted starting material such as crude glycerol [66]. Al_2O_3 has favourable textural properties such as high surface area, high pore volume, and high pore-size distribution, as well as its acid base characteristics [67]. Based on the previous research, doped Pt/Al_2O_3 results in an H_2 selectivity of approximately 24.5% from Pt-Re/C to as high as 129.9%, achieved with $Pt-Cu/Al_2O_3$. While some of the alkane selectivity is not recorded, the selectivity of alkanes for Pt-based catalysts is around 1.3 to 40%. The finding obtained is common for Pt-based catalysts, which are more selective to H_2 production rather than alkane production. The use of metal nickel (Ni) as an alternative exhibits lower H_2 selectivity range of 36.5 to 68.9%, as compared to using Pt [68]; however, the alkane selectivity for each catalyst is not reported. It is observed that the commonly produced liquid products for APR are C_1 to C_3 products such as alcohols, diols, acids, and ketones. 1,3-propanediol is not observed in most APR of glycerol, possibly due to H_2 being the focused product rather than a liquid product. The 1,3-propanediol is possibly obtained in trace amounts, and hence not reported by researchers. As analysed, some of the catalysts used also are not suitable for production of 1,3-propanediol. Most of the reaction temperatures used for APR is also too high, potentially breaking down the obtained 1,3-propanediol into smaller products [69]. Comparing them with aqueous phase reforming, the other reforming techniques require extremely high reaction temperatures and pressures for catalytic reforming. As observed in Table 1, only some findings yield 1,2-propanediol, but they have relatively high reaction temperature requirements [70–72]. Comparatively, there are no observed techniques that can yield 1,3-propanediol effectively.

Table 1. Aqueous phase reforming of glycerol with other thermochemical techniques.

Catalyst	Technique	Temperature (°C)/Pressure (Bar)	H_2 Selectivity (%)	Alkane Selectivity (%)	Liquid Products	Ref.
$Pt/CoAl_2O_3$	APR	260/50	32	40	Ethanol, acetone, propanol, propionic acid	Reynoso, et al. [73]
Ru-Pt-NMC3	APR	250/40	82.2	Not reported	Not reported	Gogoi, et al. [74]
Pt-Ni/MWNT Cu-Ni/MWNT	APR	240/40	90.9 85.6	Not reported	Acetol, lactic acid	Rahman [75]
Pt/Al_2O_3 $Pt-Ni/Al_2O_3$ $Pt-Co/Al_2O_3$ $Pt-Cu/Al_2O_3$ $Pt-Fe/Al_2O_3$	APR	225/27.6	40.4 52.1 50.9 129.9 54.6	6.8 13.6 8.4 1.3 9.8	Not reported	Guo, et al. [76]
Ni/Al_2O_3 $Ni-P/Al_2O_3$ $Ni-Cu/Al_2O_3$ $Ni-Mo/Al_2O_3$	APR	250/75	39.6 60 36.5 68.9	Not reported	Not reported	Chen, et al. [68]

Table 1. *Cont.*

Catalyst	Technique	Temperature (°C)/Pressure (Bar)	H$_2$ Selectivity (%)	Alkane Selectivity (%)	Liquid Products	Ref.
Pt-Re/C	APR	225/29	24.5	Not reported	Ethylene glycol, propylene glycol, 1-propanol, 2-propanol, ethanol, methanol, acids	King, et al. [69]
Ni/α-Al$_2$O$_3$	Steam reforming	450–600/1	Not reported	Not reported	1-hydroxy-2-propanone, acetic acid, 1-2 propanediol, propanol, 2-methyl-2-cyclopentenone	Buffoni, et al. [70]
Ni/Al$_2$O$_3$	Steam reforming	500–600/1	Not reported	Not reported	Acetaldehyde, acrolein, propanal, acetone, acetic acid, methanol, ethanol, 1,2-propanediol	Iriondo, et al. [71]
Not reported	Pyrolysis	650–700/1	Not reported	Not reported	Acrolein, acetaldehyde, formaldehyde, acetol, 3-hydroxypropanal	Hemings, et al. [77]
Ni/α-Al$_2$O$_3$	Pyrolysis	700–900/1	Not reported	Not reported	Not reported	Shahirah, et al. [78]
Ru/ZrO$_2$	Gasification	510–550/350	Not reported	Not reported	Acetic acid, acetaldehyde, hydroxyacetone	May, et al. [79]
Raney Ni/K$_2$CO$_3$	Gasification	650–800/230–270	Not reported	Not reported	Acetaldehyde, propionaldehyde, acrolein, allyl alcohol, hydroxyacetone, propionic acid,	Li, et al. [80]
La-Ni/Al$_2$O$_3$	Dry reforming	750/1	Not reported	Not reported	Not reported	Siew, et al. [81]
Re-Ni/CaO	Dry reforming	600–900/1	Not reported	Not reported	Not reported	Mohd Arif, et al. [82]
Rh/Ce	Partial oxidation	600/2–6	Not reported	Not reported	Methylglyoxal, acetaldehyde, hydroxyacetone, ethylene, acetic acid, glycols, benzene, acetone	Rennard, et al. [83]
Pt/Al$_2$O$_3$	Partial oxidation	100/5	Not reported	Not reported	Glyceric acid, glycolic acid, lactic acid, oxalic acid, tartronic acid, formic acid, glyceraldehyde, dihydroxyacetone	Skrzyńska, et al. [84]
Rh-Ce/γ-Al$_2$O$_3$	Autothermal reforming	500–1050/1	Not reported	Not reported	Not reported	Dauenhauer, et al. [85]
Pd/Ni/Cu/K supported on γ-Al$_2$O$_3$	Autothermal reforming	550–850/1	Not reported	Not reported	Not reported	Swami and Abraham [86]
Pt-Ni/Al$_2$O$_3$	Catalytic reforming	380–500/250	Not reported	Not reported	Glycerol, 1,2-propanediol, acetaldehyde, ethanol	Chakinala, et al. [72]
Ni supported on La$_2$O$_3$/α-Al$_2$O$_3$/γ-Al$_2$O$_3$/ZrO$_2$/YSZ	Catalytic reforming	450–580/250	Not reported	Not reported	Acetaldehyde, acetic acid, methanol, acetol	Pairojpiriyakul, et al. [87]

Figure 3 shows the overall reaction pathway for aqueous phase reforming of glycerol, where there are two pathways observed: a dehydrogenation route from metal sites and a dehydration–hydrogenolysis route on acid sites. The metal site reaction is the route focusing more on diol, acrolein, acetones, aldehydes, and acids, where glycerol loses H$_2$ to become either dihydroxyacetone or glyceraldehyde. The resultant H$_2$ gas will then react with CO or CO$_2$ via methanation to form methane and water. At acid sites, after enough H$_2$ is generated, glycerol undergoes dehydration to form both hydroxyacetone, which is a stable compound, and 3-HPA, which is unstable. These intermediate compounds will then undergo hydrogenolysis using the H$_2$ formed from dehydrogenation, APR, and WGS to

form 1,2-propanediol and 1,3-propanediol. These diols can further break down into smaller products. Due to its unstable nature, 3-hydroxypropionaldehyde can also break down into other unwanted products such as propanol and acetone.
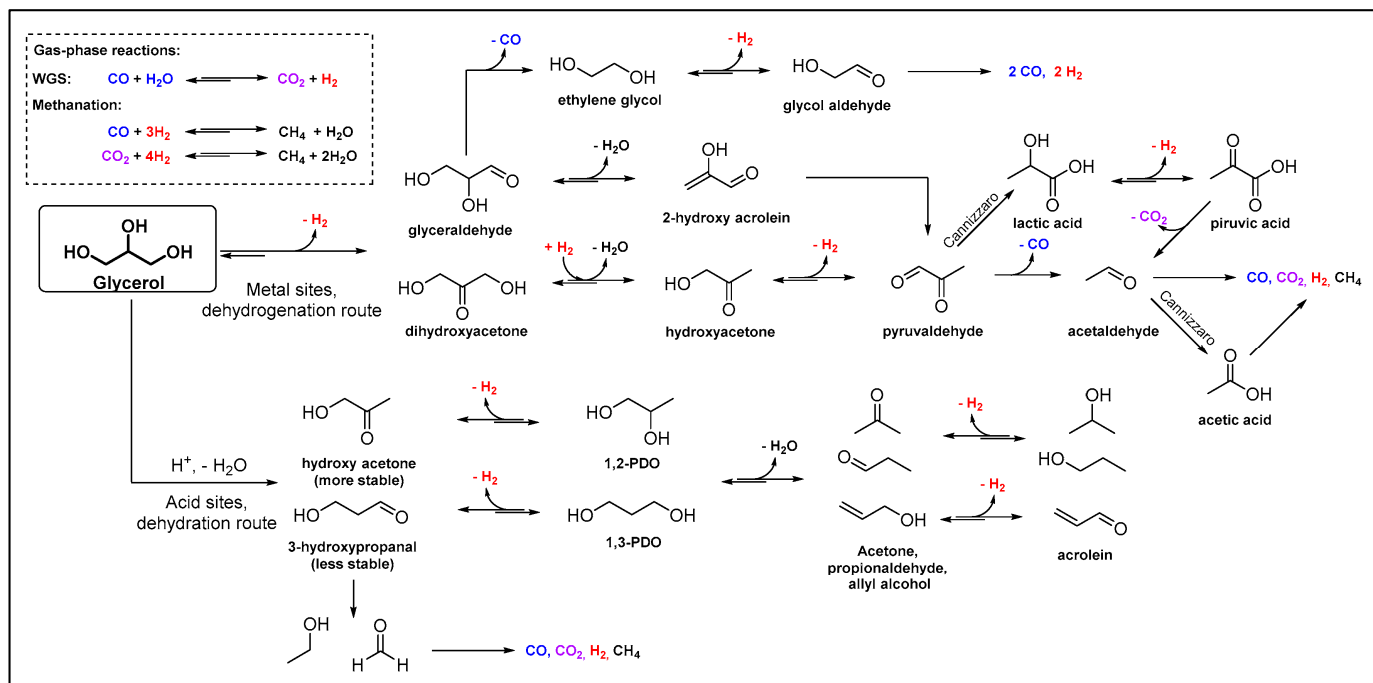

Figure 3. Reaction pathway for aqueous phase reforming of glycerol. Reprinted/adapted with permission from Fasolini, et al. [88], MDPI, 2019.

It is possible to produce 1,2-propanediol and 1,3-propanediol through APR without the need for external, expensive H_2 gas feeding via in situ glycerol hydrogenolysis [61,88,89]. In this reaction, the H_2 from APR of glycerol at metal sites is used up for the dehydration–hydrogenolysis of glycerol into 1,2-propanediol, 1,3-propanediol, and other potential products at the acid sites. The hydrogenolysis reaction is a part of a reduction process involving the dissociation of chemical bonds (C-C or C-O) in an organic compound with the subsequent addition of H_2 to the resultant molecular fragments [90]. While C-C hydrogenolysis reactions have gained commercial importance in petroleum refineries, C-O hydrogenolysis reduces the oxygen content and is an important area of research for biomass conversion into fuels and chemicals. In this research, C–O hydrogenolysis is clearly one of the most attractive routes in the chemical conversion of glycerol [91]. Figure 4 shows the potential products of glycerol hydrogenolysis of both C-C and C-O hydrogenolysis. Hydrogenolysis of glycerol from the breaking of C-O chemical bonds, which is the preferred pathway in this research, yields both 1,2-propanediol and 1,3-propanediol. However, both 1,2-propanediol and 1,3-propanediol have the potential to subsequently undergo hydrogenolysis into 1-propanol, 2-propanol, or propane gas. Through a C-C hydrogenolysis process, glycerol is converted into ethylene glycol, ethanol, methanol, ethane, and methane. While these products are very useful in the industry, they are not the targeted products and are considered undesired.

Figure 5 shows the general dehydration–hydrogenolysis mechanism of glycerol. Glycerol will undergo dehydration in the presence of acid sites on the catalyst into either acetol or 3-HPA; acetol is more stable thermodynamically and hence more favoured as compared to dehydration of glycerol to 3-HPA. As mentioned by Martin et al. [61], operating under acid conditions should bring about higher selectivity of 1,2-propanediol and 1,3-propanediol. The problem comes from the selective and controlled cleavage of the C-O bond to remove the secondary hydroxyl bonded to the central carbon [92]. The secondary

hydroxyl reactivity for glycerol is reduced sterically, due to the presence of the two primary hydroxyls, making it less accessible to the catalyst's active sites. Consequently, removal of the secondary hydroxyl is kinetically and thermodynamically less favourable [93]. Making matters worse, the activation energy for dehydrating hydroxyls is similar, making dehydration of glycerol to acetol a more favourable route [94]. The resulting acetol and 3-HPA then undergo hydrogenolysis with the help of the noble metal sites into 1,2-propanediol and 1,3-propanediol, respectively. In conclusion, 1,2-propanediol is usually perceived as the major product as compared to 1,3 propanediol, which is considered the minor output. As reported by da Silva Ruy et al. [95], the reaction must be performed under mild conditions, generally below 200 °C, as high temperatures result in further dehydration and hydrogenolysis of 1,2-propanediol and 1,3-propanediol into various mono-alcohols and alkanes which are not the targeted products.
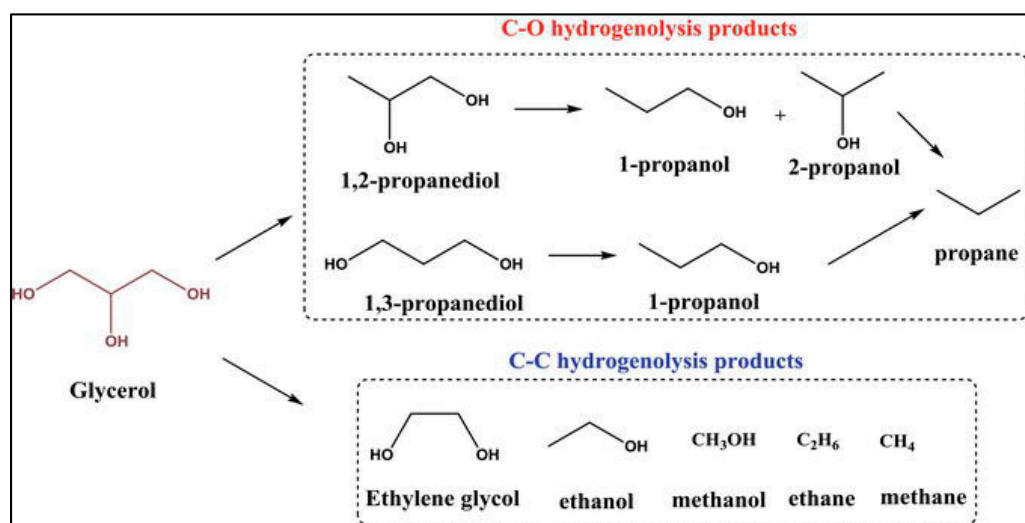

Figure 4. Products obtained from glycerol hydrogenolysis. Reprinted/adapted with permission from Samudrala [90], IntechOpen, 2018.
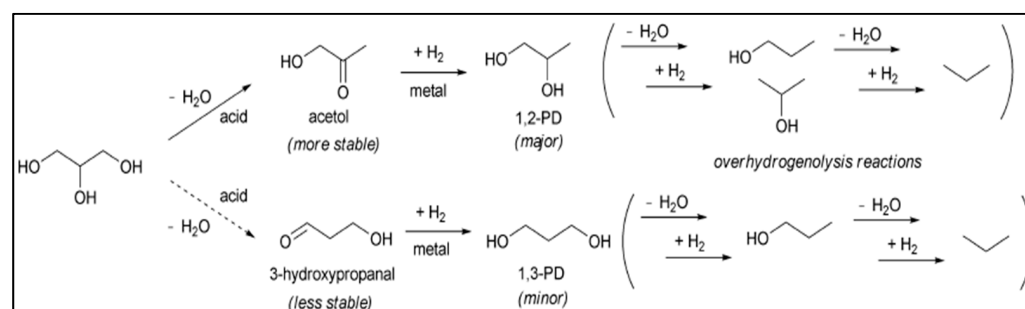

Figure 5. General dehydration–hydrogenolysis mechanism for glycerol.

Figure 6 shows the expanded mechanism for the glycerol hydrogenolysis reaction; da Silva Ruy et al. [95] suggests that ain addition to the solid catalyst's acid strength, the nature of the acid sites (Lewis or Brønsted) plays a key role in determining the selectivity of glycerol hydrogenolysis for 1,2-propanediol and 1,3-propanediol. Brønsted acid sites are more selective towards the production of 3-HPA for the production of 1,3-propanediol, and Lewis acid sites are more selective for hydroxyacetone to 1,2-propanediol. However, the total acid sites are also important for higher glycerol adsorption and conversion; hence, it is important to find the perfect ratio of Brønsted acid to Lewis acid sites. The diagram as compared with Figure 5 shows the extra presence of dehydration of glycerol to acrolein, which will then become 3-hydroxypropanal or hydroxyacetone. As mentioned by Nakagawa and Tomishige [91], weak or medium Brønsted acid sites promote acrolein formation. The

resulting acrolein will then have its hydroxyl group of the secondary carbon protonated, resulting in the elimination of a molecule of water and forming 3-HPA, similar to the Degussa route. Lewis acid sites, however, promote the dehydration of the primary carbon, which results in the production of hydroxyacetone. However, 3-HPA has the potential to convert into 1,3-dihydroxyopropene in a reversible reaction and irreversibly to acetaldehyde via dehydration, which potentially reduces the overall selectivity for 1,3-propanediol. In addition, 3-HPA is a very unstable intermediate that quickly dehydrates to acrolein in a reversible reaction, while hydroxyacetone has a direct pathway to 1,2-propanediol via hydrogenolysis. The resulting 1,2-propanediol and 1,3-propanediol can also dehydrate into other products, and hence it is important to find the suitable temperature to prevent conversion into smaller products.
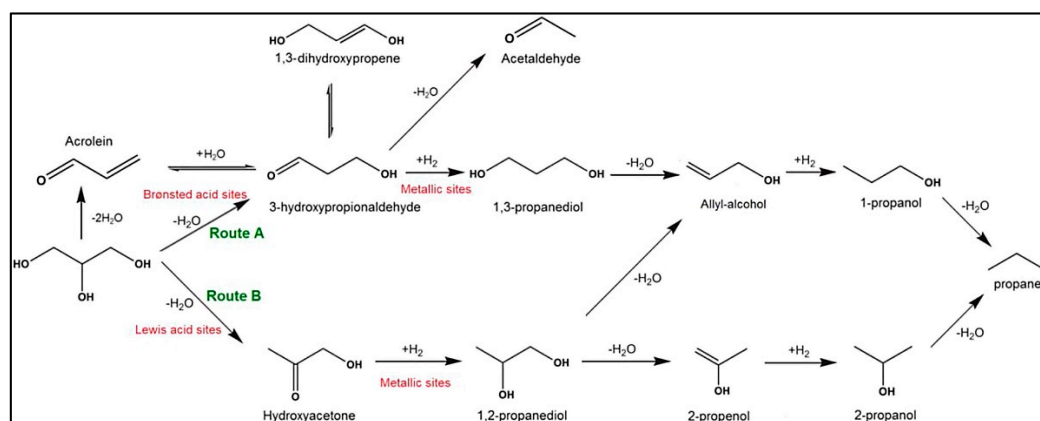

Figure 6. Expanded mechanism for the glycerol hydrogenolysis reaction using an acid-based catalyst. Reprinted/adapted with permission from da Silva Ruy et al. [95], Elsevier, 2020.

In addition to the glycerol hydrogenolysis route of dehydration and hydrogenolysis, 1,2-propanediol can also be produced from another glycerol hydrogenolysis pathway via glycerol dehydrogenation, dehydration, and hydrogenation to 1,2-propanediol as observed in Figure 7; copper (Cu)-based catalysts are generally used for this matter. Cu metal first assists the dehydrogenation of glycerol to glyceraldehyde. The basic support then dehydrates the glyceraldehyde to pyruvic aldehyde. Subsequent hydrogenation at a Cu site will result in 1,2-propanediol as the final product, with acetol as the intermediate product. However, glyceraldehyde can also be converted to 2-hydroxymalonaldehyde at a Cu site, with subsequent retro-Claisen reaction and hydrogenation to ethylene glycol, a shorter diol chain. Glycerol dehydrogenation to glyceraldehyde is assumed to be the rate-limiting step.
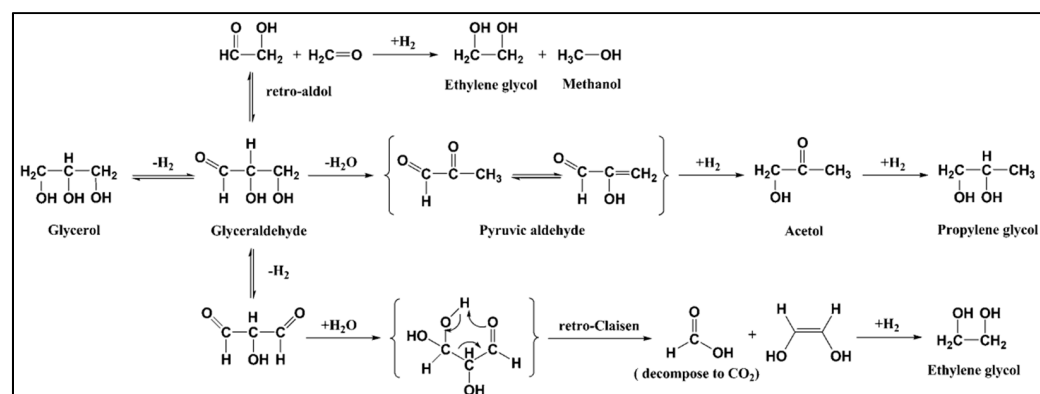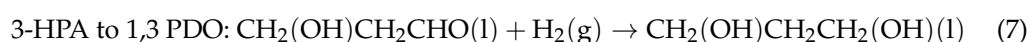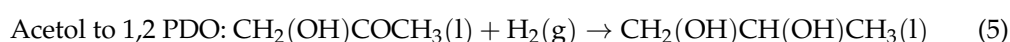

Figure 7. Glycerol dehydrogenation, dehydration, and hydrogenation to 1,2-propanediol using an alkali support. Reprinted/adapted with permission from Wang and Liu [96], Wiley, 2010.

In general, production of 1,2-propanediol is more versatile because there is not much restriction in terms of the catalyst utilized, which is oftentimes a metal catalyst, whether Cu-based or another metal acid-based catalyst; both acidic and basic support can be used, with varied intermediate products and pathways. On the other hand, 1,3-propanediol is hypersensitive to catalyst composition and nature; Brønsted acid catalysts are selective, and this causes difficulty in optimizing catalyst composition for good yield and selectivity of product. According to a thermodynamic analysis prepared by Ouyang et al. [89], as seen in the equations below, it is observed that in addition to glycerol APR, which yields H_2 and CO_2, glycerol can be converted via dehydration into either acetol or 3-HPA.

$$\text{Glycerol to acetol: } C_3H_5(OH)_3(l) \rightarrow CH_2(OH)COCH_3(l) + H_2O(g) \tag{4}$$

$$\text{Acetol to 1,2 PDO: } CH_2(OH)COCH_3(l) + H_2(g) \rightarrow CH_2(OH)CH(OH)CH_3(l) \tag{5}$$

$$\text{Glycerol to 3-HPA: } C_3H_5(OH)_3(l) \rightarrow CH_2(OH)CH_2CHO(l) + H_2O(g) \tag{6}$$

$$\text{3-HPA to 1,3 PDO: } CH_2(OH)CH_2CHO(l) + H_2(g) \rightarrow CH_2(OH)CH_2CH_2(OH)(l) \tag{7}$$

Aqueous Phase Reforming of Glycerol: Hydrogen Gas vs. Liquid Products

APR has always been primarily concerned with converting polyols into green hydrogen as an energy source, with liquid products often considered as the by-products. This is due to the fact that APR is considered a promising technology for meeting future global hydrogen energy needs because it is environmentally clean and efficient for energy conversion, compared to conventional gasoline and diesel engines [97]. However, the general perspective needs to be changed to shift the focus from hydrogen yield to liquid yield. Currently, hydrogen energy remains the energy source with the lowest impact and with the least certainty of utility. Hydrogen energy in the form of fuel cells continues to promise too much but deliver too little. Although hydrogen energy is still a promising source of energy for the future, in its current form, it is still considered a risky source of energy with huge safety issues and high infrastructure costs [98].

Due to these circumstances, it is proposed that the hydrogen produced from glycerol aqueous phase reforming be used for the production of propanediols via in situ glycerol hydrogenolysis, which uses the formed hydrogen for hydrogenolysis. These liquid products have certainties of utility and impact on current industrial needs. In addition to the industrial usage of propanediol, other possible products of glycerol hydrogenolysis have their own benefits, such as propanol and acrolein. Propanol is used in solvents, rubbing alcohol, cosmetics, and even fuels. Acrolein is used for making acrylic acid and for water treatment. In addition to the issue mentioned above, based on a thorough market study, the total liquid product has a higher market value compared to hydrogen. Currently, the hydrogen market's value was found to be USD 820 million in 2020 [99]. As for the liquid products, in the year 2020, the market value was USD 4 billion for propylene glycol [100], USD 484.8 million for 1,3-propanediol [101], USD 1.5 billion for acrolein [102], and USD 4.5 billion for both 1-propanol and 2-propanol [103]; other small products have not been the subjects of a market analysis, but the total liquid product market share is more than 10 times that of the hydrogen market share. It is a waste to solely focus on hydrogen selectivity, as these liquid products have greater overall value.

4. Production of Propanediols via Glycerol Hydrogenolysis

From Table 2, the popular metal catalysts for glycerol hydrogenolysis to 1,2-propanediol are Cu and Ru, with some small usages of Ni, cobalt (Co), calcium (Ca), palladium (Pd), and cerium (Ce) as either a metal or a promoter, which has high selectivity with good conversion; more than half of the catalysts reported have selectivity towards 1,2-propanediol above 90%. Congruently, glycerol conversion was observed to achieve 95% on one catalyst. The result obtained is far superior in terms of conversion and selectivity compared with other technologies such as biochemical conversion of glycerol to 1,2-propanediol. The supports used were quite varied, ranging from the ever-popular Al_2O_3, an amphoteric

metal, to the rare carbonate minerals dolomite and bentonite, which are moderately basic supports. To prevent overhydrogenolysis of 1,2-propanediol into smaller product, glycerol hydrogenolysis is usually performed in a low temperature range, as observed in the table, from 180 °C up to 260 °C using a rather low glycerol concentration [44]. Based on observations, all findings reportedly comply with the temperature range. Cu-based catalysts have been reported to exhibit excellent selectivity towards 1,2-PDO. This is attributed to the properties of Cu metal. Cu tends to selectively cleave the C-O bond rather than the C-C bond. Cu metal assists in cleaving the C-O bond of the primary hydroxyl group of glycerol to form acetol with simultaneous H_2 addition via hydrogenolysis without attacking C-C bond of glycerol molecules. This phenomenon is a prerequisite of selective 1,2-propanediol formation [104,105]. Furthermore, Cu is cheaper than noble metals such as Pt and Re, with similar glycerol conversion and 1,2-propanediol selectivity, which is an advantage in its utilization in glycerol hydrogenolysis [106]. It can be concluded that hydrogenolysis of glycerol to 1,2-PDO requires both metal sites for the activation of hydrogen and acid sites or basic sites for dehydration. Balance between hydro-dehydrogenation and dehydration centres in catalyst is vital for good selectivity of 1,2-propanediol [107]. To date, there are still debates on which type of support is better for the production of 1,2-propanediol, acidic or basic supports, as both of them will lead to different pathways [108].

However, the findings from Table 2 show that basic support has slightly better selectivity of 1,2-propanediol as compared with acid support. Only a few findings reported their yield of 1,2-propanediol, which ranges from 13 up to 66.1%, which is produced by Cu supported with alumina (Al_2O_3); it is reported to be able to produce 20.1% 1,2-propaendiol even in a third catalyst cycle with 50.9% conversion [109]. Based on the observations, findings were mostly obtained through the batch process, with some findings obtained using the fixed-bed process from Tanielyan et al. [110] using highly commercialized Raney Cu and a flow process with an excellent 100% conversion and with a selectivity of 96.3%.

Table 2. Heterogeneous catalyst used for glycerol hydrogenolysis to 1,2-propanediol (X = conversion, S = selectivity, Y = yield).

Catalyst	Temp. (°C)	Reactor	X (%)	S [a] (%)	Y (%)	Ref.
Cu/Dolomite			78.5	79	Not reported	
Cu/Al_2O_3	200	Batch	28	66.8	Not reported	Azri, et al. [111]
Cu/Bentonite			68.8	14.6	Not reported	
Cu/Al_2O_3	220	Batch	55.5	91.7	66.1	Kunthakudee, et al. [109]
Cu/SBA-15	230	Batch	90.3	97.3	Not reported	Shan, et al. [108]
CuMgFe-xLDO	180	Batch	47.8	97.5	Not reported	Yu, et al. [112]
Co-Ca/Al_2O_3	210	Batch	95	90	Not reported	Gong, et al. [113]
Ce-Ni/SBA-15	200	Batch	51	29	24	Jiménez-Morales, et al. [114]
Ru/Al_2O_3			32.8	41.7	Not reported	
Ru/ZrO_2	200	Batch	30.1	69.8	Not reported	Soares, et al. [115]
Ru-Cu/ZrO_2			45	94	Not reported	
Raney Cu	225	Fixed-bed	100	96.3	Not reported	Tanielyan, et al. [110]
Ni/SiO_2-C	260	Batch	56	84.7 [b]	43.3	Gatti, et al. [116]
Pd/m-ZrO_2 + ZnO	220	Batch	Not reported	94.1 [c]	Not reported	Sun, et al. [117]
PtSn	200	Batch	16	84	13	Barbelli, et al. [118]

[a] Total liquid product selectivity [b] Reported C3-based selectivity is 77.3% [c] Reported C3-based selectivity is 94.1%.

Table 3 shows various heterogeneous catalysts used for glycerol hydrogenolysis to 1,3-propanediol. It can be observed that the most popular noble metals are iridium (Ir), rhodium (Rh), rhenium (Re), and platinum (Pt), which yield relatively good selectivity of 1,3-propanediol. They are commonly supported by tungsten oxide (WO_x), silica (SiO_2), or Al_2O_3, in line with statement by da Silva Ruy et al. [95] that in order to obtain high 1,3-PDO selectivity, an appropriate metallic site combination (Pt, Ir, and Rh) with Brønsted acids (MoO_x, ReO_x, and WO_x) with supports (SiO_2, ZrO_2, or Al_2O_3) is required. There are also other metals used as dopants, such as Cu, niobium (Nb), and gold (Au). As

observed, tungsten (W) is a popular precursor metal and is widely utilized as a support or as a dopant due to its selective conversion of glycerol into 1,3-PDO; Zheng et al. [119] discovered that bimetallic tungsten catalysts are active for hydrogenolysis. Based on research by Liu et al. [94], WOx is known to exert the best effect on the selective conversion of glycerol into 1,3-PDO. Similarly, Zheng et al. [119] discovered that bimetallic W catalysts are active for hydrogenolysis. Bimetallic catalysts comprise W and a metal from group 8, 9, or 10 of the periodic table, both supported on activated carbon, delivered promising results concerning the yield and selectivity for products. However, the amount of W affects the activity, showing volcano-curve dependence, where too much W doping resulted in overhydrogenolysis into smaller chain chemicals [120]. Similarly, most laboratory-scale experiments are carried out using glycerol diluted in water solutions, at temperatures in the range of 120 to 200 °C, as temperatures higher than 200 °C are observed to lead to subsequent reactions to alkanes, and dilution of glycerol is important to avoid its degradation with the formation of oligomers at high temperatures. Coincidentally, the temperatures are in the range of the APR temperature range of around 200–300 °C. The conversion of glycerol ranges from as low as 12.7% to as high as 83.4%, and the selectivity ranges from as low as 6% to as high as 64.6%. There are three standout findings observed by Zhu et al. [121], Numpilai et al. [122], and Liu et al. [123]; all of them have high conversion rates, good selectivity, and yields above 30%. The similarity between these findings is that two of them use W as a support or dopant with Pt as the metal catalyst, together with other metals and supports. W is observed to be very effective for glycerol conversion to 1,3-propanediol. This is attributed to its good physicochemical properties, activity in the production of 1,3-propanediol, ability to generate Brønsted acid sites, and having a synergistic effect with Pt metal [93]. The highest yield of 36% uses a titanium oxide (TiO$_2$) support with a combination of Ir and Re metal, which is another good catalyst combination. Similarly, Amada et al. [124] with similar metal but a different support, SiO$_2$, reported 1,3-propanediol selectivity of 64.6%. The selectivity and yield of 1,3-PDO obtained via hydrogenolysis aer as competitive as the selectivity of 1,3-PDO obtained biochemically, yet thermochemically having the advantages of faster formation of 1,3-PDO and the catalyst not being temperature-sensitive. Similarly, the batch process is the popular reaction process due to its relatively higher yield and conversion. However, at the industrial scale, batch reactors are less competitive, as they present disadvantages such as the need to replace the spent catalyst periodically, tedious loading and unloading procedures, as well as the huge size of the equipment decreasing the annual operation time [95].

Table 3. Heterogeneous catalyst used for glycerol hydrogenolysis to 1,3-propanediol.

Catalyst	Temp. (°C)	Reactor	X (%)	S [a] (%)	Y (%)	Ref.
AuPt/WO$_x$	140	Batch	81.4	57.1 [b]	29.3	Zhao et al. [125]
Cu-HSiW/SiO$_2$	210	Batch	83.4	32.1	Not reported	Huang et al. [126]
Cu-WO$_x$-TiO$_2$	180	Batch	12.7	32.3	Not reported	Li et al. [127]
Ir–ReO$_x$/SiO$_2$	120	Batch	22.6	64.6	Not reported	Amada et al. [124]
Ir-ReOx/rutile TiO$_2$	120	Batch	80	69	36	Liu et al. [123]
Pt/Nb-WO$_x$	160	Batch	40	29.7	11.9	Yang et al. [128]
Pt/ZrW	180	Batch	10.4	30.6	~5	Zhou et al. [129]
Pt-HSiW/SiO$_2$	200	Batch	81.2	38.7	31.4	Zhu et al. [121]
Pt/WO$_x$/Al$_2$O$_3$	220	Batch	78	48	32.8	Numpilai et al. [122]
Rh/C + H$_2$WO$_4$	180	Batch	21	6	1.3	Chaminand et al. [130]
Ru-Ir-ReO$_x$/SiO$_2$	120	Batch	60.7	33.7	20	Tamura et al. [131]

[a] Total liquid product selectivity [b] Reported C-based selectivity is 51.6%.

5. Production of Propanediols via In Situ Glycerol Hydrogenolysis on Aqueous Phase Reforming of Glycerol

Due to 1,2-propanediol being the major product of glycerol hydrogenolysis, there is not much restriction on catalyst selection, even for APR. It has been reported that Cu-based catalysts are good for APR of glycerol to 1,2-propanediol despite supported noble metals

showing excellent activity for glycerol hydrogenolysis, as the selectivity for 1,2-propanediol is significantly affected by their higher ability for catalysing C–C cleavage, causing lower atom economy [105]. Reports have also shown that it is also possible to produce 1,2-propanediol from glycerol in a continuous system without the presence of H_2, with good selectivity and conversion [132]. Comparable to glycerol hydrogenolysis, metal catalysts (noble or non-noble) with supports (acid or base) are important in ensuring good yield of 1,2-propanediol [90,132]. Acid supports with good physicochemical properties such as zeolites, alumina, and silica-alumina have been used for this purpose, and similarly, basic catalysts such as yttrium and tin have been selected due to their good physicochemical properties [114]. Contrary to glycerol hydrogenolysis, Table 4 shows that Ni, Pt, and Cu are the most popular metal catalysts for the APR of glycerol. As for supports, Al_2O_3 is the most popular one due to its cheap price and high yield. The temperature ranges from as low as 180 up to 260 °C. Reactions are mostly done using batch reactors, with one study performing the reaction using a continuous reactor with a promising 1,2-propanediol selectivity of 75% and conversion up to 65%. Yun et al. [133] have also managed to achieve 76.6% glycerol conversion with a relatively good selectivity of 55.3% and a yield of 42.4% using a Cu-Ni catalyst, which combines the ability of Cu metal to selectively target C-O bonds for higher 1,2-propanediol selectivity with the ability of Ni metal to generate H_2 via APR. Compared to glycerol hydrogenolysis, APR has the added advantage of not requiring an expensive, external H_2 supply.

Table 4. Heterogeneous catalysts used for glycerol APR to 1,2-propanediol.

Catalyst	Temp. (°C)	Reactor	X (%)	S [a] (%)	Y (%)	Ref.
Cu-Al	220	Continuous	65	75	Not reported	Mane and Rode [105]
Cu-Ni	220	Batch	76.6	55.3	42.4	Yun et al. [133]
Cu-Zn/Al_2O_3	200	Batch	43	69	Not reported	Mishra et al. [134]
Ni/SiO_2-Al_2O_3	240	Batch	80~	~64	22.0	Seretis and Tsiakaras [135]
Pt/Fe_2O_3-Al_2O_3	250	Batch	93.8	43.3	39	Yfanti et al. [136]
Pt/NaY	239	Batch	85.4	76.19 [b]	Not reported	D'Hondt et al. [137]
Pt-HT [c]	250	Batch	74.4	77.5	Not reported	Pendem et al. [138]
Pt-Ir-ReOx/SiO_2	190	Batch	81	32	53	Liu et al. [139]
Pt-Ni/Al_2O_3	220	Batch	71.4	52.4	Not reported	Yan et al. [140]
Pt-Sn	200	Batch	49	63	31	Barbelli et al. [118]
Ru-Pt/Al_2O_3	227	Batch	50.1	83.5 [d]	Not reported	Roy et al. [141]
Raney-Ni	180	Batch	100	43	Not reported	Yin et al. [142]

[a] Total liquid product selectivity [b] Reported carbon selectivity is 64% [c] HT—Hydrotalcite [d] Reported total selectivity is 47.2%.

Finding a perfect catalyst for in situ glycerol hydrogenolysis in APR of glycerol to 1,3 propanediol is indeed a challenge, as the catalysts required are specific, and there are two processes that need to occur at the same time: glycerol hydrogenolysis and aqueous phase reforming. As mentioned by Nakagawa and Tomishige [91], only metal-oxide-modified noble metal catalysts can selectively yield good amounts of 1,3-propanediol; da Silva Ruy et al. [95] adds that to obtain high 1,3-PDO selectivity, an appropriate metallic site combination (Pt, Ir, and Rh) and Brønsted acids (MoO_x, ReO_x, and WO_x) aiming at selectively activating the secondary glycerol hydroxyl are necessary. Among the metallic components, Pt is the most widely used on several supports, including SiO_2, ZrO_2, Al_2O_3. As mentioned by Lehnert and Claus [66], in addition to metal loading, the kind of support used for the catalyst plays an important role in the rate of H_2 production, whereas the nature of the catalyst precursor does not influence catalytic activity. The performance of the catalyst is also affected by metal loading and metal particle size. Hence, APR is a structure-sensitive process. Table 5 shows the list of catalysts used for APR that yields 1,3-propanediol. Contrary to glycerol hydrogenolysis that has external hydrogen and APR of glycerol for production of 1,2-propanediol, the selectivity for 1,3-propanediol in APR is fairly disappointing, as most of the values are either unreported or reported together

with other trace products, as the quantity is considered negligible. Generally, the focus of aqueous phase reforming itself is generally the production of hydrogen gas rather than the liquid product, which explains the low 1,3-propanediol selectivity. Two studies have managed to achieve good selectivity for 1,3-propanediol in more than trace amounts; the combinations of Ni with CeO_2 and ZrO_2 supports are among the ones with high selectivity values of 52.73 and 23.8% respectively [143,144]. In the same two studies, it was discovered that Ca addition significantly reduces the selectivity for 1,3-propanediol. The addition of Ca to the Ni-based catalysts has relatively high selectivity towards the production of 1,2-propanediol. This is because Ca is a basic metal which contradicts the requirement of 1,3-propanediol, which requires high amount of Brønsted acid sites [91,95]. This clearly shows that any further improvements on the catalyst, such as dopant addition, need to comply with the strict catalyst requirements of 1,3-propanediol production. The ratio of H_2 to glycerol and yield of product are not reported, and the reported selectivity values are calculated based on total liquid selectivity; hence, the total selectivities are predicted to be lower than the reported values. However, the fact that the value is higher than trace amounts is a feat and worthy to be reported.

Table 5. Heterogeneous catalyst used for glycerol APR to 1,3-propanediol.

Catalyst	Temp. (°C)	Reactor	X (%)	S [a] (%)	Ref.
Pt/Al_2O_3			22.5	Trace	
Pt_2-Fe/Al_2O_3	240	Batch	26.2	Trace	Soares et al. [145]
Pt-Fe/Al_2O_3			29.5	Trace	
Pt-Fe_2/Al_2O_3			33.5	Trace	
Pt/Al_2O_3	240	Batch	12	Trace	Callison et al. [146]
PtCo/CNT	230	Fixed-bed	~60	Trace	Dietrich et al. [147]
PtMo/CNT					
Ni/ZrO_2	230	Batch	50.8	23.8	Syuhada et al. [143]
Ca-Ni/ZrO_2			48.44	14.2	
Ni/CeO_2	230	Batch	54.26	52.73	Syuhada et al. [144]
Ca-Ni/CeO_2			48.2	28.39	

[a] Total liquid product selectivity

6. Discussions, Recommendations on Production of Propanediols via In-Situ Glycerol Hydrogenolysis via Aqueous Phase Reforming

Based on the findings, it is observed that production of 1,2-propanediol and 1,3-propanediol via glycerol hydrogenolysis is highly dependent on the catalyst used. The catalysts used are very different due to different requirements, especially regarding the amount of acid sites for 1,3-propanediol and acidic or basic sites for 1,2-propanediol. Acidic/basic sites and metal sites are important for the production of propanediols from glycerol because acid/basic sites assist in dehydration of glycerol and metal sites during hydrogenolysis, yielding intermediates. As mentioned, the production of 1,2-propanediol via glycerol hydrogenolysis requires a catalyst that prefers C-O bond cleavage rather than C-C bond cleavage; notably, Cu-based catalysts are usually employed with a variety of good basic supports. Differing from 1,3-propanediol, the preferred catalyst was W-based, which has high amounts of Brønsted acid sites with the presence of a metal catalyst such as Pt, Ru, or Re. It can be concluded from this that Cu and other acid-based catalysts with acidic or basic sites influence the production of 1,2-propanediol. Brønsted acid sites, on the other hand, directly influence the production of 1,3-propanediol from glycerol via hydrogenolysis [95]. However, studies have found that Brønsted acid sites are also slightly selective towards production of 1,2-propanediol, adding to the difficulty in producing 1,3-propanediol [148]. In APR of glycerol to 1,2-propanediol, the preferred catalyst shows some changes. The preference of catalyst for 1,2-propanediol production broadens from Cu-based examples, with other noble metals such as Ni and Pt being the bases of catalysts due to the requirement to produce H_2 to be consumed in situ for glycerol hydrogenolysis; these catalysts are found to be very active in APR. Only Ni-based catalysts with support

such as CeO_2 and ZrO_2 give good selectivity of 1,3-propanediol, and the other catalysts yield trace amount of 1,3-propanediol. For 1,2-propanediol, Ni-Cu is selected to be the best catalyst because it combines the best strengths of both metals, as proven by its good yield and selectivity. Some catalyst combinations are also multifunctional and can efficiently convert glycerol into 1,2-propanediol with or without H_2 feeding, as suggested by Barbelli et al. [118], who discovered that their PtSn was able to achieve 63 and 82% selectivity for hydrogenolysis and APR respectively. The situation is different with 1,3-propanediol. Glycerol needs to convert first via dehydrogenation into the main products H_2 and CO before that generated H_2 can be used in situ for hydrogenolysis on acid sites. Hence, it is important to find the right time of reaction to ensure high 1,3-propanediol yield but prevent overhydrogenolysis of 1,3-propanediol. In addition, the catalyst selected is usually not catered and selective towards yielding high selectivity of liquid products, specifically 1,3-propanediol. Similar to glycerol hydrogenolysis, Pt is the most widely used noble metal, with doping of Fe, Co, and Mo as a promoter. From the list of promoters used, Co and Mo have the potential to generate high amounts of Brønsted acid sites, which are beneficial to increase the selectivity for 1,3-propanediol [42]. The addition of Mo also resulted in increased activity, as the ratio of Brønsted acid to metal-like sites increased [149]. Mo is compatible with noble metals and is able to reduce the coke formation of bulk Ni and other noble metals [150]. Similarly, Co-based catalysts showed good performance in hydrooxygenation processes [151,152]. While very few reports focused on selective hydrogenolysis using Co catalysts, Zhang et al. [153] discovered that a cobalt-based catalyst does enhance both hydrogenolysis and hydrogenation. As for the reaction temperature, it is around the recommended hydrogenolysis temperature of 200 °C. Soares et al. [145] tested both APR using an N_2 gas feed and hydrogenolysis using an H_2 gas feed using the same catalyst and relatively similar parameters. The study obtained a selectivity for 1,3-propanediol of approximately 4% for each catalyst. Contrary to APR, only trace amounts of 1,3-propanediol were obtained. The amount of H_2 is important to encourage hydrogenolysis. Hence, the catalyst used should generate good Brønsted acid sites, while simultaneously being reactive in APR conditions and able to obtain good H_2 selectivity. Findings by Syuhada et al. [143] show that production of 1,3-propanediol via APR is not impossible, but it is very rigid in terms of the variables used, whereby the wrong catalyst combination, wrong reaction parameters, and wrong reaction time cause negative effects towards the selectivity of 1,3-propanediol and conversion of glycerol.

To further improve the overall viability of glycerol hydrogenolysis and APR for utilizing waste glycerol, various recommendations were made. Starting with the production of 1,2 propanediol via glycerol hydrogenolysis: as observed, it is in a good state, with most of the findings achieving commendable selectivity for 1,2-propanediol and glycerol conversion. Hence, the focus of future research should be on Cu-based catalysts with various supports; cheap supports such as Al_2O_3, SiO_2, or SBA-15 are preferable from an economic point of view and based on proven results. Research should also extend to a continuous process to observe whether it is viable, as continuous processes are often preferred by the industry, while also transitioning research to utilize crude glycerol obtained directly from biodiesel production. As for 1,3-propanediol, research should be based on W as a dopant or support, with noble metals such as Pt/Ru. Because the selectivity and conversion achieved are not as high as other technologies such as biochemical conversion [154], research should focus on finding the perfect catalyst ratio and perfect parameters before transitioning into a continuous process and crude glycerol utilization. It is apparent that the type of catalyst used is significant for the production of 1,2-propanediol and 1,3-propanediol via aqueous phase reforming. As discussed by Syuhada et al. [143], the metal catalyst, catalyst support, and catalyst dopant all have an effect on the yield of the desired product. Only acidic metals should be considered and not basic metals due to the negative effects of the latter. As for 1,2-propanediol, the selectivity for the product and the conversion are observed to be generally high for most catalysts; hence, further studies should be conducted on the industrial-scale aspect of the research. Tests run on pilot plants with continuous reactor

configurations are recommended to further study the effectiveness of the catalyst at the industrial level. However, further studies on catalysts for aqueous phase reforming are highly recommended to focus on Cu-based catalysts, with combination of a cheap yet effective noble metal such as Ni and a catalyst support such as Al_2O_3 [104]. Specifically a catalyst combination such as Ni-Cu/Al_2O_3 is recommended for further testing. Catalyst reusability, reaction kinetics, and pathway also need to be studied for most of the researched catalysts to ensure the competitiveness of the catalysts with the commercial catalysts. 1,3-propanediol production via APR, however, requires more thorough laboratory-scale study because the selection of the catalyst is more vital and will "make or break" the overall selectivity for the desired product. To date, only Ni-based catalysts with supports such as ZrO_2 and CeO_2 have been proven to have high selectivity for 1,3-propanediol hence; further catalytic modification study should be based on these findings as a benchmark. The addition of a catalyst dopant is highly recommended to further improve the yield of the product. Catalyst dopants that generate large amounts of Brønsted acid sites such as W [94], Mo [42], and Co [151,152] should be further studied due to the fact that these dopants are widely used in glycerol hydrogenolysis to 1,3-propanediol with great results, despite a lack of knowledge of whether these combinations will work well on APR. Other feasible metal catalysts such as Pt, Ru, and Ir should also be tested to ensure good catalytic activity and good H_2 yield, as this is also a factor to ensure efficient in situ glycerol hydrogenolysis [155].

7. Conclusions

It is necessary to further reduce the impact of oversupply of glycerol due to biodiesel production boom. Due to the lucrativeness of 1,2-propanediol and 1,3-propanediol, several technologies such as biomass conversion and various reforming technologies are studied to help biodiesel operators in handling glycerol wastes. APR is considered suitable for the production of 1,2-propanediol and 1,3-propanediol without the use of external H_2 due to its low temperature and energy requirements, as well as the reaction temperature being similar to that of glycerol hydrogenolysis. APR also yields large amounts of H_2 for in situ hydrogenolysis of glycerol on the acidic or basic sites. However, the challenges of the current production of propanediols lie in the economic and commercial feasibility of the processes. For example, biochemical conversion is difficult commercially, as it is a sensitive process using live bacteria. Glycerol hydrogenolysis, despite being very efficient commercially, requires expensive H_2 feedstock to ensure good conversion and selectivity. Aqueous phase reforming, while economically feasible, is very sensitive to catalyst choices and has lower conversion and selectivity compared to bioconversion and glycerol hydrogenolysis.

As for 1,2-propanediol, Ni and Pt were the preferred metal catalysts due to high reforming activity, and Cu was preferred due to its preference for C-O cleavage rather than C-C cleavage, and various supports such as Al_2O_3, SiO_2 were preferred. Usage of Cu or noble metals leads to a different pathway for the production of 1,2-propanediol. Ni-Cu combinations were observed to be popular, with proven and excellent results. Studies have shown that there is not much difference in terms of selectivity and conversion for the processing of glycerol with glycerol hydrogenolysis and APR. Metal catalysts such as Pt, Ir, Re, and Ni and acid catalysts with high amount of Bronsted acid sites such as W, Co, and Mo were identified to be the best at glycerol hydrogenolysis for 1,3-propanediol conversion with suitable supports such as WO_x, Mo_x, or Al_2O_x. The production of 1,3-propanediol via aqueous phase reforming of glycerol, however, poses a challenge. Studies have shown that most of APR processes do not focus on liquid products, and the catalysts used are not suitable for the production of 1,3-propanediol. Using the best catalyst combination for glycerol hydrogenolysis, however, might not yield similar optimum results as a catalyst that performs well in one process might not perform well in other processes. Currently, the study of in situ glycerol hydrogenolysis in APR should focus on industrial-scale 1,2-propanediol production and improving current Ni-based acidic supports such as ZrO_2 and CeO_2 for the production of 1,3-propanediol with catalyst dopants.

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