

Review

Chemicals Production from Glycerol through Heterogeneous Catalysis: A Review

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Abstract: Utilization of biofuels generated from renewable sources has attracted broad attention due to their benefits such as reducing consumption of fossil fuels, sustainability, and consequently prevention of global warming. The production of biodiesel causes a huge amount of by-product, crude glycerol, to accumulate. Glycerol, because of its unique structure having three hydroxyl groups, can be converted to a variety of industrially valuable products. In recent decades, increasing studies have been carried out on different catalytic pathways to selectively produce a wide range of glycerol derivatives. In the current review, the main routes including carboxylation, oxidation, etherification, hydrogenolysis, esterification, and dehydration to convert glycerol to value-added products are investigated. In order to achieve more glycerol conversion and higher desired product selectivity, acquisition of knowledge on the catalysts, the type of acidic or basic, the supports, and studying various reaction pathways and operating parameters are necessary. This review attempts to summarize the knowledge of catalytic reactions and mechanisms leading to value-added derivatives of glycerol. Additionally, the application of main products from glycerol are discussed. In addition, an overview on the market of glycerol, its properties, applications, and prospects is presented.

Keywords: glycerol; carboxylation; oxidation; etherification; hydrogenolysis; esterification; dehydration; heterogeneous catalyst



Citation: Koranian, P.; Huang, Q.; Dalai, A.K.; Sammynaiken, R.

Chemicals Production from Glycerol through Heterogeneous Catalysis: A Review. *Catalysts* **2022**, *12*, 897. <https://doi.org/10.3390/catal12080897>

Academic Editors: Charles Xu and Tianliang Lu

Received: 29 June 2022

Accepted: 10 August 2022

Published: 15 August 2022

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1. Introduction

Glycerol is an industrial chemical, which can be used as a multipurpose substance with hundreds of applications due to its unique physical and chemical properties [1]. Glycerol can be either produced by synthetic or as a by-product of biodiesel production, the soap manufacturing, and the hydrolysis reaction [2,3]. In recent years, biodiesel has emerged as a remarkable and renewable alternative to fossil fuels. The dramatic growth of biodiesel production results in an increased abundance of glycerol, which is the main by-product (about 10 wt.% of biodiesel) in the biodiesel industry [4–6]. Figure 1 shows the increase in the production of biodiesel and accumulated crude glycerol from 2003 to 2020. It can be observed that as a result of this accumulation, the price of crude glycerol has been decreased. The biodiesel-derived glycerol (crude glycerol or waste glycerol) contains various impurities such as methanol, free fatty acids, fatty acid methyl ester, salt, water, etc. [4,7,8]. The impurities limit the utilization of crude glycerol obtained from the biodiesel industry and need to be removed to increase its value [9,10]. In addition, if a large amount of crude glycerol cannot be disposed properly it can cause environmental problems. However, purification of crude glycerol is costly and not feasible for some small sized plants. Therefore, it is necessary to explore alternative use for crude glycerol to make biodiesel production more profitable. After purified to high purity product, glycerol from the biodiesel industry can be industrially applicable [9].

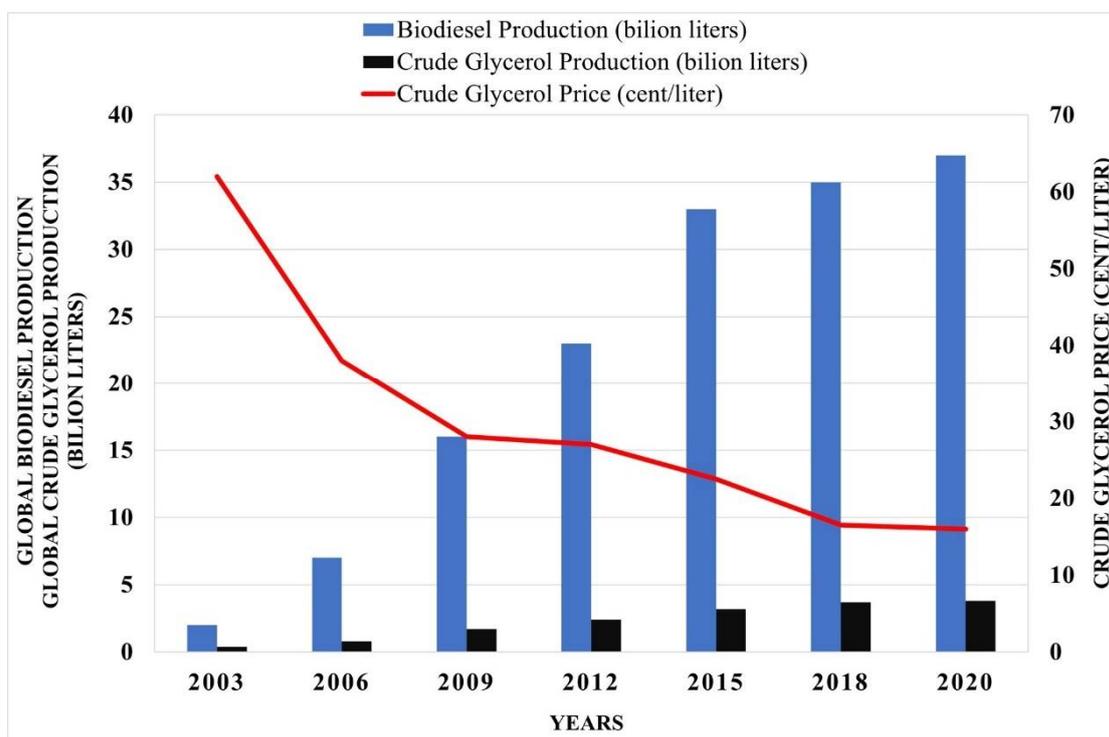


Figure 1. Global production of biodiesel and crude glycerol, and crude glycerol price between years 2003 to 2020. Data adopted from [11], open access journal of Green Chem. Lett. Rev.

Glycerol market is expected to keep growing in upcoming years [12]. Researchers showed profound interest in developing novel approaches for crude glycerol recovery and utilization. Glycerol, renewable carbon source, can be converted through bioconversion to a wide range of products [12]. The conversion of glycerol to produce commodities is viable and eco-friendly [13]. Proper utilization of glycerol will greatly improve the economic viability of biodiesel production [14]. Therefore, it becomes industrially important to find new fields to use glycerol. The attractive pricing and large availability make glycerol an appealing feedstock employed in the production of value-added chemicals such as ethanol [15], hydrogen [16], glycerol ethers [17], 1,3-propanediol [18], glycerol carbonate [19], 1,2-propanediol [20], acrolein [21], epichlorohydrin [22], citric acid [23], and lactic acid [24].

The catalytic conversion of glycerol to value-added chemicals through reactions such as carboxylation, dehydration, oxidation, hydrogenolysis, esterification, and etherification was undertaken [25,26]. Heterogeneous catalysts have been widely studied for catalytic conversion of glycerol and they are easy to be removed from products. However, the drawbacks of some heterogeneous catalysts, such as poor thermal stability, poor regeneration ability, deactivation, low surface area, and side-product formation limit their use and need to be overcome [25,27]. Several factors such as size and shape control, thermal/chemical stability, spatial distribution, electronic state, and surface composition must be considered to tailor an appropriate catalyst for conversion of glycerol to new products. This work presents detailed discussion on glycerol conversion to various chemicals via many processes, and on suitable heterogeneous catalysts for many important glycerol-derived value-added products. This review summarizes recent studies on approaches to transform glycerol to value-added chemicals. The involved heterogeneous catalysts are discussed in detail.

2. Glycerol Properties

Glycerol, synonyms of 1,2,3-propanetriol, glycerin and 1,2,3-trihydroxypropane, is a low toxicity alcohol having three hydrophilic hydroxyl groups [1,4]. The word “glycerol”

specifically refers to the pure chemical compound 1,2,3-propanetriol, while the word “glycerin” often refers to commercial products with more than 95% glycerol [28]. Glycerol is a colorless, viscous, odorless, hygroscopic liquid with sweet taste, which is very soluble in water and many alcohols because it contains three hydrophilic hydroxyl groups [1]. It is slightly soluble in ether and dioxane, partially insoluble in fatty acids, benzene, hexane and chloroform, insoluble in hydrocarbons [26,28]. Under water-free condition and 1 atm, glycerol has a density of 1.261 kg/L, melting point of 18.2 °C and boiling point of 290 °C [29]. Glycerol is a trihydric alcohol and a highly flexible molecule forming both intra- and intermolecular hydrogen bonds [29]. Glycerol can be used as a multipurpose substance in many applications due to its unique physical and chemical properties [1].

Glycerol can be produced by hydrolysis of sugars, soap production by saponification and biodiesel production by transesterification as the by-product [3]. Saponification is now less important in many countries since detergents are used instead of soap [30]. It is also derived from chemical synthesis and microbial fermentation [30,31]. Yeast fermentation as a process to produce glycerol has been well recognized. In *Saccharomyces cerevisiae*, during redox-neutral process of the fermentation of sugar to ethanol, glycerol is produced as the by-product [30]. Biodiesel-derived glycerol (crude glycerol) is produced from the transesterification of vegetable oil with alcohol by acidic, basic, or enzymatic catalysts [13]. During the transesterification process, approximately 10 wt.% glycerol and 90 wt.% biodiesel are produced [32].

3. Applications of Glycerol

The increased quantities of crude glycerol due to the expanding biodiesel production may cause environmental problems [14]. To address the challenge, more alternative applications of crude glycerol are developed. Glycerol is a renewable source with hundreds of applications. Based on different properties, glycerol has a wide range of applications in different industries such as food, medical, pharmaceuticals, personal care, botanical extracts, antifreeze, chemical intermediates, etc. [33]. Figure 2 shows the main areas of glycerol application with the percentage distribution. Glycerol is safe and suitable for food use. It can be used as a solvent, sweetener, softening agent and preservative agent for food and beverage [4]. It is a major ingredient in some personal care products such as toothpaste, skin, and hair care products to provide moisture and improve smoothness [4].

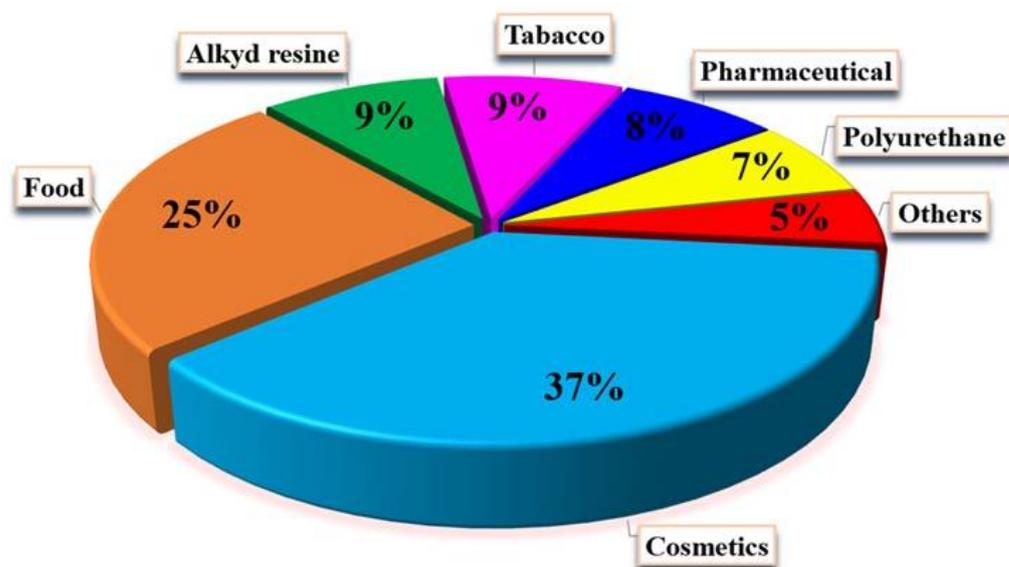


Figure 2. Percentage of glycerol application in different fields. Data collected from [34], open access journal of Membranes.

Glycerol can be supplemented for animal diets to improve energy availability [35]. Nutritional analysis of glycerol produced by the fresh oils indicated very high carbohydrate content, and glycerol could be used as a feed supplement [36]. Glycerol is a renewable feedstock in the production of value-added products. It is estimated to have more than two thousand end uses in the chemical industry [12]. Glycerol was reported to be converted to amino acids by the multifunctional catalytic system (Ru₁Ni₇/MgO) [37]. Glycerol, which is suitable for microorganisms' growth, is an excellent carbon substrate to produce commodities including 1,3-propanediol, lactic acid, docosahexaenoic acid (DHA), bioethanol, hydrogen, fuel additives, etc. [9,38]. The bioconversion of partially treated crude glycerol to useful chemicals using enzymes and microbes is eco-friendly but less productive [13].

Crude glycerol can be directly converted to derivatives such as hydrogen, propylene glycol, acrolein, polyglycerols, etc., and the effects of the impurities on the conversion performance need to be further investigated [26]. It was employed as the alternative green solvent in the aldol condensation and Pd catalyzed Heck C-C coupling reaction [39]. It was also used as a promoter in bio-oil manufacture during the liquefaction of biomass [40]. One possible use of glycerol from biodiesel production was to prepare the inexpensive deep eutectic solvents with choline chloride for the esterification of palmitic acid [41]. Crude glycerol has been studied as a supplement to the components in biogas production to increase gas production and methane contents [42]. Currently, some studies provide a considerable way to utilize crude glycerol in co-digestion and co-gasification by blending with hardwood chips, solid waste, agro-industrial by-products, and waste water [43–45].

Crude glycerol can be purified to high quality to be used as glycerol. The catalytic conversion of glycerol to high-value chemicals and catalysts development are appealing and still under investigation. It was reported that glycerol can be utilized as low-cost raw material to derive valuable chemicals such as glycerol ethers, 1,3-propanediol, epichlorohydrin, glycerol carbonate, 1,2-propanediol, etc. through carboxylation, dehydration, oxidation, hydrogenolysis, esterification, etherification, and reduction [46,47]. These conversion processes and involved heterogeneous catalysts are highlighted in the following sections.

4. Methods of Conversion

Different methods of glycerol conversion to value added products and some of the important derivatives are shown in Figure 3. Application of the products, various reactants and reaction conditions are discussed in the following sections.

4.1. Carboxylation

Carboxylation is a chemical transformation in which a carboxyl group is added to a compound. The main product which is derived from glycerol carboxylation is glycerol carbonate (CAS number: 931-40-8). Glycerol carbonate has been recognized as an important product derived from glycerol over recent years. Being inexpensive to act as a new reactant material has created an opportunity of glycerol carbonate to produce polyurethanes and polycarbonates [48]. It is also employed as a solvent, personal care product, and lubricant. One major reason for researchers' interest is its wide reactivity, which makes it appropriate for many applications. The reason of this feature of glycerol carbonate is the existence of hydroxyl and 2-oxo-1,3-dioxolane groups in its structure [49]. The physical properties of glycerol carbonate also make this material suitable to be applied in industry. The flash point of glycerol carbonate is 190 °C, therefore, it is not easily flammable. Furthermore, it is a nontoxic, bio sustainable, biodegradable, and viscous liquid with low evaporation rate [50].

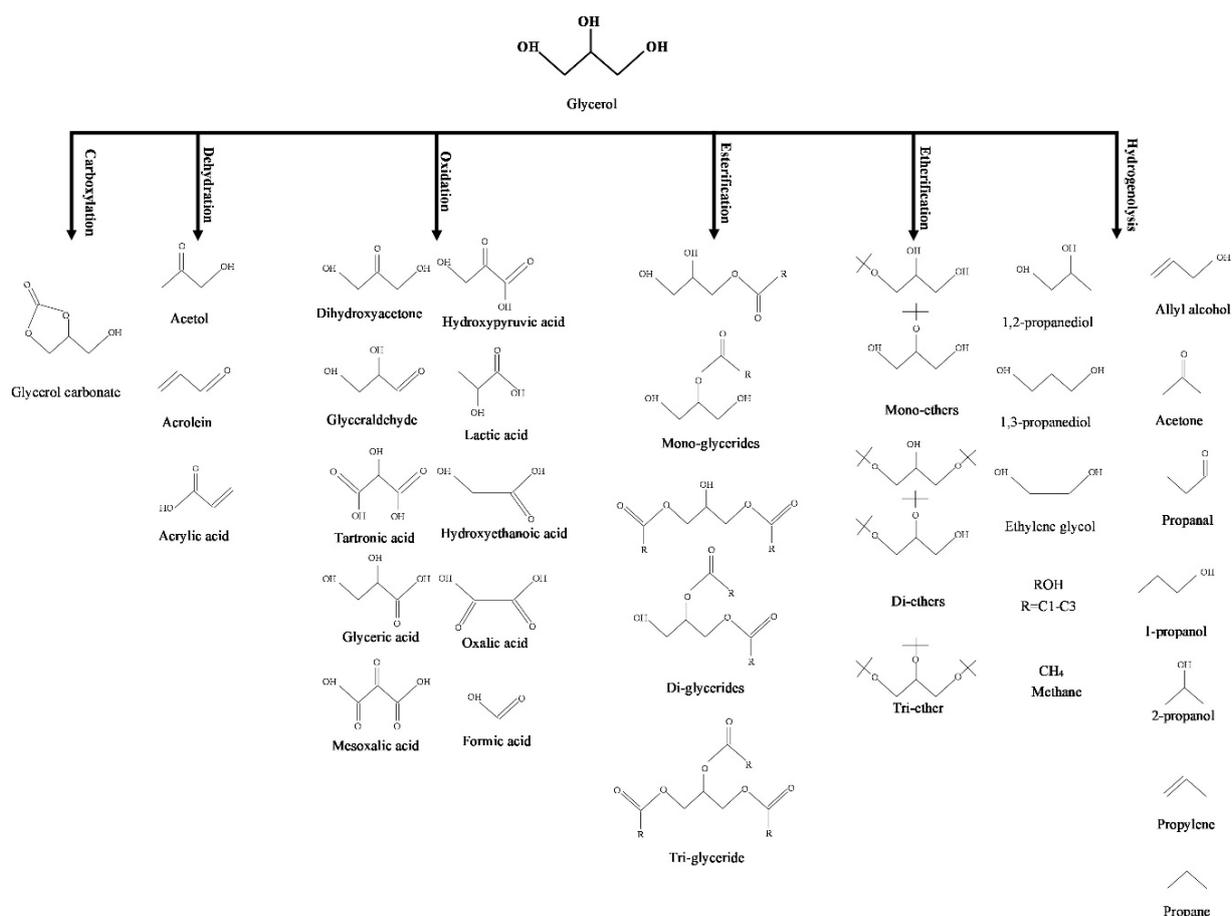


Figure 3. Main glycerol derivatives through different pathways.

Numerous reactions as well as various heterogeneous catalysts have been reported in the literature for catalytic conversion of glycerol to glycerol carbonate. Table 1 represents several pathways and the performance of different catalysts for this conversion and the reaction conditions. In each case, glycerol reacts with a carbonate source chemical to produce glycerol carbonate. The most common reactants for this purpose are carbon monoxide [51,52], carbon dioxide [53–58], urea [59–61], ethylene carbonate, propylene carbonate, dimethyl carbonate [50,62–65], diethyl carbonate [66], propylene oxide, and ethylene oxide (oxirane). Among all carbonate sources mentioned above, urea, ethylene carbonate, propylene carbonate, carbon dioxide, dimethyl carbonate and propylene oxide are relatively low-cost materials in comparison with others. Besides, urea and dimethyl carbonate are molecules synthesized from CO₂, therefore, the carboxylation of glycerol performed directly with CO₂ has one less step. Additionally, conversion of carbon dioxide and glycerol to a glycerol carbonate is a promising process since carbon dioxide is a greenhouse gas. In spite of all mentioned, there are challenges, which makes this reaction more difficult.

In some studies, carbon dioxide could not be used successfully as the reactant for the glycerol conversion to glycerol carbonate due to its inertness and thermodynamic stability. Metallic oxide catalysts have attracted attentions due to their suitable CO₂ adsorption and activation and their subsequent activity in carbon dioxide transformation. It is also noticeable that using 2-cyanopyridine or acetonitrile as dehydrator is common in the reaction between glycerol and carbon dioxide. With their use, the reaction sets a new and favorable equilibrium. When the produced water is absorbed by these chemicals, because of the reduction in water, a new equilibrium is set. Based on Le Chatelier's principle, the reaction moves towards producing more glycerol carbonate.

Table 1. Catalysts used for the synthesis of glycerol carbonate (GC).

Catalyst	Molar Ratio	Solvent	Temp. (°C)	Pressure (MPa)	Reaction Time (h)	GC Yield (wt%)	Ref.
Glycerol + CO₂		Molar Ratio G to CO ₂					
1 mol% n-Bu ₂ SnO	Excess CO ₂	MeOH	80	3.5	4	35	[53]
Bu ₂ SnO	–	Methanol/Zeolite	120	13.8	4	35	[53]
6 mol% n-Bu ₂ Sn(OMe) ₂	Excess CO ₂	free	180	5	15	7	[67]
Zn/Al/La/M (M = Li, Mg, Zr)	Zn:La:Al = 4:1:1	free	170	4	12	15.1	[56]
CeO ₂	Excess CO ₂	DMF	150	4	5	78.9	[57]
Cu/La ₂ O ₃	Excess CO ₂	Acetonitrile	150	7	12	15.2	[55]
La ₂ O ₂ CO ₃ /ZnO	La:Zn = 1:4	Acetonitrile	170	4	12	14.3	[54]
Zr-Ce Oxide	Excess CO ₂	DMF	150	3	5	36.3	[58]
Glycerol + urea		Molar Ratio G to Urea					
ZnO	1:1	free	140	–	6	57.86	[59]
ZnO/SiO ₂	1:1	free	140	–	6	64.3	[59]
MoO ₃ + SnO ₂	1:3	free	150	–	4	67	[60]
Au/Fe ₂ O ₃	1:1.5	free	150	–	4	38	[68]
Co ₃ O ₄ /ZnO	1:3	free	145	–	4	60	[60]
Zn/MCM-41	1:1	free	145	–	3	73	[61]
Ni/MCM-41	1:1	free	145	–	3	53	[61]
Cu/MCM-41	1:1	free	145	–	3	45	[61]
CaO, La ₂ O ₃ , MgO, ZrO ₂ , Al ₂ O ₃	3:2	free	150	–	3	28–93	[69]
0.5 wt% calcined La ₂ O ₃	3:1	free	140	–	1	91	[70]
manganese sulfate	1:1	free	150	–	2	61	[71]
Zinc sulfate	1:1	free	140	–	2	86	[71]
Sn/W mixed oxide	2:1	free	140	–	4	49.7	[72]
1wt% Au/MgO	1:1.5	free	110	–	4	46	[68]
1wt% Pd/MgO	1:1.5	free	110	–	4	62	[68]
1wt% Au-Pd/MgO	1:1.5	free	110	–	4	67	[68]
Cu-Mn	1:1.5	free	140	–	6	90.2	[73]
Zn-Sn	1:1	free	155	–	4	97.6	[74]
Zr-Phosphate	1:1	free	145	–	3	80	[75]
Glycerol + dimethyl carbonate		Molar Ratio G to DMC					
CaO	1:3.5	free	95	–	1.5	95	[50]
CaO	1:2	free	70	–	1.5	68	[62]
MgO	1:2	free	70	–	1.5	23	[62]
Mg _{0.9} Ca _{1.1} O ₂	1:2	free	70	–	1.5	75.4	[62]
Mg _{1.2} Ca _{0.8} O ₂	1:2	free	70	–	1.5	100	[62]
Mg-Al hydrotalcite (Mg/Al = 2)	1:3	Methanol	70	–	3	65	[64]
LiNO ₃ /Mg ₄ AlO _{5.5}	1:3	free	80	–	1.5	96	[76]
ZnO/La ₂ O ₃	1:4	free	150	–	2	97	[63]
K-zeolite	1:3	Methanol	75	–	1.5	96	[77]
Na ₂ O	1:2	free	75	–	0.5	92	[78]
trisodium phosphate (TSP)	2:1	free	70	–	1	99.5	[65]
hydrotalcite- hydromagnesite	1:5	DMF	100	–	0.5	79	[79]
Mg/Al/Zr	1:5	free	75	–	1.5	95	[80]
Mg–Al hydrotalcite	1:5	DMF	100	–	2	75	[81]

Table 1. Cont.

Catalyst	Molar Ratio	Solvent	Temp. (°C)	Pressure (MPa)	Reaction Time (h)	GC Yield (wt%)	Ref.
K ₂ CO ₃	1:3	free	75		3	97	[82]
BaCO ₃	1:5	DMF	140		2	96.4	[83]
Ti/Si	1:3	free	65		7	52	[84]
TiO ₂	1:3	free	65		7	4	[84]
Ni-Mg Oxide	1:4	free	90		1.5	82	[85]
Glycerol + carbon monoxide	Molar Ratio G to CO						
K ₂ CO ₃ /Se	Excess CO and O ₂	DMF	20	0.1	4	84	[52]
Glycerol + diethyl carbonate	Molar Ratio G to DEC						
Ce-NiO	1:3	free	85	-	8	85.6	[66]

Use of n-Bu₂Sn(OMe)₂ and n-Bu₂SnO as two metal alkoxide catalysts for this reaction led to low glycerol conversion as a result of the low activity of carbon dioxide [67]. In another research, one mol% nBu₂SnO was used as a catalyst of this reaction in presence of methanol. The results showed the glycerol carbonate yield of 35% [53]. In a previous study, Cu/La₂O₃ catalyst was prepared for this reaction while acetonitrile was used as the dehydrator. A total of 2.3% Cu additive in the catalyst showed 33.4% glycerol conversion and glycerol carbonate selectivity of 45.4% at 150 °C, 7.0 MPa and reaction time of 12 h [55]. CeO₂ catalysts in form of nanoparticles or nanorods could reach a relatively higher yield (~79 wt%) of glycerol carbonate. The amount of acidity and basicity in these catalysts impact their activities. The higher yield of glycerol carbonate is due to the presence of acidic and basic sites in the catalyst. The hydroxyl groups of glycerol are well adsorbed and activated by the Lewis acidic sites of the catalyst and carbon dioxide is adsorbed and activated by the basic sites [57].

Besides the direct carboxylation by CO₂, the indirect pathways may proceed with the reaction with more benefits. Nguyen & Demirel [86] concluded that the net present value of the glycerol carboxylation by using urea is higher than that of direct carboxylation with carbon dioxide for a duration of 12-year operation with the same capacities. The by-product of the carboxylation with urea is ammonia, which needs reduced pressure to be removed and shift the equilibrium to products' side. Krisnandi et al. [59] studied the performance of ZnO/SiO₂ catalyst on the reaction of glycerol and urea. ZnO catalyst showed high glycerol conversion of 82.38%; but the selectivity and yield of glycerol carbonate were as low as 40.46% and 33.33%, respectively. Applying a porous silica support with the ZnO catalyst enhanced the selectivity and yield of glycerol carbonate to 77.83% and 64.30%, respectively. In another study [61], wet impregnation method was applied to prepare Zn/MCM-41 catalyst for the reaction of glycerol and urea to produce glycerol carbonate. The glycerol conversion of 75% and glycerol carbonate selectivity of 98% selectivity were obtained due to the simultaneous existence of acidic and basic sites in the catalyst. Acidic sites activate glycerol and basic sites activate urea. Tin-tungsten mixed metal oxide was also used as a catalyst for the reaction of glycerol with urea. The catalysts with different tin/tungsten ratio were prepared and it was observed that the catalyst with tin/tungsten ratio of 2:1 calcinated at 500 °C showed glycerol conversion of 52% and glycerol carbonate selectivity of over 99% [72]. The catalyst with gold and palladium nanoparticles and magnesium oxide support has also been studied for the reaction of conversion of glycerol to glycerol carbonate in the presence of urea. Rahim et al. [68] concluded that 1 wt% AuPd/MgO at the reaction temperature of 150 °C showed the best result (glycerol conversion of 87%, and glycerol carbonate selectivity of 77%) among other tested catalysts including MgO, 1% Au/MgO, 2.5 wt% Au/MgO, and Pd/MgO. However, the results were not much better than using magnesium oxide as catalyst (glycerol conversion of 84%, and glycerol carbonate selectivity of 57%), but it still shows the positive synergistic effect of using two metals combined as a catalyst for glycerol conversion and glycerol carbonate selectivity.

Most studies on glycerol carboxylation have been carried out on dimethyl carbonate reactant since it reacts at mild conditions and low duration of reaction time. Several metal oxides and mixed metal oxides such as ZnO, Na₂O, CaO, MgO, MgCa-oxide, MgAl-oxide and NiMg-oxide, and metal salts such as LiNO₃, K₂CO₃ and BaCO₃ have been examined as catalysts in this reaction. Khayoon and Hameed [62] made a comparison between the efficiency of magnesium oxide and calcium oxide in the reaction. It was revealed that CaO reached a higher yield of glycerol carbonate up to 68% at 70 °C under 90 min of reaction time with 1:2 molar ratio of glycerol to dimethyl carbonate. The research of Ochoa-gomez et al. [50] concluded that by varying the reaction condition to 1:3.5 molar ratio of glycerol to dimethyl carbonate, and the temperature of 95 °C, with the same CaO catalyst, the glycerol carbonate yield of 95% was achieved. The best result was obtained from Mg_{1.2}Ca_{0.8}O₂ catalyst at 70 °C and 90 min reaction time, which led to producing glycerol carbonate with the yield of 100 wt% [62]. Figure 4 shows a possible reaction mechanism of glycerol and dimethyl carbonate (DMC) with CaO catalyst. Active Ca species in the catalyst is attacked by a glycerol molecule and a DMC molecule. This is characterized as Ca(C₃H₇O₃)(OCO₂CH₃) (II) as shown in Figure 4. Then, glycerol molecule collides with intermediate Ca species II and releases a methanol molecule, generating Ca species III. Glycerol carbonate was produced via an intermolecular nucleophilic substitution and the catalyst is generated.

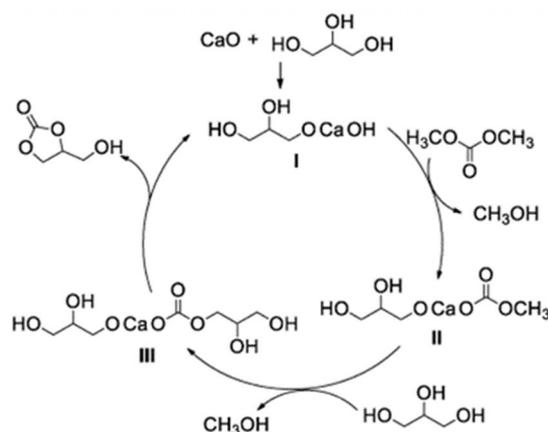


Figure 4. A plausible reaction mechanism for converting glycerol to glycerol carbonate using CaO catalyst [87], open access journal of Catalysts.

Glycerol carbonate can also be converted to glycidol through catalytic decarboxylation process [88,89], ultrasonic activation, conventional thermal activation, and microwave-assisted activation [90].

4.2. Oxidation

Oxidation refers to a reaction in which oxygen is added as a reactant, or an element loses electrons accompanied, which led to increasing the valence number of the component. General oxidation of glycerol involves oxidation by adding oxygen atoms or dehydrogenation by removing hydrogen atoms. Electrocatalysis, defined as an electrochemical reaction in which electrode acts as both catalyst and electron acceptor/donor, can be used for glycerol oxidation. A review has been performed by Coutanceau et al. [91] on different catalytic systems and conditions on glycerol electro-oxidation. They concluded that a wider potential range of the catalyst activity, and a lower glycerol oxidation onset potential are two of the essential parameters for obtaining the highest selectivity toward a desired product at the best conversion rate. The process of oxidizing glycerol can be carried out by any of the three hydroxyl groups of the component. Several products can be synthesized from glycerol by different oxidizing agents. Figure 3 shows the main derivatives of glycerol through these reactions. To study more closely, the derivatives are divided

into three categories named as C_1 , C_2 and C_3 products, based on the number of backbone carbon atoms.

One of the main C_1 products of glycerol oxidation is formic acid (CAS number 64-18-6). Commonly, formic acid is used in agriculture, pharmaceutical industry, rubber, chemical, leather, and textile manufacturing [92]. This compound also has the potential of serving a supply of hydrogen [92,93]. For this purpose, several catalytic reactions can be used to easily decompose formic acid to hydrogen and carbon dioxide under moderate conditions [94–100]. Therefore, it can be utilized directly in formic acid fuel cells or indirectly in hydrogen fuel cells [101]. Low toxicity and being liquid at ambient conditions make this chemical safer and easier to store and transport as compared to hydrogen. Due to this reason, scientists consider formic acid, as a renewable derivative of biomass to be used as an alternative to hydrogen gas [102,103].

Several catalysts have been used for the conversion of glycerol to formic acid as summarized in Table 2. Mainly, the oxidant, which is used for reaction with glycerol, is oxygen, and the reaction usually occurs at medium to high pressure. As a case study, Xu et al. [92] used $\text{Ru}(\text{OH})_4$ nanoparticles reduced on graphite in aqueous solutions of Lewis acids of FeCl_3 , AlCl_3 , CrCl_3 and ZnCl_2 to convert glycerol and oxygen to formic acid at the temperatures between 160 to 180 °C and 0.5 to 1.5 MPa pressure. It was observed that acidity of FeCl_3 had the highest synergistic effect with the $\text{Ru}(\text{OH})_4$ nanoparticles and resulted in formic acid yield of around 60%. In another study [104], catalytic oxidation reaction was carried out for conversion of glycerol to formic acid using $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ as a vanadium substituted phosphomolybdic catalyst. The formic acid selectivity of around 50% was observed at 2 MPa of oxygen pressure, 150 °C and 1 wt% initial glycerol concentration during 3h reaction time. In this reaction, glycerol was completely consumed. Phosphomolybdic acid performs as a catalyst to catalyze the oxidation reaction. Results also were attributed to the selective oxidative cleavage of C–C bonds by the vanadium atoms. Ntho et al. [105] investigated the effects of gold catalyst particle size on glycerol oxidation. Using $\text{Au}/\text{Al}_2\text{O}_3$, it was observed that the formic acid was obtained as the major product when Au particles were large up to 20 nm.

Another reactant, which has been utilized for the conversion of glycerol to formic acid, is hydrogen peroxide. A cost-benefit point by selecting H_2O_2 as reactant is that atmospheric pressure is used since the oxidant is liquid. Lin et al. [106] used gold nanoparticles and phosphotungstic acid (PTA) located inside nano channels of mesoporous silica as catalyst in conversion of glycerol to formic acid in the presence of hydrogen peroxide. At 80 °C and 24 h reaction time, selectivity of 79.2% was achieved, with formic acid yield of 26.6%. Kong et al. [107] also investigated using H_2O_2 as the oxidant and different metal (III) triflate-based catalysts. Among metals such as Bi, Ce, Zn, Ag, Y, In, Al, and Sn, aluminum (III) triflate had the highest catalyst performance in conversion of glycerol to formic acid. At conditions of 70 °C and 12 h reaction time, glycerol was consumed completely and formic acid yield of 72% was achieved. Farnetti and Crotti [108] studied glycerol oxidation using H_2O_2 with iron salts. They succeeded to obtain both glycerol conversion and selectivity of formic acid up to 99% by using $\text{Fe}(\text{OTf})_2$ catalyst.

Oxone as another oxidant has been used as well [109], but this reaction showed lower selectivity of formic acid production since the reaction produced more side-products [101].

Glycolic acid or hydroxyethanoic acid (CAS number: 79-14-1) and oxalic acid or ethanedioic acid (CAS number: 144-62-7) are the two most important C_2 oxygenated products derived from glycerol. Oxalic acid is applied in cleaning or bleaching. Glycolic acid is highly soluble in water and has been employed in skincare manufactured goods [110]. The main C_3 products of glycerol oxidation are lactic acid (CAS number: 50-21-5), mostly used for preservation and flavoring; dihydroxyacetone (CAS number: 96-26-4) principally applied as a constituent in tanning products and cosmetic industry; glyceraldehyde (CAS number: 497-09-6), which is an intermediate in carbohydrate metabolism; tartronic acid (CAS number: 80-69-3), which is applied in the reaction of catalytic oxidation with air to produce mesoxalic acid; glyceric acid (CAS number: 473-81-4), as its derivatives are

significant intermediates in reaction of glycolysis; and hydroxypyruvic acid (CAS number: 1113-60-6), an intermediate in metabolism of glycine and serine, and mesoxalic acid (CAS number: 473-90-5).

Table 2. Catalysts used for C₁ derivative by glycerol oxidation and the reaction conditions.

Catalyst	Molar Ratio	Temp. (°C)	Pressure (MPa)	Reaction Time (min)	Formic Acid Yield (wt%)	Ref.
Glycerol + oxygen H ₄ PVMo ₁₁ O ₄₀	Molar Ratio of O ₂ to G -	150	2.0	180	Around 50	[104]
Ru(OH) ₄ / Reduced graphite oxide + FeCl ₃	Excess O ₂	160	0.5	60	Around 60	[92]
Glycerol + hydrogen peroxide Au-phosphotungstic acid/Silica nanoparticles	Molar Ratio of H ₂ O ₂ to G 5:1	80	-	1440	26.6	[106]
Aluminum (III) triflate	10:1	70	-	720	72	[109]
Fe(OTf) ₂ *	11.2:1	21	-	36	98	[108]
Fe(OTf) ₂ + BPA **	11.2:1	21	-	280	92	[108]
Fe(OTf) ₂ + BPA	2.8:1	21	-	90	6	[108]
FeCl ₂	4.2:1	21	-	6	94	[108]
FeCl ₃	4.2:1	21	-	6	96	[108]
Glycerol + oxone NHC–Pd complex	Molar Ratio of oxone to G 1:1	room	-	360	Glycerol conversion 10	[109]

* Tf = trifluoromethanesulfonate, ** bis(2-pyridinylmethyl)amine.

In most of the research, a variety of products have been obtained through glycerol oxidation. Therefore, the selectivity of each product in a mixture is usually reported. Table 3 presents the results of studies on glycerol oxidation reactions using a variety of catalysts. Carretin et al. [111] enhanced the reactivity of the catalysts by increasing the purity of oxygen as the oxidant of the reaction. Pd, Pt and Au nanoparticle catalysts with graphite or activated carbon supports were used for oxidation of glycerol in a batch mode at the temperature of 60 °C and pressure of 1 bar, employing air as oxidant. It was observed that Au catalysts were inactive, and Pd and Pt catalysts generated by-products such as CO₂, HCHO, and HCOOH, which are not favorable. Using pure oxygen instead of air at the pressure of 3 bar enhanced the reactivity and adding NaOH to the reaction led to the elimination of C₁ by-products. They also used Au/activated carbon and Au/graphite with 1 wt.% of Au, 100% selectivity of glyceric acid, and 54–56% conversion of glycerol were achieved, respectively. The most common catalysts used in oxidation of glycerol are Au, Pt, Ag, Pd, and Pb. In a study carried out by Skrzynska et al. [112], noble metals were used as catalysts for pure glycerol oxidation reaction. The alumina was used as a support and Ag (up to 1.13 wt.%), Au (up to 0.98 wt.%), Pd (0.96 wt.%) and Pt (0.95 wt.%) were used as catalysts. Additionally, a comparison was made between applying pure glycerol and the glycerol with impurities. After 2 h of reaction, it was observed that the most efficient catalyst for the reaction using impure glycerol was Au/Al₂O₃ with 50% glycerol conversion loss for the reaction and the selectivity of 80–90% towards glyceric acid. Au/Al₂O₃ catalyst showed the highest activity considering the initial rate of reaction.

Table 3. Performance of different catalysts used in oxidation of glycerol.

Catalyst	Glycerol Conv. (%)	Selectivity (%)							Ref.
		Glycolic Acid	Oxalic Acid	Glyceral Dehyde	Dehydroxy Acetone	Glyceric Acid	Tartronic Acid	Formic Acid	
Pt-Bi/SBA-15 (0.4 wt.% Bi)	63.2	-	-	-	63.3	5.4	-	-	[113]
Ag-Pd/CeO ₂	37.1	44.9	0.0	-	-	25.8	4.8	24.5	[114]
Ag-Au/CeO ₂	43.8	46.2	0.0	-	-	23.3	1.8	25.2	[114]
Ag-Pt/CeO ₂	54.2	51.0	0.0	-	-	18.9	2.7	27.4	[114]
Ag/Al ₂ O ₃	30.0	44.8	0.0	-	-	27.2	0.0	28.0	[112]
Au/Al ₂ O ₃	30.0	20.7	0.2	-	-	60.4	0.9	12.5	[112]
Pd/Al ₂ O ₃	30.0	2.6	0.3	-	-	85.8	5.7	1.0	[112]
Pt/Al ₂ O ₃	30.0	9.9	2.6	-	-	74.0	5.1	8.1	[112]
Pt/C	70.3	8.0	0.0	1.3	9.2	66.4	-	-	[115]
5% Pt-3% Bi/C	74.4	6.6	19.5	0.0	46.5	10.2	-	-	[115]
5% Pt-5% Bi/C	91.5	0.0	39.9	0.0	49.0	5.4	-	-	[115]
5% Pt-7% Bi/C	72.0	14.1	18.6	0.0	38.8	15.6	-	-	[115]
Au-Pt (1:3)/hydrotalcite	57	10	0.5	12	-	72	5	-	[116]
V ₂ O ₅	5	1	0.0	-	-	1	-	22	[117]
Au/V ₂ O ₅	20	4	0.0	-	-	29	1	3	[117]
Ta ₂ O ₅	2	6	0.0	-	-	3	-	2	[117]
Au/Ta ₂ O ₅	13	6	0.0	-	-	6	3	3	[117]
TiO ₂ (P25)	~36	-	-	13	7.5	-	-	8	[118]

The synergistic effect of bi-metallic catalysts has shown higher glycerol conversion and selectivity of some derivatives. The effect of using bimetallic Pt-Cu catalyst in comparison with using Pt over carbon nano tube in glycerol oxidation has been investigated by Ribeiro et al. [119]. Products such as dihydroxyacetone or glyceric acid were obtained from the oxidation reaction of glycerol using Pd and Pt catalysts with carbon nanotube support. Glycerol conversion of approximately 90% and a selectivity of 60–70% towards glyceric acid was obtained in alkali medium. Pt-Cu catalyst and Pt catalyst were compared for a reaction, which produced glyceric acid, dihydroxyacetone and glyceraldehyde, in base-free circumstances when carbon nanotube was used as the support. It was observed that the Pt-Cu catalyst over carbon nano tube (CNT) support showed a higher efficiency than the Pt catalyst over the same support in the oxidation of glycerol. Another study [114] has investigated the performance of synergetic bimetallic catalyst for the glycerol oxidation producing glycolic acid. The effect of metal additives on silver catalyst with CeO₂ support was studied, and it was noticed that addition of 5% platinum to the silver catalyst enhances the catalyst performance with a glycerol conversion of approximately 54% and glycolic acid selectivity of 51% at the reaction temperature of 60 °C after 5 h. This selectivity was the highest among the results of the other side-products including glyceric acid, formic acid, oxalic acid, and tartronic acid.

The effects of acidic/basic sites of support in oxidation reaction of glycerol have been investigated by Xu et al. [116] using Au-Pt catalyst. Several acidic and basic supports such as TiO₂, CeO₂ (acidic supports), MgO and Mg(OH)₂ (basic supports), and amphoteric supports such as Al₂O₃ and hydrotalcite were employed. The products selectivity was affected by the acidic/basic properties of the catalyst support. For catalysts with supports containing more basic sites, glyceraldehyde's selectivity decreased and the selectivity of tartronic acid, glycolic acid, or glyoxalic acid increased. Glyceric acid's selectivity was not affected by the acidic or basic sites of the support. Reaction pH is important to influence the reaction. Primary alcoholic groups are produced in basic circumstances while secondary alcoholic groups are produced in acidic circumstances. Production of glyceraldehyde and tartaric acid occurs at basic pH. Strongly acid pH is favorable for the production of dihydroxyacetone and hydroxypyruvic acid [33].

Augugliaro et al. [118] examined glycerol photocatalytic oxidation using a cylindrical photoreactor under TiO₂ P25 (Degussa) photocatalyst in an aqueous suspension. In photocatalytic reaction, TiO₂ P25 was used as a standard material, which comprises of anatase and rutile phases (ratio of about 4 to 1). The liquid products from glycerol oxidation were formic acid, glyceraldehyde, and 1,3-dihydroxyacetone. Glycerol conversion of 36% was

obtained after 10 h. The highest selectivity of 13 wt.% of glyceraldehyde was achieved from this process.

4.3. Etherification

Etherification is defined as a transformation of glycerol molecules to form polyglycerols. For instance, condensation of two glycerol molecules leads to the formation of diglycerol with linear, branched, or cyclic isomers [120]. Etherification is associated with development of mono-, di-, and tri-tert-butylglycerol ether mixtures [121] as shown in Figure 3. In etherification process, glycerol reacts with alcohols or alkenes to produce branched compounds with oxygen atoms such as tert-butyl ethers, which can be used as fuel additives. Production of fuel additives and the intermediates applied in pharmaceuticals, non-ionic surfactants, and agrochemicals directly through glycerol etherification has made this process appealing among various processes for glycerol conversion [122,123]. Poly-substituted ethers (di- and tri-ethers) are ideal fuel additives because of their potential miscibility with commonly used diesel fuels. When these additives are used in blending with diesel fuels, they make the engine's performance better by reducing the production of suspended matter, carbon dioxide, and hydrocarbons. They also help to decrease the release of unregulated aldehydes [123,124].

A list of some catalysts used in etherification of glycerol has been shown in Table 4. Heterogeneous catalysts used in this reaction might be either acidic or basic. Mostly, acidic catalysts are used in etherification of glycerol due to their fast speed of reaction. This class of catalysts also make higher conversion of glycerol in comparison with basic catalysts. When the reaction takes place with acidic catalysts and in presence of tert-butyl alcohol as the reactant, water is produced as a side product which infers the necessity of catalyst to be active in water [125]. Studies on etherification of glycerol with isobutene and tert-butanol revealed that the reaction with isobutene brought a higher conversion value in various temperatures. Glycerol was fully converted when reacted with isobutene in presence of silica catalysts [33]. Applying sulfonated graphene as the catalyst in etherification of glycerol with isobutene led to complete conversion of glycerol with a high selectivity of nearly 92 mol% of di- and tri-substituted ethers after 7 h [126]. The reaction conditions were temperature range of 333–343 K, catalyst loading of 4 wt.% and isobutene to glycerol ratio of 4 (molar basis). High activity of this catalyst in water makes it suitable for the etherification reaction with tert-butyl alcohol. Miranda et al. [125] used the sulfonated reduced graphene oxide in the reaction of glycerol with tert-butyl alcohol. The highest conversion of glycerol of 77% was obtained with the selectivity of 73% towards MTBG (3-tert-butoxy-1,2 propanediol and 2-tert-butoxy-1,3 propanediol), and 27% towards DTBG (2,3-di-tert-butoxy-1-propanol and 1,3-di-tert-butoxy-2-propanol) after 10 h.

Table 4. Performance of different catalysts used in etherification of glycerol.

Catalysts	Reactant	Time (h)	Glycerol Conv. (%)	Selectivity (%)			Ref.
				Mono Glycerol Ether	Di Glycerol Ether	Tri Glycerol Ether	
SnSO ₄	tert-butyl alcohol	4	~30	~15	0	0	[127]
Sn _{1.5} PW ₁₂ O ₄₀	tert-butyl alcohol	4	~90	~72	~24	~1	[127]
Sn ₂ SiW ₁₂ O ₄₀	tert-butyl alcohol	4	~57	~53	~22	~1	[128]
Sn ₃ PMo ₁₂ O ₄₀	tert-butyl alcohol	8	~71	~71	~28	~1	[129]
Montmorillonite-Al-Pillared	tert-butyl alcohol	6	~86	~75	~0	~25	[130]
Montmorillonite-K-10	tert-butyl alcohol	6	~92	~87	~4	~4	[130]
Montmorillonite-KSF/O	tert-butyl alcohol	6	~95	~83	~10	~2	[130]
Amberlyst-15	Ethanol	4	90	87	5	8	[131]
Amberlyst-15	Ethanol	8	96	65	19	16	[131]
H-Beta zeolite	Ethanol	8	92	71	17	12	[131]
H-ZSM-5 zeolite	Ethanol	8	61	94	4	2	[131]
Sulfonate graphene	Isobutene	7	99.7	7.9	56.4	35.7	[126]
sulfonated reduced graphene oxide	Tert-butyl Ether	10	77	73	27	-	[125]
Cs/ZSM-5	-	8	13	100	0	0	[123]
Cs/ZSM-5	-	24	42	80	20	0	[123]

Utilization of acid zeolites has been investigated by Veiga et al. [132]. The performance of acid zeolite catalysts on etherification of glycerol has been examined with ethyl alcohols and tert-butyl alcohol. It was observed that the catalysts containing Lewis acid and Bronsted acid sites can be efficiently used for this conversion. The catalysts with the best performances showed glycerol conversion of up to 75% with tert-butyl alcohol and 81% with ethyl alcohol. Pinto et al. [131] focused on glycerol etherification with the reactant of ethanol. They used some solid acid catalysts such as zeolites, sulfonic resins, and clays in the etherification reaction of glycerol with ethanol, and the products were mono-glycerol-ethers, di-glycerol-ethers, and tri-glycerol-ethers, which are applied as constituents of biodiesel fuel. The best glycerol conversion and ethyl ether selectivity (96% and 80%, respectively) were obtained using the catalyst of Amberlyst-15 acid resin with the temperature of 180 °C, ethanol glycerol ratio of 3 (molar basis) and reaction time of 4 h.

The selectivity cannot be effectively controlled in glycerol etherification process when an acid catalyst is applied since a mixture of linear or cyclic polyglycerols, a mixture of di- to hexa-glycerol chemicals, are produced [133]. Using a basic catalyst is shown to be more effective than applying acidic catalysts in a reaction with cyclic polyglycerols since there are some drawbacks for the acidic catalysts with this reaction. Some disadvantages include low selectivity and a drop in product quality due to secondary reactions such as dehydration and oxidation leading to intermediate products [134].

In case of using basic catalysts in etherification of glycerol, zeolite catalysts such as ZSM-5, and zeolite type X, Y, and A have been applied by Clacens et al. [123]. When Cs/ZSM-5 was used, selectivities of 80% for diglycerol and 20% for triglycerol were achieved at the temperature of 260 °C and 1000 Si/Me ratio. Si/Al ratio was investigated as a factor in etherification of glycerol reaction using ZSM-5 catalyst and a considerable effect was observed due to the variation in acidity and basicity of the catalyst. Zeolite Y, another form of zeolite, is extensively applied in industry because of its good stability and its ability to accommodate molecules with diameters higher than 1.2 nm [135]. Gholami et al. [134] reported 2 wt.% catalyst as the optimum value for etherification of glycerol. They noticed that increasing the catalyst amount did not improve the product's yield.

4.4. Hydrogenolysis

Hydrogenolysis of glycerol is a reaction in which a hydrogen molecule causes a breaking down (meaning of lysis) of C-C or C-O bonds of glycerol. This process begins with dehydration which includes cleavage of C-O and C-H bonds. This step is promoted by catalysts which contain acidic sites. Lewis acids bring about dehydration at primary hydroxyl groups while Bronsted acids cause dehydration at secondary hydroxyl groups [136]. It is followed by a hydrogenation step in which C-H and O-H bonds are formed and/or another dehydration step occurred.

By hydrogenolysis of glycerol with hydrogen, a variety of products with different number of carbons are produced. The main products are methanol (CAS number: 67-56-1), methane (CAS number: 74-82-8), ethylene glycol (CAS number: 107-21-1), 1,2-propanediol (1,2-PDO) (Propylene Glycol) (CAS number: 57-55-6), 1,3-propanediol (1,3-PDO) (CAS number: 504-63-2), allyl alcohol (CAS number: 107-18-6), acetone (CAS number: 67-64-1), propanal (propionaldehyde) (CAS number: 123-38-6), 1-propanol (CAS number: 71-23-8), 2-propanol (CAS number: 67-63-0), propylene (CAS number: 115-07-1), and propane (CAS number: 74-98-6). Among these products, 1,2-PDO and 1,3-PDO have been investigated in several research studies due to their applications. 1,2-PDO is applied in pharmaceutical, antifreeze and tobacco industries and 1,3-PDO is applied in the production of polymers such as polytrimethylene terephthalate (PTT), numerous polyesters and copolyesters [137].

Transition metals such as Cu, Co and Ni have been active and selective for 1,2-PDO production when used as catalysts of hydrogenolysis of glycerol. The catalysts based on Cu are commonly used for this reaction due to their activity and selectivity for cleavage of the C-O bond [138]. Cost-effective transition metal catalysts have shown high selectivity and yield for 1,2-PDO, while numerous noble metals showed good performances to produce

1,3-PDO. When the reaction is controlled in a way that just one hydroxyl is dissociated, C-C cleavage is prevented and cleavage of the C–O bond occurs, then high values of propanediol yield can be attained. Hence, it is crucial to control the bifunctional properties of a catalyst such as hydrogenation and dehydrogenation function of the metals and the hydrolysis function of acidic and basic sites [139].

Table 5 presents results of studies on glycerol hydrogenolysis reaction using a variety of catalysts. In a study, by Shan et al. [140], Cu catalysts with SBA-15 support were used for hydrogenolysis of glycerol in the liquid phase, and the selectivity of 1,2-propanediol was observed to be about 97%. NaY-zeolite supports were used by De andrade et al. [141], with 20 wt.% metal catalysts of Cu, Ni and Cu-Ni for hydrogenolysis reaction of glycerol in an alkaline condition. The reaction occurred in continuous flow mode for 30 h at a temperature of 260 °C and pressure of 4.6 MPa. Cu-Ni was found as the most effective catalyst to produce 1,2-propanediol. By adding NaOH to the reaction, the yield for 1,2-propanediol could be enhanced. Using glycerol to NaOH ratio of 5 (molar basis) led to glycerol conversion of 96.4% and 1,2-propanediol yield of 31.8%. Pandey and Biswas [142] employed Cu-Ru/MgO catalyst for propylene glycol (1,2-propanediol) production, and it was observed that this product can be produced at high reaction pressures, while atmospheric pressure is more suitable for hydroxyacetone (acetol) production. 6Cu–4Ru/MgO catalyst showed the performance that almost a full conversion and propylene glycol selectivity of approximately 75% at H₂/glycerol ratio of 66.8 (mole basis) under reaction pressure of 0.8 MPa. A novel catalyst of 3Cu/2Zn/1Cr/3Zr was used by Sharma et al. [143] at 240 °C and 4 MPa for the same reaction. Propylene glycol selectivity enhanced to 97% and glycerol was fully converted after 10 h.

Table 5. Performance of different catalysts used in hydrogenolysis of glycerol.

Catalyst	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion of Glycerol (%)	Selectivity			Ref.
					1,2-PDO	1,3-PDO	1-Propanol	
Ni/ γ -Al ₂ O ₃	220	-	5	100	87.0	-	0.1	[144]
Ni/CS-P *	260	-	5	100	0.0	-	71.0	[144]
Ni/CS-P *	260	-	2	100	0.0	-	91.0	[144]
Ni/Y-Zeolite	260	4.5	23–30	95.6	42.9	-	-	[141]
Cu/Y-Zeolite	260	4.5	23–30	71.1	12.6	-	-	[141]
Ni-Cu/Y-Zeolite	260	4.5	23–30	96.4	43.9	-	-	[141]
Cu/SBA-15	230	4	1.5	90.3	97.3	-	-	[140]
Ag/Al ₂ O ₃	220	1.5	10	46.0	96	-	-	[145]
Pt/SiO ₂ -Al ₂ O ₃	220	4.5	24	19.8	32	-	-	[146]
Ru/CeO ₂	180	5	10	85.2	62.7	-	-	[147]
Cu/ZnO	200	2	16	37.0	92	-	-	[148]
Cu/Al ₂ O ₃	220	5	6	61	93.3	-	-	[149]
Cu/MgO	180	3	20	72	97.6	-	-	[150]
Cu/MgAlO	180	3	20	80	98.2	-	-	[151]
Cu-Pd/MgAlO	180	2	10	77	97.2	-	-	[152]
Pt(0.5)-Ir-ReOx/SiO ₂	190	2	17	30	19	-	4.1	[153]
Ir-ReOx/SiO ₂	120	8	36	81	-	46	-	[154]
Pt-WO ₃ /ZrO ₂	170	8	18	86	-	28	-	[155]
Pt/WO ₃ -TiO ₂ /SiO ₂	180	5.6	12	15.3	-	50	-	[156]
Pt/WOx-TiOx	180	5.6	12	18.4	-	40.3	-	[157]
Ir/ZrO ₂ with HZSM-5 **	250	1	2	100	-	-	-	[158]

* Phosphorous-impregnated carbon composite, ** Gives propene selectivity 85%.

Some noble metal-based catalysts such as Pt-Re and Pt-WO_x have shown to be effective for the production of 1,3-propanediol [139]. Catalysts containing Pt, WO_x and Al₂O₃ were used for glycerol hydrogenolysis, and it was observed that Pt and W content have significant effects on the yield of 1,3-propanediol and the highest yield of 28.4 wt.% was obtained at Pt/W ratio (molar basis) of 6/12.9 [159]. Different supports such as C, CeO₂, TiO₂, Al₂O₃, ZrO₂, and MgO were also employed with Ir-ReOx catalyst to produce 1,3-propanediol through glycerol hydrogenolysis and it was observed that 1,3-propanediol productivity depended on the metal loading. Ir loading of 6 wt.% with 6 m²/g rutile TiO₂ support demonstrated the highest catalyst activity [160].

Two main drawbacks of the process are the batch mode of the reaction and a high pressure of hydrogen, which is required to attain an acceptable performance in terms of conversion and selectivity [161]. Furthermore, hydrogen is available at refineries and is produced from fossil fuel sources. Another drawback is the potential hazard of using hydrogen due to its flammability and diffusivity at high pressures. Two methods of hydrogen production are glycerol reforming in aqueous phase and catalytic transfer hydrogenation by hydrogen donors. In situ production of propanediol from glycerol and hydrogen is discussed in a review by Martin et al. [137].

Allyl alcohol is another value-added product derived from hydrogenolysis of glycerol. This product can be obtained from acrolein hydrogenation [136] as well as from glycerol transformation and dehydration of both 1,2-propanediol and 1,3-propanediol [162]. 1,2-propanediol dehydration leads to production of acetone, propanal, and allyl alcohol. When an acid catalyst is applied for 1,2-propanediol dehydration, propanal would be the major product. One limitation in production of allyl alcohol is its hydrogenation into 1-propanol in presence of hydrogen gas. Therefore, a hydrogen transfer reaction with mono alcohol or acids, which are H donors, are used in place of hydrogen gas for production of allyl alcohol from glycerol. For example, Arceo et al. [163] used formic acid H donor in hydrogenolysis of glycerol and obtained the allyl alcohol yield of 89% at 230–240 °C. Formic acid also played a role as the catalyst in this reaction.

Propylene (also called propene) is another value-added product of glycerol, which can be synthesized by dehydration of both 1-propanol and 2-propanol. This product is extensively applied in petrochemical industry [162] and its synthesis from renewable resources is not studied well. There is not much research on producing this product from glycerol hydrogenolysis. Mota et al. [164] studied preparation of green propene using metallic catalysts with supports in the reaction of glycerol and hydrogen. The conversion was approximately full, and the selectivity was reliant on the catalyst composition. When activated carbon was used as a support, Ru and Ni/Mo catalysts majorly produced propane, Pd majorly produced methane/ethane and Zn/Mo and Cu/Mo catalysts on activated carbon brought about production of oxygenated intermediates. Fe/Mo catalyst with activated carbon support showed up to 90% propene selectivity. This formation might be due to weak reducibility of iron-molybdenum catalyst.

4.5. Esterification

Esterification is a chemical reaction in which two reactants form an ester as a reaction product. Generally, any reaction between glycerol and a fatty acid, counts as an esterification reaction which can lead to produce monoglycerides, diglycerides, and/or triglycerides. Monoglyceride can also be obtained from triglyceride by glycerolysis reaction via base catalysts or enzymes or methyl ester and glycerol trans-esterification reaction. This product is a good surfactant and can be employed in pharmaceutical, food and cosmetic industries [165]. It is possible to convert waste oils to distilled fatty acids through two process steps: splitting and distillation. The product can be employed for synthesis of value-added products via esterification of glycerol [166]. Oleic acid, acetic acid and lauric acid are some of the fatty acids which have been used in esterification [167,168]. The structures of the products are shown in Figure 3.

Biocatalysts, multivalent metal catalysts, acidic and basic catalysts have been mostly used for glycerol esterification [169]. Table 6 presents results of studies on glycerol esterification reaction using a variety of catalysts. Corma et al. [170] examined the effect of using Lewis acid catalyst and Brønsted basic catalyst on the yield of monoglycerides in this reaction. It revealed that the yield of monoglycerides was 60% by using Lewis acid catalyst, while it improved to 80% by changing the catalyst with Brønsted basic catalyst at the same conditions.

Table 6. Performance of different catalysts used in esterification of glycerol.

Catalyst	Reactant	Acid/Glycerol Ratio	Temp. (°C)	Time (h)	Glycerol Conv. (%)	Selectivity (%)			Ref.
						Mono	Di	Tri	
Glycerol-based carbon catalyst	Acetic acid	1:3	110	3	99	-	88	≈5	[171]
Layered double hydroxide of MgAlCO ₃	Oleic acid	2:1	180	2	≈63	≈51	≈44	≈5	[172]
Layered double hydroxide of MgAlCO ₃	Oleic acid	3:1	140	2	≈56	≈88	≈10	≈0	[172]
MgAlCO ₃	Lauric acid	3:1	180	2	99	90 mono- and di-laurine		-	[173]
HPW/SBA-15	Lauric acid	1:4	160	6	70	50	-	-	[174]
ZnO/Zeolite	Oleic acid	1:4	150	6	85	70	-	-	[165]
Sn-EOF (Organic framework)	Oleic acid	1:1	150	20	40	98	-	-	[175]

Several studies have focused on the catalysts containing metal oxides/salts for this reaction. Bombos et al. [176] made a comparison for catalysts including zinc oxide, tin (II) oxide, and ferrous oxide. Zinc oxide was observed as the most likely catalyst for glycerol and oleic acid esterification. Nevertheless, there is a leaching problem for zinc oxide powder. Since Zn particles were leached in the solution, Singh et al. [165] used ZnO on a zeolite support to prevent the leaching. Oleic acid esterification led to monoglyceride selectivity of 70–80% and the conversion of 60–90%. When zeolite was used as a support, less leaching of metal catalysts is observed compared to alumina and silica supports [177]. In another study [175], Sn leaching was successfully controlled by keeping the oleic acid at lower amount in the initial mixture. A Sn–organic framework catalyst was employed in esterification of glycerol in the presence of oleic acid. The catalyst acted highly selective towards mono-glyceride with 98% selectivity at oleic acid conversion of 40% at the reaction condition of 150 °C for 20 h.

Hamerski et al. [172] examined the effect of reaction temperature while using layered double hydroxide catalysts for glycerol esterification. It was revealed that at higher temperature (180 °C), a darker product was achieved and glycerol conversion and product selectivity (in order of mono-, di, and tri-olein) were higher in comparison to that of lower temperature (160 °C). Esterification reaction of glycerol without using a solvent has been investigated in some research [173,178]. Hamerski and Corazza [173] tried esterification of glycerol with lauric acid using a layered double hydroxide, Mg-Al-CO₃, as the catalyst in absence of solvent. The reaction was carried out under the conditions of temperature between 100 to 180 °C, lauric acid/glycerol molar ratio (1:1 to 3:1) and catalyst amount of 2 to 8 wt%. A high glycerol conversion of 99% was obtained for the reaction, and the product was monolaurine and dilaurine. Ahmad et al. [179] claimed that in transesterification reactions, those reactions, which are carried out without a solvent, showed higher reaction rate in comparison with those using the solvents with low methyl ester solubility, which makes the reaction slower.

4.6. Dehydration

Glycerol dehydration is a reaction in which one or more water molecules are removed from glycerol structure. It is possible to selectively convert glycerol to acrolein (CAS number: 107-02-8) or acetol (hydroxyacetone) (CAS number: 116-09-6) through dehydration reaction using appropriate catalysts and reaction conditions. Besides acrolein and acetol, which are commercially key compounds, dehydration of glycerol also produces acrylonitrile (CAS number: 107-13-1) and acrylic acid (CAS number: 79-10-7) [180]. Acrolein is applied as a source of polyester fibre production as well as its application as an herbicide and a detergent [179]. Acrolein can also be employed as an intermediate or chemical reactant to synthesize materials such as methionine, acrylic acid, esters, propanol, allyl alcohol, and propanal [181]. Acetol is another value-added product which is a source compound for 1,2-propanediol. This chemical is environmentally friendly and reactive, has a wide range of applications due to its hydroxyl and carbonyl functional groups. Some applications include solvent usage, hydrogen production industry and textile industry [180].

At dehydration of glycerol, heterogeneous catalysts such as oxides and mixed oxides, as well as liquid catalysts such as mordenite, are commonly used. Some of different catalysts used in dehydration of glycerol are listed in Table 7. A study has been carried out by Stosic et al. [182] on the effect of varying Ca/P ratio (1.39 to 1.77) in calcium phosphate catalyst during dehydration reaction of glycerol. They observed that changing the Ca/P ratio influences the acidic and basic properties of the catalyst. Their investigation revealed that for selectively production of acrolein, the catalyst needs to have more number and higher strength of acidic sites and the amount of by-product (acetol) increase as the basic sites rise. To increase the number of acidic sites of the catalyst and gain benefit from this fact to increase acrolein yield in dehydration reaction, Garcia-Sancho et al. [183] investigated the effect of phosphoric acid treatment on the performance of Nb₂O₅ catalyst with zirconium doped silica support (Si/Zr = 5). The molar ratio of Nb/P varied between 0.1 and 1. Characteristic tests revealed the presence of zirconium hydrogen phosphate on the surface of the catalyst which enhanced the stability of the catalyst and the yield of acrolein production as well, because of the acidic sites. The best result of this study was 74% of acrolein selectivity at 350 °C. Another study [181] investigated conversion of glycerol to acrolein through dehydration reaction by hiring three catalysts using zeolite-Y including HY, LaY, and Pd/LaY. The activity analysis of the catalysts was carried out in the presence of hydrogen, and it was observed that both glycerol conversion and acrolein yield were enhanced with La ions exchanged in the zeolite-Y. With the reaction progress for 3 h, glycerol conversion was constant because of the presence of Pd metal and hydrogen gas in the feed. Since the reaction is exothermic below 480 K, acetol production was favored and a complete conversion was obtained. At the temperatures higher than 480 K, more energy is consumed in the system which promotes acrolein generation with a maximum concentration at the temperature of 600 K. As given in Table 7, temperature range of 200–320 °C is suitable for dehydration reaction of glycerol to produce acrolein. Temperature lower than 200 °C is needed for production of acetol.

Table 7. Performance of different catalysts used in dehydration of glycerol.

Catalyst	Temp. (°C)	Reaction Time (h)	Glycerol Conv. (%)	Selectivity (%)		Ref.
				Acrolein	Acetol	
Al ₂ O ₃ -PO ₄	280	10	100	42	23	[184]
TiO ₂ -PO ₄	280	10	98	37	30	[184]
SAPO-34	280	10	59	72	6.8	[184]
Ca/Ca ₁₀ (PO ₄) ₆ (OH) ₂	350	1.5	85	9	22	[182]
P/Ca ₁₀ (PO ₄) ₆ (OH) ₂	350	1.5	97	35	19	[182]
Zr	325	2	91	25	5	[183]
ZrNb	325	2	80	36	8	[183]
ZrNbP _{0.2}	325	2	100	56	10	[183]
WO ₃ /ZrO ₂ at SiC	250	-	100	71.1	8.1	[185]
30 wt% HPW/MSU-x	300	4	100	69.5	7.5	[186]
30 wt% HPW/SBA-15	300	4	100	61	4.5	[186]
nanosheet MFI zeolite (Si/Al = 30)	320	8	98.3	82.8	8.4	[187]
nanosheet MFI zeolite (Si/Al = 50)	320	4	99.8	85.4	4.9	[187]
SiCuCr ₄₀ -Ce ₅	200	3	98.6	-	60.35	[188]
Hydrotalcite type-M ²⁺ /M ³⁺ = 4	240	1–9	6.9	-	39	[189]
5.0% Cu-Hydrotalcite type-M ²⁺ /M ³⁺ = 4	240	1–9	64.1	-	52.2	[189]

A sample for observing the effect of acidity is Suprun et al.'s work [184]. They compared the performance of aluminum oxide and titanium oxide supports, which are modified by phosphates, with SAPO-34 catalyst. They expressed that the selectivity of acrolein as a product and glycerol conversion are dependent on the amount of acidity and the textural properties of the catalyst. The first couple of catalysts have relatively lower acidity amount (170 μmol NH₃/g for Al₂O₃-PO₄ and 150 μmol NH₃/g for TiO₂-PO₄), and

acidity of SAPO-34 was 280 $\mu\text{mol NH}_3/\text{g}$. It was observed that higher natural acidity of catalyst lead to higher acrolein selectivity and lower acetol selectivity. It is noteworthy to mention that glycerol conversion in $\text{Al}_2\text{O}_3\text{-PO}_4$ and $\text{TiO}_2\text{-PO}_4$ was nearly complete, while it was 59% by using SAPO-34. Production of acrolein through glycerol dehydration can take place in liquid or gas phase; but it seems that in both, the major obstacle in the industrial manufacture pathway is the fast deactivation of the catalysts by carbon deposition [190].

The production of acetol, another product of glycerol dehydration, has been investigated by Basu et al. [188]. CuCr catalyst over silica support was promoted by different amount of cerium. It has been reported that $\text{SiCuCr}_{40}\text{-Ce}_5$ catalyst showed the highest acetol selectivity (60.4%). It seems that Ce promotion caused higher glycerol conversion, lower reaction temperature and more acetol selectivity. Pathak et al. [191] examined some acid catalysts for dehydration of glycerol at 380 °C. The maximum product of acrolein, around 25/100 g feed, was obtained by using γ -alumina, while using silica-alumina led to maximum amount of acetaldehyde product, almost 24.5/100 g feed. The highest amount of acetol (14.7/100 g feed) and formaldehyde (9/100 g feed) was achieved with the catalysts of HY and silica-alumina, respectively.

5. Industrial Prospects and Barriers

The market price of glycerol is dependent on the supply. The downward trend of glycerol price is caused by the growth of biodiesel plant in which glycerol is produced as a by-product [4]. Crude glycerol plays an important role in bio-refining industry based on oilseeds [192]. The glycerol production from biodiesel industry promoted the applications of glycerol in value-added chemicals production, which offset biodiesel production cost and expand the existing market. Utilization of glycerol generated by biodiesel industry will benefit the local and global economy and environment [13]. Glycerol utilization can also change the market of other industries, which relies on the glycerol production [5]. The advancement in glycerol utilization will help to move towards a circular bioeconomy [13].

The economic studies of glycerol purification after biodiesel production indicated that glycerol purification process could reduce wastewater treatment cost and get benefits from glycerol recovery [193]. The potential benefits of conversion purified glycerol to value-added fuel additives, solketal and glycerol carbonate, was evaluated by Chol et al. [194]. In simulation process, solid catalyst Amberlyst-15 and dibutyltin oxide were used for ketalization and carboxylation of glycerol. The simulation results showed the estimated annual revenue (USD 80.36/kg) was higher than annual cost (USD 50.45/kg), and the process was more profitable when more glycerol was converted to solketal and glycerol carbonate. Thus, it's worth investing in extra process of glycerol purification and conversion in addition to a biodiesel plant [194].

Though utilization of crude glycerol for high value product formulation has been widely investigated, these processes are not widely commercialized [13]. Enzyme properties and low product yield and low conversion limit its industrial application in conversion of glycerol. The homogeneous catalysts may cause disposal, recycling, and corrosion problems, which may increase the production cost [25]. The heterogeneous catalyst can be easily recovered and reused; hence intensive research trend to focus on heterogeneous catalyzed process to convert glycerol to value added products. The deactivation of some heterogeneous catalysts limits their utilization. Thus, the reusability and stability must be further improved for industrial application. The reusable heterogeneous catalysts with high stability and capacity during the reaction process are highly desirable in industry. The reusability is generally studied for heterogeneous catalysts. The anhydrous trisodium phosphate catalyst was repeatedly used for nine cycles without deactivation in glycerol carbonate synthesis from glycerol and dimethyl carbonate [65]. The preserved crystalline phase after the nine times indicated high structural stability of trisodium phosphate catalyst. Transesterification of glycerol over Mg-Al hydrotalcites catalysts was studied by Zheng et al. [64]. The catalyst activity decreased slightly but can be maintained by regeneration after each experiment. $\text{ZnO/La}_2\text{O}_3$ mixed oxides, catalysts used in the production

of glycerol carbonate from glycerol, can be fully regenerated by calcination [63]. The catalyst HSiW/ZrO₂ was used for acetylation of glycerol, and the catalytic activity remained constant for all the cycles [195]. The heterogeneous Ti-SBA-15 catalyst was used to convert glycerol to glycerol carbonate, and the reusability study showed that this catalyst was stable and economically feasible [84]. The transformation of glycerol to valuable products by appropriate heterogeneous catalysts has commercialization potential [84]. To be reused with constant activity, various methods such as solvent wash, oven drying and calcination were developed to regenerate the above-mentioned catalysts [25,63,64,195]. In general, deactivation problem caused by leaching, harsh conditions, or contaminants deposition in activity sites need to be considered in design of catalysts. Effective and simple regeneration need to be developed for glycerol conversion catalysts to enhance feasibility and economic viability in industry. The transformation of glycerol to valuable products by appropriate heterogeneous catalysts, which have low leaching and high stability and can be easily recovered, is promising and competitive for industrialization.

The price of crude glycerol is much lower than that of purified glycerol. Direct conversion of crude glycerol to value-added products seems to be more cost-effective. The glycerol transformation commercialization might be limited by the high price of pure glycerol. Currently, crude glycerol instead of purified glycerol was studied to be directly converted to various value-added derivatives [196–198]. However, the yield, selectivity and catalysts performance need to be improved. The production cost, feedstock quality, followed by separation and purification need to be considered [26]. The viability of crude glycerol conversion to value added products still needs to be enhanced [33].

6. Discussion on the Products

Applications of biofuels as an alternative for fossil fuels has attracted attentions to reduce carbon dioxide emission and its subsequent global warming. An increase in demand for biodiesel has led to the production and accumulation of glycerol, which is a high value commercial chemical with a verity of applications in personal care and pharmaceutical products, chemical industry, textile industry, food industry and food supplements for animals. There are numerous chemical products which can be produced by the conversion of the excess produced glycerol. Being a molecule with three hydroxyl group gives a valuable opportunity to be converted via carboxylation, oxidation, etherification, hydrogenolysis, esterification, and dehydration as the most important processes.

The main product of glycerol carboxylation is glycerol carbonate. There are many carbonate source materials which have been considered to react with glycerol to produce glycerol carbonate. Important factors such as accessibility and price, being eco-friendly, reaction conditions and reactivity lead to select a reactant for this reaction. In reaction with carbon dioxide, the main by-product is water, so, using two dehydrators is common: acetonitrile and 2-cyanopyridine. The reaction with carbon dioxide needs high pressure, while using urea needs a slight vacuum to remove gaseous by-product, ammonia. Dimethyl carbonate is the most frequently used chemical in recent decades to react with glycerol and produce glycerol carbonate, because of its relatively low price and mild reaction conditions. Among heterogeneous catalysts, which have been used to produce glycerol carbonate with any carbonate source, metal oxides and mixed metal oxides have shown relatively better results due to their co-existence of acidic and basic sites on the catalyst. Glycerol oxidation takes place when glycerol reacts with oxygen or hydrogen peroxide as the main oxidant. In the reaction with oxygen, medium to high pressure is needed. The most common catalysts using in glycerol oxidation are Au, Pt, Ag, Pd, and Pb. Bimetallic catalysts have shown higher conversion of glycerol during the reaction. Products' selectivity is highly affected by the feature of acidic or basic nature of the catalyst. For catalysts with higher number of basic sites, the selectivity of glycolic acid, tartronic acid, or glyoxalic acid increase, while the selectivity of glyceric acid is not affected by acidity or basicity of the catalyst.

Reaction pH is another important factor, which affects the formation of intermediates of the reaction. Primary alcoholic groups are formed in basic conditions, while secondary

alcoholic groups are produced in acidic circumstances. Production of glyceraldehyde and tartaric acid occurs at basic pH. Strongly acid pH is favorable to produce dihydroxyacetone and hydroxypyruvic acid. Etherification of glycerol occurs when glycerol reacts with alcohols or alkenes. Reaction with isobutene bring higher conversion compared with tert-butanol.

Products from etherification reaction are mono-, di-, and tri-glycerol ethers. Generally, using acidic catalysts in etherification reaction leads to faster reaction and higher conversion, but low selectivity; in contrast, by using basic catalysts, the reaction will be slower, but have more selectivity. Hydrogenolysis of glycerol occurs when hydrogen reacts with glycerol, and advances to a variety of products. Two of the most important ones are 1,2-PDO (propylene glycol) and 1,3-PDO. Most transition metals such as Cu, Co, and Ni have been active for production of propylene glycol, while noble metals such as Pt have shown better performance in 1,3-PDO synthesis. The common reaction condition from these studies is the temperature range of 120–260 °C, and high pressure up to 50 atm. Due to flammability and diffusivity of hydrogen under high pressure condition, H donors such as formic acid may be used instead of hydrogen.

Esterification of glycerol occurs while glycerol reacts with oleic acid, acetic acid, or lauric acid. The products classify in three groups: mono-, di-, and tri-glycerides. Most of the studies in this review show the temperature range of 110–180 °C. It has been observed that with increasing the temperature, more glycerol conversion can be achieved. Additionally, hiring basic catalysts lead to more monoglyceride selectivity. Metal and mixed metal oxides are common catalysts which have been used for this reaction. Leaching, as the main problem, has been solved to some extent, by using supports or keeping the amount of the reactant to a lower concentration.

Two main products named acrolein and acetol are produced during glycerol dehydration. Generally, temperatures less than 200 °C are suitable for synthesis of acetol, and the range of 200–320 °C shows better results of acrolein production. On the other hand, higher catalyst acidity results in higher acrolein selectivity and lowers conversion of glycerol. The opposite works for acetol, means lower catalyst acidity leads to higher acetol selectivity and higher glycerol conversion.

7. Conclusions

The surplus of crude glycerol due to the expanding biodiesel production makes it urgent to explore alternative applications of crude glycerol. Glycerol is an appealing feedstock employed in the production of value-added chemicals. Conversion of waste glycerol is a favorable way to produce value-added products as well as overcome the problem of accumulation of glycerol, as the bottleneck of biodiesel production process. There are some major categories of the conversion of glycerol for instance carboxylation, oxidation, etherification, hydrogenolysis, esterification, and dehydration, based on the changes which are applied to the structure of the glycerol molecule, which are studied in detail in this review.

Heterogeneous catalysts play a crucial role to enhance the yields of the desired products along these reactions. Different factors of the catalyst such as the amount of acidity or basicity, the catalyst phase, surface area, and catalyst synthesis parameters, must be adjusted for production of the specific desired outcome. For instance, metal oxide and mixed metal oxide catalysts have shown better performance towards the production of glycerol carbonate, and esterification reaction of glycerol. Precious metal catalysts have mostly shown better performance in glycerol oxidation rather than other catalysts, while noble metals are favorable to produce 1,3-PDO, and transition metals showed better functioning towards the production of propylene glycol. Strong basic catalysts are more suitable to produce glycolic acid, tartronic acid, glyoxalic acid or monoglyceride, while moderate basic ones are appropriate for glyceraldehyde production. Hydroxypyruvic acid and dihydroxyacetone have shown more yield in presence of strong acidic catalysts. Acidic catalysts are also favorable in etherification of glycerol since they provide more glycerol conversion.

The heterogeneous catalysts have been widely studied for glycerol conversion to value added products. Their performances are acceptable, and they are easy to be separated and reused. However, the direct conversion of crude glycerol by heterogeneous catalysts needs more effort to be enhanced. Expanding the areas of glycerol and crude glycerol consumption will help to have more circular bioeconomy. It can also affect the market of other industries, which are dependent to glycerol as their feedstock.

Author Contributions: P.K.: Conceptualization, methodology, validation, investigation, formal analysis, resources, data curation, writing original draft preparation. Q.H.: Conceptualization, methodology, validation, investigation, resources, data curation, writing original draft preparation. A.K.D.: Conceptualization, writing—review and editing, supervision, project administration, funding acquisition. R.S.: writing—review and editing, supervision, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Canada Research Chair (CRC) Program and Natural Sciences and Engineering Research Council of Canada (NSERC), and Agriculture Development Funds (ADF#20190145).

Acknowledgments: The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chairs (CRC) program, and Agriculture Development Funds (ADF#20190145) for supporting this research. The first author is also thankful to the university of Saskatchewan for awarding the Dean's scholarship for the graduate program.

Conflicts of Interest: The authors declare no conflict of interest.

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