

Review

An Overview of Recent Research in the Conversion of Glycerol into Biofuels, Fuel Additives and other Bio-Based Chemicals

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Abstract: The depletion of fossil fuels has heightened research and utilization of renewable energy such as biodiesel. However, this has thrown up another challenge of significant increase in its byproduct, glycerol. In view of the characteristics and potentials of glycerol, efforts are on the increase to convert it to higher-value products, which will in turn improve the overall economics of biodiesel production. These high-value products include biofuels, oxygenated fuel additives, polymer precursors and other industrial bio-based chemicals. This review gives up-to-date research findings in the conversion of glycerol to the above high-value products, with a special focus on the performance of the catalysts used and their challenges. The specific products reviewed in this paper include hydrogen, ethanol, methanol, acetin, glycerol ethers, solketal, acetal, acrolein, glycerol carbonate, 1,3-propanediol, polyglycerol and olefins.

Keywords: biodiesel; glycerol; biofuels; oxygenated fuel additives; chemicals; catalysts

1. Introduction

Since the beginning of the industrial revolution, fossil fuels have been the major source of energy and industrial chemicals. At any point in time, the yardstick for development of any country has been attributed to the level of consumption of fossil fuels. It is becoming clearer that fossil fuel reserves are finite in nature. The International Energy Agency (IEA) forecasted that the world maximum oil production will be attained between 1996 and 2035 [1,2]. Some experts have predicted that the current oil may completely be depleted by 2050 [3]. The finite nature, coupled with the challenges of the skyrocketing cost of conventional oil, global warming, and other environmental pollution problems, has led to the current in-depth research into the use of alternative fuels that are renewable and sustainable [4,5].

Renewable energy sources such as solar, wind, geothermal and biomass are considered to be viable alternatives to conventional oil [2]. However, energy from biomass is considered to be more sustainable, especially for the transportation sector. Biofuel is a general name for fuels from biomass, which include bioethanol, biodiesel, biomethanol, biogas, biohydrogen, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), synthetic biofuels (hydrocarbons) and bio-oil (vegetable) [6–8]. Of all the biofuels, biodiesel is the most researched and it is still work in progress despite the level of its development. This enormous interest by researchers, industrialists and governments worldwide may not be unconnected with the inherent advantages. It is biodegradable,



nontoxic, and renewable, has high cetane number, in-built oxygen content, higher combustion without or with low sulfur, aromatic components and other regulated emissions, complete carbon cycle, and availability of raw materials, and fits into existing engines with little or no modification and with a high flash point [9,10].

Biodiesel is a monoalkyl ester of fatty acids obtained from vegetable oil or animal fat through esterification or transesterification reaction with alcohol in the presence of catalyst. This has been reported by several authors [11–15]. Specifically, it is a reversible reaction involving triglyceride with methanol (most commonly) or ethanol (less commonly) in the presence of NaOH, KOH or H_2SO_4 as catalyst. The reaction is shown in Scheme 1. The use of sodium or potassium methoxide (CH₃ONa or CH₃OK) as catalyst has recently become more preferred. This is to substantially minimize or avoid the moisture content associated with biodiesel production [9].



Scheme 1. Conversion of glyceride to biodiesel and glycerol.

To complement the already-dwindling petroleum products, developed countries have responded to the production and use of biofuels, especially with the directive of European Union (EU) that conventional fuels should have an addition of at least 5.75% biofuels by 2010, with the possibility of increasing it to 20% by 2020 [8]. The foregoing directive, in addition to the compliance with the Kyoto Agreement that member nations should reduce the level of CO₂ emission to below 8% of 1990 level by 2012, has sharply increased the production of biodiesel [16]. Efforts by the EU can be seen from the available data from various sources. Biodiesel production in EU member countries was put at 1.93 million tons in 2004, and after ten years, in 2013, it was put at 10.37 million tons, moving up to 11.58 million tons in 2016, with Germany and France taking the lead [17]. Figure 1 presents a pictorial representation of EU biodiesel production for the period 2004 to 2016, indicating the capacity and actual growth pattern. Similarly, the United States biodiesel production grew from 0.5 million gallons in 1999 to 250 million gallons in 2006 [18], and later to 2.89 billion gallons in 2016 [19]. Figure 2 shows the US biodiesel growth pattern from 2006 to 2016. However, the global status report 2016 [20] indicates that in 2015, the world biodiesel production was 30.1 billion liters, with the United States, Brazil, Germany, France and Argentina being the top five producers. The biodiesel global production of the top 16 countries in 2015 is shown in Figure 3. Some of these countries have already made it mandatory through legislation to have an addition of 2-5% biodiesel to the existing conventional diesel, as stipulated by the EU [3,21]. However, this directive has been reviewed more recently. EU member countries are to ensure that energy from renewable sources forms at least 10% of the transportation fuels by the year 2020 [22]. This is to improve energy efficiency and reduce greenhouse gas emission. It has also been reported in several works that biodiesel production will soar in the coming years and this is evident from the series of diversified global research activities in boosting biodiesel production both in the areas of feedstock and catalysis. On feedstock, research is focused on the use of edible, non-edible and waste oils [23–25]. Recent reviews have shown that more than 350 oil-bearing crops are potential feed stocks for biodiesel production [26,27]. Meanwhile, with regard to catalysis, research is now focused on the use of heterogeneous solid catalysts (acid and base) and enzymes [28,29].



Figure 1. EU biodiesel production for the period 2004 to 2016 [17].



Figure 2. United States biodiesel growth pattern for the period 2006 to 2016 [19].



Figure 3. The biodiesel global production of the top 16 countries in 2015 [20].

Despite the diversification of research in biodiesel production, the cost is still not favorable when compared to conventional fuels. It was reported that the cost of biodiesel unit price is 1.5–3.0 times higher than that of petroleum-derived diesel fuel, depending on the type of feedstock used [30]. In addition, the high production of biodiesel produces large volumes of waste, with glycerol as the major product. It has been reported in various literature that 10–20% of the total volume of biodiesel produced is made up of glycerol. That is, for every 100 kg of biodiesel produced, 10 kg of glycerol is generated [31,32]. The growing biodiesel production will definitely lead to an excess supply of glycerol, which has been described as having a low commercial value because of its low quality [33]. There are also social and environmental concerns when discarded without adequate treatment; hence,

a lot of research is focused on the conversion of glycerol into high value and useful products. This, in the view of researchers and industrialists, will enhance the economics of biodiesel by lowering its cost of production. The versatility of glycerol is well known in view of its applications in almost all the fields of human endeavors [34,35], as indicated in Table 1. However, for glycerol to be used in food, pharmaceutical, cosmetics and other personal care industries, it must be pure. Unfortunately, the purification process, which involves filtration, chemical treatment and vacuum distillation, is expensive, especially to the small and medium production plants, and therefore not commensurate with its current low market value [21,36]. It is, therefore, not surprising that great attention has recently been directed towards the utilization of crude glycerol or partially-treated raw glycerol in the production of higher-value products. This is expected to promote integrated biodiesel and other chemical production which concept is now known as biorefinery. There are several recent reviews showcasing some of these conversions [35,37–40]; however, some of them are on certain products via bioconversion, while some have emphasized the reaction type or the nature of the glycerol used.

The present review, in addition to providing up-to-date findings of research outcomes, places emphasis on products with applications directed at non-personal care areas, such as biofuels, oxygenated fuel additives, polymers and some industrial bio-based precursor chemicals, with special focus on the performance of the catalysts and techniques used for such conversions. Figure 4 illustrates the applications of the products reviewed in this paper.

Medical, Pharmaceutical and Personal Care Industries	Food Industry	Automotive and Chemical Industries	Other
Cough syrups, expectorant and elixirs Mild laxative Allergen treatment Plasticizer Lubrication Flavor Additive Toothpaste Mouth washers Skin and hair care Moisturizer Softener Soap	Humidifier/Humectant Flavor Solvent Emulsifier Antioxidant Lubricant Sweetener Preservation Thickening agent	Antifreeze hydraulic and lubricating agents Tannins prevention Alcohol free alternatives Preserving agent Explosives Synthesis of resins and many compound Polymers and fuels	Denitrification Enzymatic reagents Cryoprotectant Animal feed

 Table 1. Industrial applications of glycerol [31,35,41].



Figure 4. Applications of some glycerol derivatives.

2. Glycerol, Its Uniqueness and Availability

Glycerol (propane-1,2,3-triol) is a sweet-tasting oily liquid discovered in 1779 by Swedish chemist Carl Wilhelm Scheele. It was named 'glycerin' (Greek: glukeros meaning 'sweet') in 1823 by French chemist Michel Eugene Chevreul and was given the formula C₃H₈O₃ in 1855 by Charles-Adolphe Wurtz [42]. When pure, glycerol is water-soluble, clear, almost colorless, odorless, viscous, non-toxic, and hygroscopic, with a high boiling point. Glycerol is a polyhydric alcohol with three hydrophilic hydroxyl groups, each attached to carbon which is responsible for its stable, versatile reactions and applications [43,44]. Some of its major properties are shown in Table 2, as reported by several authors. In the market, there are three categories of glycerol, namely crude glycerol, purified/refined glycerol, and commercially synthesized glycerol. Crude glycerol is of lower purity when compared to the purified and synthesized glycerol. Crude and purified glycerol are products of biodiesel production, while synthesized glycerol is obtained through a different route, commonly from propene [41]. Crude glycerol, unlike purified and synthesized glycerol, cannot be used in sensitive areas such as food, medicine and cosmetics, because of its level of purity (60-80%) [21,39]. Table 3 shows the different categories of glycerol and some of their contents. The composition of crude glycerol varies with the type of catalyst, feedstock employed, the efficiency of the process and the recovery of methanol and/or catalysts used [34]. Several studies have also confirmed this as exhibited in the typical compositions of crude glycerol from different sources [45–47]. Typical composition of different crude glycerol is shown in Tables 4 and 5.

CINI	Proportios	Values Reported by Different Authors				
5/N	rioperties	[44]	[36]	[41]		
1	Form and color	Liquid and colorless	na	na		
2	Formula weight	92.09	92.09	92.09		
3	Specific gravity/Density (20 °C)	$1.260^{50/4}$	1.261 g/cm^3	1.261 g/cm^3		
4	Melting point	17.9 °C	18.17 °C	18.0 °C		
5	Boiling point	290 °C	290 °C	290 °C		
6	Solubility in 100 parts					
	Water	Infinity	na	na		
	Alcohol	Infinity	na	na		
7	Viscosity of liquid glycerol at 100% purity	10 cP	1499 cP at 20 °C	1.410 Pa·s		
8	Difusivity in (DL \times 105 sqcm/s)					
	i-Amyl alcohol	0.12	na	na		
	Ethanol	0.56	na	na		
	Water	0.94	na	$1.33 \times 10{-}11 \text{ m}^2/\text{s}$		
		na	0.0025 mmHg at 50 °C	<0.0001 kPa at 20 °C		
0	Vanour processo	na	0.195 mmHg at 100 °C	0.03 kPa at 100 °C		
9	vapour pressure	na	4.3 mmHg at 150 °C	0.67 kPa at 152 °C		
		na	46 mmHg at 200 °C	6.67 kPa at 204 °C		
10	Refractive index	na	1.474	1.474		
11	Surface tension (20 °C)	na	63.4 dyne/cm	63.4 mN/m		
12	Compressibility (28.5 °C)	na	2.1×10 MPa	$2.1 imes 10^{-4}~\mathrm{MPa}$		
12	Heat of vaporization	na	21,060 cal/mole at 55 °C	88.2 KJ/mol		
15	rieat of vaporization	na	18,170 cal/mole at 195 °C	76.1 KJ/mol		
14	Heat of formation	na	159.6 Kcal/gm mole	-669 KJ/mol		
15	Heat of combustion	na	1662 KJ/mole = 18.05 MJ/kg	-1662 KJ/mol		
16	Heat fusion (18 °C)	47.49 cal/g	18.3 KJ/mole	18.3 KJ/mol		
17	Heat of solution	na	na	−5.8 KJ/mol		
18	Thermal conductivity	na	0.29 w/°K	0.29 W/m/K		
19	Flash point	na	177 °C	177 °C		
20	Fire point	na	204 °C	204 °C		
21	Relative dielectric constant (25 °C)	na	na	42.48		
22	Autoignition temperature on glass	na	na	429 °C		
23	Calorific value	na	na	18 KJ/g		
24	Specific electrical conductivity (20 °C)	na	na	0.1 μS/cm		

Table 2. Physico-chemical properties of glycerol reported by different authors.

na = not available.

S/N	Parameters	Crude Glycerol	Purified Glycerol	Refined/Commercial Glycerol
1	Glycerol content (%)	60-80	99.1–99.8	99.2–99.98
2	Moisture content (%)	1.5-6.5	0.11-0.8	0.14-0.29
3	Ash (%)	1.5-2.5	0.054	<0.002
4	Soap (%)	3–5	0.1-0.16	na
5	Acidity (meq/100 g)	0.7-1.3	0.10-0.16	0.04-0.07
6	Chloride (ppm)	BDL	1.0	0.6–9.5
7	Color (APHA)	Dark	34–45	1.8–10.3

Table 3. Quality parameters of different categories of glycerol (adapted from [48]).

BDL = Below detection limit, na = not available.

Table 4. Elemental analysis of a typical crude glycerol produced in biodiesel industry (adapted from different authors).

					Eler	nent					
Feedstock	C (wt%)	H (wt%)	N (wt%)	O (wt%)	Na (ppm)	K (ppm)	P (ppm)	Ca (ppm)	Mg (ppm)	Fe (ppm)	Reference
na	52.77	11.08	< 0.0001	36.15	na	na	na	na	na	na	[49]
SB oil (1)	24.3	na	0.3	na	11,769	118.8	38.7	BDL	BDL	31.6	
SB oil (2)	44.3	na	0.6	na	19,361	140.5	101.3	8.4	3.7	34.2	[45]
SB oil (3)	46.8	na	0.7	na	19,108	1057	24.7	4	BDL	52.8	[43]
WV oil	54.2	na	0.9	na	16,263	486.2	233.8	20.5	14.2	92.1	

BDL = Below detection limit, SB = Soybean oil, WV = Waste vegetable oil, na = not available.

Table 5. Qualit	y of various cruc	le glycerol from [biodiesel plants b	y different authors
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Feedstock	Glycerol Content (%)	Methanol Content (%)	Moisture Content (%)	Ash Content (%)	Soap Content (%)	рН	Appearance	Reference
Commercial pure glycerol	99.5	na	0.5	0	0	6.7	Colorless liquid	
Crude palm oil	88.56	na	3.41	7.12	0.91	6.68	Dark brown liquid	[4]
RBDP oil (1)	85.2	na	8.11	5.26	1.43	7.73	Dark brown semi solid	[40]
RBDP oil (2)	93.4	na	1.43	3.43	1.74	12.13	Dark brown semi solid	
Mixture of vegetable oils	71.7	25.7	na	na	na	na	na	[50]
SB oil (1)	63	6.2	28.7	2.7	BDL	6.9	na	
SB oil (2)	22.9	10.9	18.2	3.0	26.2	9.7	na	[4]]
SB oil (3)	33.3	12.6	6.5	2.8	26.1	9.5	na	[43]
WV oil	27.8	8.6	4.1	2.7	20.5	9.4	na	
Waste cooking oil	83.4	BDL	11.6	2.7	1.3	na	na	[51]

RBDP = Refined, bleached and deodorized palm oil, BDL = Below detection limit, SB = Soybean oil, na = not available.

Prior to the advent of biodiesel production, glycerol was commonly obtained from fatty acids and soap production, its availability was not commensurate with it demands, hence it had a relatively good market value [38,44]. However, this has now changed. It is believed that since 1995, there has been an oversupply of glycerol in the world market, and the current increase in biodiesel production has further increased the level of glycerol. It has been estimated that by the year 2020, production will be six times higher than demand [41]. It was reported that the worldwide crude glycerol obtained from biodiesel production increased from 200,000 tons in 2004 to 1.224 million tons in 2008 [34]. Garlapati et al. [52] reported that it was forecasted that 4 billion gallons of crude glycerol will be produced as a byproduct of biodiesel by 2016.

From the foregoing, it is clear that the availability of glycerol is not in doubt, in fact, it is generally believed that due to the upsurge in biodiesel production, the glycerol production will continue to grow, hence, the conversion of glycerol into other useful products is timely and of essence due to overall improvement on the economics of biodiesel production.

3. Biofuels from Glycerol

Biofuels may be liquid or gaseous fuels produced from biomass resources to meet energy needs, especially in transportation, electricity and other stationary sectors. These biofuels are considered to be

efficient, biodegradable, non-toxic or less toxic, and free of sulfur and aromatics [53,54]. Reports have shown that many biofuels have been produced from glycerol via different chemical and biological catalysts. Some of them are reviewed below.

3.1. Hydrogen and Syngas

Hydrogen is considered an ideal fuel for the future; as such, it is of intense interest to researchers and industrialists because of its excellent burning ability and its resultant byproduct, water; hence, it is eco-friendly [38,55]. In addition to the -friendliness, hydrogen has extensive applications in industry for the production of ammonia and methanol, and in petroleum processing. It can also be used to generate electricity in gas turbines and fuel cells for portable electronics [56]. Syngas is considered a versatile intermediate, containing a mixture of hydrogen and carbon monoxide. It is a precursor to many important fuels and chemicals such as methanol and liquid hydrocarbons through Fischer-Tropsch synthesis [32].

The conversion of glycerol into hydrogen and syngas follow a similar protocol. In the past, the conversion was carried out via combustion, but the method was found to be uneconomical, unsafe and technically deficient in view of the high temperature used, obnoxious gas emission and complex product composition [18,36,38,57]. On the contrary, reforming methods have gained acceptance by researchers and industrialists in view of its efficiencies. The reforming methods include steam reforming, partial oxidation, autothermal reforming, aqueous phase reforming and supercritical water reforming [38,56,58–60]. The reforming methods essentially follow a similar basic principle, in line with Scheme 2.

$$C_3H_8O_3 + xH_2O + yO_2 \xrightarrow{Catalyst} aCO_2 + bCO + cH_2O + dH_2 + eCH_4 + \dots$$

Scheme 2. Conversion of glycerol to hydrogen and syngas by catalytic reforming.

Steam reforming is carried out in a gas phase (in Scheme 2, x > 0 and y = 0), usually at atmospheric pressure and a temperature of 400 °C or above [61]. Aqueous phase reforming (APR) is done with glycerol in the liquid phase at higher pressures (1.6–4.0 MPa) and moderate temperatures (200–250 °C) [62]. In APR, x = 0 and y = 0 in Scheme 2. When a partial oxidation process takes place in the presence of oxygen x = 0, y > 0 in Scheme 2. Autothermal reforming is the combination of both steam and partial reforming, which involves the trio of fuel, air and water [63]. Therefore, in Scheme 2, x > 0, y > 0. Supercritical water reforming is more recent, and the process is carried out at temperature \geq 374 °C and pressure \geq 22.4 MPa [63–66]. Extensive research on the conversion of glycerol into hydrogen and syngas using the above methods with or without catalyst has been reported. However, it is the general consensus that better and higher yields are obtained in the presence of catalysts particularly transition metal-based catalysts. Some of the recent findings are reviewed below.

Steam reforming of glycerol to hydrogen is the most commonly used method due to simultaneous removal of hydrogen from the water molecule and the resultant high yield from the reaction [59,60,67]. The use of metal-alumina support catalysts in steam reforming has been reported. Demsash and Mohan [68] used the combination of low loading of ceria and nickel ($10Ni/Al_2O_3/5CeO_2$), and were able to achieve high selectivity of H₂ (85.7%) at 650 °C after 16 h of reaction time in a continuous-flow packed-bed reactor. High yield of H₂ has also been reported by several researchers using Pt-doped alumina with other metal oxides such as Pt/La₂O₃/Al₂O₃ and Pt/CeO₂/Al₂O₃ [69,70]. The use of bimetal-metal oxide support catalysts in steam reforming of glycerol has been reported. Sanchez and Comelli [71] investigated the use of 4Ni/Al₂O₃, 4Co-4Ni/Al₂O₃ and 12Co-4Ni/Al₂O₃ catalysts at three different temperatures, 300, 500, and 700 °C, 0.1 MPa, 10 h⁻¹ WHSV, 6:1 WGMR, 0.17 mL min⁻¹ glycerol solution feed flow rate (FFR) and time-on-stream of 8 h. The main product obtained was H₂, which was favored at 300 °C, followed by CO₂, CO and CH₄ in smaller proportions.

Ni supported on ZrO₂, La₂O₃, SiO₂, Al₂O₃ and MgO catalysts prepared by the wet-impregnation method were used in glycerol steam reforming to produce hydrogen [72]. At reaction conditions of

650 °C, water:glycerol molar ratio of 6 and FFR of 1 mL/min, maximum hydrogen selectivity of 75.1% and glycerol conversion of 80% were exhibited by Ni/Al₂O₃ catalyst. The good performance was due to the large surface area, small crystal size and high dispersion of Ni on the alumina support material, while the catalyst stability was attributed to the high basicity. Similarly, fly ash (a solid waste of thermal power plants) impregnated with various amounts of nickel were also used as catalyst in hydrogen production [73]. The catalyst containing 7.5 wt% Ni on fly ash showed highest activity and very good stability resulting in the highest hydrogen yield. A maximum yield of 5.8 mol of hydrogen per mole of glycerol fed was produced at 550 °C with steam:glycerol molar ratio of 12:1, and a space-time of 8.4 kg cat h/k mol of glycerol fed. This resulted in glycerol conversion of 98.6%.

Good results were also reported with an aqueous phase reforming system that did not require pre-vaporization. Özgür and Uysal [74] used Pt/Al₂O₃ as catalyst in an aqueous phase reforming system in an autoclave reactor and a continuous fixed-bed reactor. The optimum temperature and FFR were found to be 230 °C and 0.1 mL/min, while hydrogen concentration in the gas product increased with decreasing glycerol concentration in the feed. At less than 45 wt% glycerol concentration, the hydrogen concentration was about 67%. In another study on Pt-based catalysts supported on different oxides (Al₂O₃, ZrO₂, MgO and CeO₂), Menezes et al. [75] found all the catalysts to be active in hydrogen production. However, the catalysts supported on MgO showed the highest activity in hydrogen production (71.9%), with low concentration of undesired hydrocarbons. Contrary to the above yields, Seretis and Tsiakaras [76] obtained only 14.1% H₂ yield under optimum conditions of 1 g of 5% Pt/Al₂O₃, 1 wt% glycerol solution, 240 °C and 4 h of reaction time. However, high glycerol conversion of \approx 84% was obtained. Other gaseous and liquid compounds were found to be present, such as CO, CH₄, CO₂, acetaldehyde, acetone, methanol, ethanol, 1-propanol, acetol, lactic acid, propylene glycol and ethylene glycol. From the foregoing, it can be seen that the level of H_2 production, as well as glycerol conversion, obtained using aqueous phase reforming were lower when compared to the steam reforming. Aqueous phase reforming also has the challenge of selectivity, in view of the fact that alkane is highly favored due to the low temperature involved. However, aqueous phase reforming is excellent for crude glycerol feedstock because it does not require pre-vaporization of water, thereby saving energy [76]. Table 6 shows the summary of the performance of some catalysts in the conversion of glycerol to hydrogen as recently reported in some literature.

Table 6. Performance of some catalysts in the conversion of	of glycerol to	hydrogen as	reported in some literature
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Catalyst (A)	Operation Parameters	Performance	TOF	Reference
7.5 wt% Ni/Fly ash (10.4)	T = 550 °C, WGMR = 12:1, Cat = 1 g, ST = 8.4 kg cat h/kmol G	GC = 98.6%, Y = 5.8 mol/mol G, S = na	nd	[73]
10 wt% Ni/Al ₂ O ₃ (123.4)	T = 650 °C, t = 5 h, Cat = 0.3 g, WGMR = 6:1	GC = 80%, Y = na, S = 75.1%	nd	[72]
$5\% \text{ Pt}/\text{Al}_2\text{O}_3$ (na)	$T = 240 \degree C$, $t = 4 h$, $Cat = 1 g$	GC = 84%, Y = 14.1%, S = na	2.1	[76]
Ni-Co/Al-Mg (na)	$T = 680 \degree C$, $t = 2 h$, $Cat = 3 g$	GC = 95%, Y = 67 vol%, S = 91%	58	[77]
1.44 wt% Pt/MgO (221)	T = 225 °C, P = 2.3 MPa. t = 3 h, Cat = 100 mg	GC = na, Y = 71.9%, S = na	* 24	[75]
$1 \text{ wt\% Pt/Al}_2O_3$ (na)	T = 230 °C, P = na. t = na, Cat = 2 g, LHSV = 0.73 h ⁻¹	GC = na, Y = 67 mol%, S = na	nd	[74]

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, WGMR = Water Glycerol Molar Ratio, W/LHSV = Water/Liquid Hourly Space Velocity, t = time, GC = Glycerol Conversion, Y = Yield, S = Selectivity, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion/* product yield per gram catalyst per total reaction time (h), na = not available, nd = not determined.

The use of microwave plasma in the gasification of biodiesel-derived glycerol to syngas was investigated by Yoon et al. [78]. The results showed high production of syngas (57% H₂ and 35% CO) and the composition decreased as the oxygen-to-fuel ratio increased. Similarly, co-gasification of glycerol with other biomass to produce syngas with improved yield has been reported by many researchers. Skoulou and Zabaniotou [79] reported syngas improvement from 0.4 to 1.2 Nm³/kg on mixing crude glycerol with olive kernel in a fixed-bed reactor at 750–850 °C. This led to increase in H₂ concentration from 19 to 33% (v/v).

Guo et al. [80] also investigated the supercritical water gasification of glycerol in a continuous flow tubular reactor in the range 487–600 °C and 25 MPa over a short residence time (3.9–9.0 s) over different alkali catalysts (NaOH, Na₂CO₃, KOH and K₂CO₃). The effects of reaction temperature, residence time,

glycerol concentration and type of catalyst on gasification were also studied. Results revealed that gasification was favored by higher temperatures, long residence times and lower glycerol concentration. The alkali catalysts enhanced the water–gas shift reaction, with NaOH being the most active. No char was observed in any of the experiments. In a similar work, Dianningrum et al. [81] studied the effect of different operating conditions (temperature (500–650 °C), concentration (5–20 wt%) and residence time (15–120 min)) on pure glycerol and two different types of crude glycerol in supercritical water gasification. Results showed decreased hydrogen production in all the feedstocks with increase in concentration, and increased hydrogen with increase in temperature and residence time. However, the tar/char was high in crude glycerol when compared with pure glycerol due to the presence of alkali salts. When the authors used the same feedstocks in a continuous reactor at 650 °C, 5 wt% for different residence times, complete gasification was achieved.

It is important to note that the syngas produced can be converted to pure hydrogen via the water–gas shift reaction, as indicated in Scheme 3. Haryanto et al. [82] reported the thermodynamic analysis for upgrading syngas derived from biomass gasification using the minimization of Gibbs free energy function. The results indicate that syngas upgrading to hydrogen was best achieved in a temperature range of 627–827 °C, pressure range of 0.1–0.3 MPa, and at different carbon:steam ratios. As much as 43–124% hydrogen increment can be achieved with negligible methane yield and coke formation, as well as decreased production of carbon dioxide.

$$CO + H_2O \longrightarrow CO_2 + H_2$$



Similarly, the use of partial oxidation and autothermal reforming have been reported in several other works with >70% H₂ yield and >80% glycerol conversion [59,65,83–86].

The use of microorganisms to produce hydrogen has also been studied and reported over the years, and findings have shown enhanced crude glycerol utilization without undergoing the high cost of the purification process associated with having pure glycerol. The use of *Enterobacter* spH1, *Enterobacter* spH2 and *Citrobacter freundii* H3 [87], *Escherichia coli* K12 [88], *Clostridium freundii* H3 [89], *Klebsiella pneumonia* TR 17 [90], *Thermotoga maritime* and *Thermotoga neapolitana* [91] have shown relatively large quantities of H₂ (>70%) under varying conditions. However, the details of microbial hydrogen production are beyond the scope of this review.

3.2. Ethanol

Ethanol is a colorless, flammable oxygenated hydrocarbon [92]. It is a well-known solvent in industry. It is the largest alternative renewable fuel and/or fuel additive for gasoline.

Efforts have been made to synthesis ethanol from glycerol via a chemical route, but production via biological means (fermentation) remains the most common. Typically, ethanol is produced from sugarcane and corn in Brazil and United States, and the argument of food versus fuel has been a limiting factor [92]. Therefore, with the availability of crude glycerol, its conversion into ethanol will drastically eliminate the food versus fuel debate, with the advantage being that it will reduce cost. In fact, Amaral et al. [93] reported that the use of glycerol in ethanol production could reduce the cost by over 35%, when compared with production from corn, and this was confirmed by the work of Posada and Cardona [94], which simulated and economically assessed both the production and purification of ethanol from raw glycerol (60 wt%), crude glycerol (88 wt%) and pure glycerol (98 wt%) using *Escherichia coli*. Results showed that the lowest bioconversion costs were compared with the commercial prices of glycerol and fuel ethanol from corn and sugarcane, the purification cost of raw glycerol was lower than previously reported values due to the methanol recovery.

The fermentation of glycerol using *Escherichia coli* K12 also revealed that a maximum ethanol yield of 0.40 g/g glycerol was obtained when 10 g/L concentration of glycerol was used under membrane headspace conditions [88]. Similarly, Loaces et al. [95] used *E. coli* to improve ethanol production and glycerol conversion using heterologous genes (metagenomic fragment) obtained from anaerobic purge sludge. The LY180 strain carrying G1 fosmid produced the highest concentration (75 g/L) of ethanol at a specific production rate of 0.39 g/h/L after a 24 h fermentation period using 50% crude glycerol dilution. In comparison with other isolates (*Escherichia coli* SS1, *Escherichia coli* BL 21, BW 25113 and *Enterobacter aerogenes* HU101), *E. coli* SS1 gave the highest ethanol yield of 1.0 mol/1.0 mol glycerol, which was found to be higher when glucose was used as substrate [96].

The use of *Klebsiella* strains have also been reported in the efficient conversion of crude glycerol to ethanol. Oh et al. [97] used *Klebsiella penumoniae* mutant, and 21.5 g/L of ethanol was generated with a productivity of 0.93 g/L/h. While Metsoviti et al. [98] employed *Klebsiella oxytoca* (FMCC-197) to obtain a mixture of 25.2 g/L ethanol, 50.1 g/L 1,3-propanediol and 16.8 g/L lactic acid using fed-batch fermentation. Metsoviti et al. [99] also used an isolated strain of *Citrobacter freundii* (FMCC-207) to produce ethanol from glycerol. Results revealed that 14.5 g/L of ethanol was produced at a yield of 0.45 g/g with a productivity of 0.7 g/L/h.

More recently, researchers have shown the potential of *Enterobacter aerogenes* for ethanol production. Jitrwung and Yargeau [100] showed that under anaerobic conditions, pH 6.4, 500 rpm, fresh feed rate 0.44 mL/min, liquid recycling ratio 0.33 and 18.5 g/L crude glycerol (15 g/L glycerol), ethanol at 0.75 mol/mol glycerol was obtained. However, ethanol enhancement has also been obtained through genetic engineering [101]. The resultant mutant strain *Eneterobacter aerogenes* SUMI014 from *Enterobacter aerogenes* ATCC 29007 increased ethanol yield 1.5-fold. 34.22 g/L ethanol was obtained under optimum conditions of fermentation of 34 °C and pH 7.5 after 78 h reaction time by mutant strain, as against 13.09 g/L produced by the wild type. The use of thermotolerant yeast, namely *Ogataeo polymorpha*, in glycerol conversion to ethanol was reported by Kata et al. [102]. Low concentration of ethanol (0.8 g/L) was obtained with the wild-type strain of *Ogataeo polymorpha*, but on overexpression with the pyruvate decarboxylase (PDC1) gene, it enhanced the ethanol concentration to 2.91 g/L. When the wild-type strain (WT) was overexpressed with both PDC1 and alcohol dehydrogenase (ADH1) genes, the ethanol concentration increase in temperature to 45 °C slightly improved ethanol production. The summary of the performance of the biocatalysts in the conversion of glycerol to ethanol as recently reported in some literature is shown in Table 7.

Biocatalyst	Operating Parameters	Performance	Reference
Ogataeo polymorpha	T = 37 °C, pH = na, rpm = 140, t = na	$\label{eq:c} \begin{split} C &= 0.80 \pm 0.100 \; g/L, Y = 0.077 \pm 0.036 \; g/g, \\ P &= 0.007 \pm 0.001 \; g/L/h \end{split}$	[102]
Ogataeo polymorpha/PDC1		$\label{eq:c} \begin{split} C &= 2.91 \pm 0.240, \ \dot{Y} = 0.270 \pm 0.159 \ g/g, \\ P &= 0.022 \pm 0.002 \ g/L/h \end{split}$	
Ogataeo polymorpha/PDC1/ADH1		$C = 4.29 \pm 0.040, Y = 0.357 \pm 0.073 \text{ g/g},$ P = 0.036 ± 0.000 g/L/h	
Enterobacter aerogenes ATCC 29007 Enterobacter aerogenes SUMI1014 Enterobacter aerogenes SUMI2008	T = 34 °C, pH = 7.5, t = 78 h	C = 13.09 g/L, Y = 0.156 g/g, P = 0.161 g/L/h C = 34.54 g/L, Y = 0.428 g/g, P = 0.439 g/L/h C = 38.32 g/L, Y = 0.479 g/g, P = 0.491 g/L/h	[101]
Enterobacter aerogenes ATCC 35029	T = 34 °C, pH = 6.4, rpm = 500, t = 20–24 h	C = na, Y = 0.75 mol/mol, P = na	[100]
Escherichia coli SS1 Escherichia coli BL 21 Escherichia coli BW25113 Enterobacter aerogenes HU101	T = 37 °C, pH = na, rpm = 120, t = 24 h	$\begin{split} C &= 9.23 \pm 0.6 \text{ g/L}, \text{ Y} = 1.00 \text{ mol/mol}, \text{ P} = \text{na} \\ C &= 9.50 \pm 0.67 \text{ g/L}, \text{ Y} = 0.991 \text{ mol/mol}, \text{ P} = \text{na} \\ C &= 5.33 \pm 1.00 \text{ g/L}, \text{ Y} = 0.592 \text{ mol/mol}, \text{ P} = \text{na} \\ C &= 3.98 \pm 0.27 \text{ g/L}, \text{ Y} = 0.594 \text{ mol/mol}, \text{ P} = \text{na} \end{split}$	[96]
Mixed culture	T = 37.5 °C, pH = 7.9, t = na Optimization	C = 6.75 g/L, Y = na, P = na C = 26 g/L, Y = na, P = na	[103]
Escherichia coli MG1655	$T = 37 ^{\circ}C, pH = na, t = 110 h$	C = 4.00 g/L, Y = 0.40 g/g, P = na	[88]

Table 7. Performance of some biocatalysts in the conversion of glycerol to ethanol as reported in some literature.

T = Temperature, t = time, C = Concentration, Y = Yield, P = Productivity.

3.3. Methanol

Methanol is a versatile chemical that has applications in various industries. It can be directly used as fuel or as an additive to gasoline, and can also be used as an intermediate for the production of various chemicals. It has been reported that the use of methanol grew by 1% from 2003 to 2008 and was predicted to have further increased by 2% by 2013 [104]. Currently, methanol is deployed in the production of biodiesel through transesterification of vegetable oil. With the increased production of biodiesel worldwide, it is obvious that the demand for methanol will definitely increase. So if the byproduct of biodiesel production, glycerol, can be converted to methanol, it will amount to recycling back into the transesterification system, thereby saving costs and ultimately reducing the cost of biodiesel. Efforts are on the increase in the conversion of glycerol to methanol via synthesis gas, hydrogenolysis over transition metal catalyst, and steam reforming of oxygenated hydrocarbons over specific catalyst at 380 °C [104].

Haider et al. [105] demonstrated a new potential method for methanol production from crude glycerol. They reacted both refined and crude glycerol separately with water over simple basic and redox oxide catalysts (MgO, CaO, SrO, LaO and CeO₂) at 250–407 °C and atmospheric pressure. Results revealed high yield of methanol from both feedstocks with CeO₂.

The use of supercritical water conditions of 450 °C and 30 MPa was reported by Carr et al. [106]. After 30 min of reaction, 1 mol of methanol was produced per mole of glycerol fed.

4. Fuel Additives

Fuel additives are substances added or blended with fuels especially gasoline, diesel and or biodiesel to improve their fuel properties leading to excellent performance. When added to fuels it can reduce harmful emissions such as hydrocarbons, particulate, CO_2 and NO_x emissions. It improves viscosity, antiknock, octane, cetane and cold flow properties of the fuels as well as improves the thermal stability, cleanliness and prevents corrosion of engines and engine parts [43,107,108].

There are variety of fuel additives that are petroleum and biomass-based; however, the interest in this review is the oxygenated additives that are glycerol-based.

The oxygenated additives produced from glycerol are many and are biodegradable, non-toxic and renewable. They can be classified into three broad groups namely acetin (acetyl glycerol), glycerol ethers and glycerol formal [109]. In view of their importance in improving engine performance, they have the potential to replace the existing petroleum-based additives such as methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE). These oxygenated additives are receiving great attention from industrialists and researchers.

4.1. Acetin (Glycerol Esters)

Acetin is the product of glycerol esterification with acetic acid or carboxylic acid in the presence of homogeneous or heterogeneous catalyst [43,107]. Acetin can also be produced through acetylation of glycerol with acetic anhydride as well as direct transesterification of either triglyceride or glycerol with methyl acetate [110,111]. Some of reactions are exemplified in Schemes 4 and 5.



Scheme 4. Conversion of glycerol to acetin by esterification with carboxylic acid.



Scheme 5. Conversion of glycerol to acetin by acetylation with acetic anhydride.

Acetin can be monoacetin, diacetin or triacetin. Monoacetin is a monoacetyl glycerol (2-monoacetyl-1,3-propanediol or 3-monoacetyl-1,2-propanediol), diacetin is a diacetyl glycerol (1,2-diacetyl-3-propanol or 1,3-diacetyl-2-propanol) and triacetin is a triacetyl glycerol (1,2,3-triacetylpropanol) [112]. All the acetins are of versatile application. Monoacetin and diacetin are used in cosmetics, medicines and food industries as humectant and emulsifier. They are also used as monomer for the production of biodegradable polyesters. While triacetin is most basically used as fuel additive to improve viscosity, as an antiknock and to meet the standard flash point and oxidation stability in gasoline [113]. Some authors have also reported the use of diacetin as fuel additive [114]. Triacetin has also been reported to be used as solvents and plasticizers. Series of research in the past have been undertaken with good yield using both homogeneous and heterogeneous catalysts but the heterogeneous catalyst has an edge in view of its advantages.

Acetylation of glycerol with acetic acid over different solid acid catalysts (Amberlyst-15, K-10 montmorillonite, niobic acid, zeolites (H-beta, HZSM-5 and HUSY)) have been investigated by different researchers. Results showed that Amberlyst-15 was the most active catalyst, with over 90% glycerol conversions and selectivity of 31%, 54% and 13% towards mono-, di- and triacetin respectively which was attributed to the strong acid sites on the catalyst surface but low pore size. The poor performance of the zeolites was attributed to diffusion problem of the acetylated esters inside the cavities [114,115].

However, when acetic anhydride was used as the acetylating agent, H-Beta and K-10 produced 100% selectivity to triacetin within 20 min at low temperature of 60 °C and was attributed to the accessibility of the acylium ion resulting from anhydride by the catalysts unlike the intermediate from acetic acid. Amberlyst-15 acid resin also yielded 100% triacetin, but only after 80 min of reaction at 60 °C. Silva et al. [115] also reported that niobium phosphate (NP) catalyst can also yield 100% triacetin but at a much higher temperature120 °C. Improved performance in the production of triacetin was also observed with Amberlyst-15 when compared with zeolite HZSM-5 and HUSY in the reaction of glycerol with acetic acid as reported by Zhou et al. [116]. The authors reported that Amberlyst-15 showed high activity as well as high selectivity towards di- and triacetin, corresponding to 98.47% glycerol conversion and 8.65%, 46.56% and 44.79% selectivity towards mono-, di-, and triacetins at optimum conditions of 110 °C and acetic acid:glycerol molar ratio 9:1 as predicted by the non-linear

model, which were found to be closed to the experimental values (97.1% glycerol conversion, 47.7% diacetin and 44.5% triacetin. This performance was attributed to the high acidic sites and sufficient pore volume to contain big molecules such as di- and triacetin. Considerable improvement was also reported when yttrium was incorporated into SBA-3 catalysts [117]. 100% glycerol conversion and selectivity of 34% and 55% towards di- and triacetin were obtained under similar reaction temperature at lower molar ratio of glycerol to acetic acid of 1:4 with 3% Y/SBA-3 catalyst. The catalyst was confirmed to be stable even after being reused three times. The improved triacetin was unconnected with the strong acidity, while the high surface area with large pore size makes the diffusion of both the substrates and products possible. However, the catalyst activity decreased in the fourth cycle with reduction in glycerol conversion to 80% and triacetin reduced to 50% attributing it to reaction conditions and mass transfer limitations.

A two-step method involving esterification and acetylation of glycerol with acetic acid (in the first step) and acidic anhydride (in the second step) over synthesized sulfonic acid functionalized solid acid catalyst which is glycerol-based was reported [118]. Results showed 100% triacetin was obtained after an initial production of 22, 67, and 11% monoacetin, diacetin, and triacetin respectively at 100% glycerol conversion. The authors further showed that the first step was time depended. The greater the time, the more triacetin was produced. The developed catalyst was found to be highly stable and recyclable. Sun et al. [119] also obtained 100% glycerol conversion and 99.0% selectivity to triacetin using synthesized magnetic solid acid catalyst calcined at 400 °C (Fe-Sn-Ti(SO₄^{2–})-400) with acidic anhydride as the acetylating agent at molar ratio of 6:1 with glycerol at 80 °C within 30 min. The catalyst activity remains unchanged even after reused for three times. This may not be unconnected to the high surface area and pore volume exhibited by the catalyst. However, when acetic acid was used as an acetylating agent at the same reaction conditions, the glycerol conversion was reduced drastically to 32.3% while the selectivity to monoacetin was 100%. When the temperature increased to 140 °C, the conversion improved and the selectivity of 75.7% and 90.3% towards mono- and diacetin were achieved.

The catalytic activities of heteropolyacids were improved with the use of supported materials. Zhu et al. [120] reported complete glycerol conversion (100%) and selectivity of 6.4%, 61.3% and 32.3% towards mono-, di- and triacetin respectively at 120 °C and 4 h of reaction time when zirconia supported $H_4SiW_{12}O_{40}$ catalyst (HSiW/ZrO₂) was used. The catalyst activity was consistent for four consecutive reaction cycles and was resistance to impurities (water, NaCl and methanol) in crude glycerol which was attributed to good surface Bronsted acid sites and hydrothermal stability indicating its good potential for industrial application.

The use of micro and mesoporous structure materials in catalysis has aided catalytic activity in view of their high surface areas. In some, additional treatments of these materials help to increase their selectivity to a particular product as exhibited by some researchers. Khayoon and Hameed [112] developed a solid catalyst by functionalizing β -MoO₃ species into the framework of hybrid mesostructured silica by the thermal decomposition of molybdophosphoric acid (MPA) over the mesoporous support. When the resultant catalyst was tested in the esterification of glycerol with acetic acid, the mesoporous support with 15 wt% MPA exhibited a superior catalytic activity with complete conversion of glycerol (100%) with a selectivity of 14%, 67% and 19% towards mono-, di- and triacetin at 110 °C, 6:1 molar ratio of acetic acid to glycerol in 3 h. The catalyst was recycled four times and was found to be stable. The use of supported iron oxide nanoparticle system of a mesoporous aluminosilicate (Fe/Al-SBA-15) catalyst with >99% glycerol conversion to a mixture of 71% di- and 28% triacetin was reported [121]. Though levulinic acid was used as against the conventional acetic acid but the catalyst remains stable even after five consecutive cycles. Dalla Costa et al. [122] compared the catalytic activities of microporous zeolites (H-ZSM-5 and H-Beta) and mesoporous material (SBA-15 functionalized with propylsulfonic groups). The Propyl-SO₃H-SBA-15 catalyst performed with high glycerol conversion (96%) and combined selectivity to di- and triacetin (87%) in 2.5 h. The performance was attributed to balance between the level of acid sites and the formation of molecules on the surface

of the mesoporous structure. Unfortunately, the catalyst was not stable because of the leaching of sulfonic group and coke deposition occurring right from the second cycle.

Deployment of metal oxide-based catalysts has shown high selectivity towards oxygenated diand triacetin. This can be seen in the work of Reddy et al. [123], Reddy et al. [124] and Zhang et al. [125]. Zirconia-based catalysts, namely ZrO_2 , TiO_2-ZrO_2 , WO_x/TiO_2-ZrO_2 and MoO_x/TiO_2-ZrO_2 , were deployed in glycerol acetylation [123]. Results showed that the MoO_3/TiO_2-ZrO_2 catalyst exhibited highest catalytic activity ($\approx 100\%$ glycerol conversion) with a combined selectivity of 49.97% diand triacetin. It was also noticed that the glycerol conversion and selectivity towards di- and triacetin increased with increased temperature from 40 to 120 °C. The authors further increased the reaction time and observed that as the selectivity of monoacetin decreased, that of di- and triacetin increased. After 60 h of the reaction time, selectivity of $\approx 80\%$ triacetin was obtained and no more. This was attributed to further conversion of mono- and diacetin to triacetin during the acetylation. Similarly, SO_4^{2-}/CeO_2 -ZrO₂ catalyst exhibited the highest activity with $\approx 100\%$ glycerol conversion and selectivity of 25.8%, 57.7% and 16.5% towards mono-, di- and triacetin, respectively in a shorter reaction time of 1 h when compared with other cerium-based catalysts (CeO₂–ZrO₂, CeO₂–Al₂O₃, $SO_4^{2-}/CeO_2-Al_2O_3$ [124]. When SO_4^{2-}/CeO_2-ZrO_2 catalyst was allowed in the acetylation reaction for 40 h, \approx 90% selectivity towards triacetin was obtained [124]. On testing the reusability of the catalyst, it was found to be relatively stable but continue to depreciate after each successive run.

Zhang et al. [125] also compared a commercial solid acid catalyst, $SO_4^{2-}/ZrO_2-Al_2O_3$, with a prepared diatomite-loaded SO_4^{2-}/TiO_2 in the esterification of oleic acid with glycerol at 210 °C, 0.1% catalyst loading and oleic acid to glycerol mass ratio of 2:1. The prepared diatomite-loaded SO_4^{2-}/TiO_2 performed better than the commercial solid acid catalyst, $SO_4^{2-}/ZrO_2-Al_2O_3$ with 59.6% of diacetin in 6 h. The metal oxide-based catalysts were stable, reusable, not expensive and are sustainable over wide range of temperatures.

To save cost in biodiesel production, transesterification of methyl acetate with glycerol was carried out to produce acetin simultaneously with the biodiesel using Ca and Sn mixed metal hydroxides as catalyst [126]. CaSn(OH)₆ catalyst performed much better when compared to other hydroxy stannates and metal oxides like MgSn(OH)₆, ZnSn(OH)₆, SrSn(OH)₆, Ca(OH)₂, CaO, MgO, etc. The high glycerol conversion (78.2%) was attributed to higher basicity exhibited by the CaSn(OH)₆ catalyst contrary to the expectation since it is basic in nature.

More recently, other novel catalysts have been explored in glycerol acetylation. Okoye et al. [127] used crude glycerol as a carbon precursor to synthesize solid acid catalyst via partial carbonization and sulphonation. This in turn was used to catalyze glycerol acetylation with acetic acid to produce mixture of diacetin and triacetin. 99% glycerol conversion and 88% combined diacetin and triacetin selectivity was achieved at 110 °C in 3 h reaction time. Okoye et al. [127] also reported that the catalyst was reused in seven cycles without significant deactivation. The catalyst's high activity was attributed to high surface acid sites density. Table 8 shows the summary of the performance of some catalysts in the conversion of glycerol to acetin as recently reported in some literature.

Catalyst (A)

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Operation Parameters

Diatomite loaded $0.3\%SO_4^{2-}/TiO_2$ (na) $0.3\%SO_4^{2-}/TiO_2$ (na) $0.3\%SO_2^{2-}/ZrO_2-Al_2O_2$ (na)	T = 210 °C, P = 0.002 MPa, Cat = 0.1% wt Oleic acid, t = 6 h, 200 rpm, Crude Glycerol/Oleic acid (1:2)	GC = na, MA = na, DA = 59.1 ± 0.6 , TA = na GC = na, MA = na, DA = 41.4 ± 1.0 , TA = na GC = na, MA = na, DA = 39.9 ± 0.7 , TA = na	* 2955 * 2070 * 1995	[125]
Sulphonated glycerol-based carbon catalyst (na)	T = 110 °C, Cat = 2 wt%CG, t = 3 h, Crude Glycerol/Acetic Acid (1:3)	GC = 99, MA = 12, DA+TA = 88	165	[127]
Pr-SO ₃ HSBA-15 (366)	T = 120 °C, P = atm. press., Cat = 4 wt% G, t = 2.5 h, Glycerol/Acetic Acid (1:6)	GC = 96, MA = 13, DA+TA = 87	** $16.25 \mathrm{S}^{-1}$	[122]
CaSn(OH) ₆ (3.95)		GC = 78.2, MA = 67.3, DA = 32.6, TA = na		
MgSn(OH) ₆ (18.1)		GC = 65.4, MA = 66.1, DA = 33.8, TA = na		
$ZnSn(OH)_6$ (7.0)		GC = 40, MA = 62.5, DA = 37.5, TA = na		
SrSn(OH) ₆ (5.0)	T = 30 °C, Cat = 7 wt% G, t = 2 h, Glycerol/Methyl Acetate (1:10)	GC = 25.2, MA = 70.1, DA = 30.2, TA = na	nd	[126]
Ca(OH) ₂ (12.0)		GC = 52.1, MA = 87.1, DA = 12.9, TA = na		
CaO (62.0)		GC = 47.2, MA = 90.2, DA = 9.6, TA = na		
MgO (44.4)		GC = 25.2, MA = 99.8, DA = na, TA = na		
Fe-Sn-Ti (SO ₄ ²⁻) (16.96)		GC = 58, MA = 83, DA = 17, TA = 0	348	
Fe-Sn-Ti (SO ₄ ²⁻)-400 (18.88)		GC = 100, MA = 0, DA = 1, TA = 99	600	
Fe-Sn-Ti (SO ₄ ²⁻)-500 (16.55)		GC = 99, MA = 0, DA = 3, TA = 97	594	
Fe-Sn-Ti (SO ₄ ²⁻)-600 (14.91)	T = 80 °C, Cat = 0.05 g, t = 0.5 h, Glycerol/Acetic Anhydride (1:6)	GC = 99, MA = 0, DA = 4, TA = 96	594	[119]
Fe-Sn-Ti (SO ₄ ²⁻)-700 (11.65)		GC = 68, MA = 82, DA = 17, TA = 1	408	
Amberlyst-15 (na)		GC = 99, MA = 0, DA = 1, TA = 99	594	
Blank		GC = 49, MA = 48, DA = 46, TA = 6	-	
3 wt% Al-SBA-15 (747)	T = 120 °C Cat = 50 mg/mmol t = 8 h 1000 mm Clycorol /Lavulnic Acid (1:4)	GC = 78, MA = 94, DA = 5, TA = 1	2	
0.63 wt% Fe/Al-SBA-15 (688)	$1 = 120^{\circ}$ C, Cat = 50 mg/ mmor, t = 6 n, 1000 rpm, Giyteror/ Levumic Acid (1.4)	GC = >99, MA = 0, DA = 71, TA = 28	2	[121]
0.63 wt% Fe/Al-SBA-15 (688)	T = 140 °C, Cat = 50 mg/mmol, t = 8 h, 1000 rpm, Glycerol/Levulnic Acid (1:4)	GC = >99, MA = 0, DA = 80, TA = 20	2	[121]
0.63 wt% Fe/Al-SBA-15	T = 100 °C, Cat = 50 mg/mmol, t = 8 h, 1000 rpm, Glycerol/Levulnic Acid (1:4)	GC = -, MA = -, DA = -, TA = -	nd	
1% Y/SBA-3 (na)		GC = 65, MA = 95, DA = 5, TA = 0	54	
2% Y/SBA-3 (na)		GC = 68, MA = 82, DA = 11, TA = 7	56	
2.5% Y/SBA-3 (na)	T = 110 °C. Cat = 0.2 g. t = 3 h. Glycerol/Acetic Acid (1.4)	GC = 82, MA = 54, DA = 26, TA = 20	68	[117]
3% Y/SBA-3 (1568)	1 110 0, cut 0.2 g, t 011, cifector, recut ricu (11)	GC = 100, MA = 11, DA = 34, TA = 55	83	[117]
3.5% Y/SBA-3 (1622)		GC = 94, MA = 24, DA = 34, TA = 55	78	
Blank		GC = 20, MA = 71, DA = 28, TA = 1	-	
Glycerol Based Carbon Catalyst (na)	T = 115 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:4)	GC = 100, MA = 22, DA = 67, TA = 11	217	
	T = 115 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:6)	GC = 100, MA = 15.8, DA = 72.2, TA = 12	217	[118]
	T = 115 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:8)	GC = 100, MA = 12.3, DA = 73.2, TA = 14.5	217	[]
	T = 115 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:10)	GC = 100, MA = 8.4, DA = 71.8, TA = 19.8	217	
Amberlyst-15 (1. 6wt) (37.6)		GC = 97, MA = -, DA = 47.7, TA = 44.5		
Amberlyst-15 (3.2 wt) (37.6)		GC = 93.5, MA = -, DA = 43.2, TA = 38.3		
HZSM-5 (368)	T = 110 °C, Cat = 82.86 mmolH ⁺ /L, t = 4.5 h, Glycerol/Acetic Acid (1:9)	GC = 85.6, MA = -, DA = 25.7, TA = 7.7	nd	[116]
HUSY (552)		GC = 78.4, MA = -, DA = 20.6, IA = 5.6		
Blank		GC = 73.2, $MA = -$, $DA = 13.8$, $IA = 1.5$		
$2rO_2(59.7)$		GC = 72.4, MA = 48.3, DA = 45.4, IA = 6.3		
$20 \text{ wt\% H51W} / 2rO_2 (48.7)$	T = 120 °C, Cat = 0.3 g, t = 4 h, 250 rpm, Glycerol/Acetic Acid (1:10)	$G_{C} = 100, MA = 6.4, DA = 61.3, IA = 32.3$	nd	[120]
$20 \text{ wt/o} \text{ fir W} / 2\text{IO}_2 (52.5)$		GC = 99.2, $MA = 7.3$, $DA = 62.6$, $IA = 29.9$		
20 Wt% ΠΓΝΙΟ/ ΔrU ₂ (49.3)		GC = 96.2, $MA = 12.0$, $DA = 62.0$, $A = 26.0$		

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
0.01 mmol H ₃ PW ₁₂ O ₄₀		GC = 96, MA = 66, DA = 34, TA = 0	** 5.3 min ⁻¹	
0.01 mmol H ₃ PW ₁₂ O ₄₀ -calcined 200 °C	T = 60 °C, P = 0.101 MPa, Cat = 0.03 mmol, t = 8 h,	GC = 93, MA = 65, DA = 35, TA = 0	** $4.28 \min^{-1}$	[128]
0.03 mmol PTSA	Glycerol/Acetic Acid (1:3)	GC = 85, MA = 86, DA = 8, TA = 0	** 3.1 min ⁻¹	[120]
0.015 mmol H ₂ SO ₄		GC = 98, MA = 54, DA = 27, TA = Trace	** $4.1 \min^{-1}$	
CeO ₂ -Al ₂ O ₃ (101)		GC = 59.4, MA = 88.1, DA = 11.6, TA = 0.3	119	
CeO_2 -ZrO ₂ (49)	T = 120 °C Cat = 5 wt ⁶ /C t = 1 h Clycoral / A catic Acid (1:6)	GC = 68.1, MA = 75.2, DA = 22.7, TA = 2.1	136	[124]
$SO_4^{2-}/CeO_2-Al_2O_3$ (136)	$1 = 120^{\circ}$ C, Cat = 5 wt/6 G, t = 1 II, Glycerol/Acetic Acid (1.6)	GC = 79.9, MA = 58.9, DA = 35.5, TA = 5.6	160	[124]
SO ₄ ²⁻ /CeO ₂ -ZrO ₂ (92)		$GC = \approx 100$, MA = 25.8, DA = 57.7, TA = 16.5	200	

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, MA = Monoacetin selectivity, DA = Diacetin selectivity, TA = Triacetin selectivity, TOF (mmol g^{-1} cat. h^{-1}) = Turnover frequency calculated based on the glycerol conversion/* product yield per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.

Glycerol ethers are highly alkylated glycerol with several applications. In addition to being used as oxygenated fuel additives, they are also used as solvents in reactions and as cleaning agent in industry. Glycerol ethers are highly branched and are synthesized through etherification of glycerol with alkenes (most commonly isobutene) and alcohols (most commonly *tert*-butanol) in the presence of homogeneous or heterogeneous catalyst (Schemes 6 and 7) [107]. For ease of reference, glycerol ethers may be classified as protic (3-alkoxy-1,2-propandiols (monoether) and 1,3-dialkyoxy-2-propanols (diether)) and non-protic (1,2,3-trialkyoxypropanes (triether)) [129].



Scheme 6. Conversion of glycerol to glycerol ethers by etherification with alkene (isobutene) (MTBG: mono-tert-butylglycerol, DTBG: di-tert-butylglycerol, TTBG: tri-tert-butylglycerol).



Scheme 7. Conversion of glycerol to glycerol ethers by etherification with alcohol (tert-butanol).

In view of its usage as oxygenated fuel, etherification of glycerol has received massive attention over the years and several studies involving different catalysts have been reported.

Goncalves et al. [130] prepared sulfonated carbon-based catalysts from agro-industrial wastes (sugar cane bagasse, coconut husk, and coffee grounds), and they proved to be highly efficient. In fact, the sugar cane bagasse-based catalyst was more effective than the commercially available Amberlyst-15. Glycerol conversion and selectivity to di-tertiary butyl glycerol and tri-tertiary butyl ether glycerol of 80.9% and 21.3%, respectively, were achieved after 4 h. The performance of the catalysts was attributed to the sulfonic groups present.

When different homogeneous alkali catalysts (LiOH, NaOH, KOH and Na₂CO₃) were tested in the glycerol etherification, complete glycerol conversion were achieved but after 8 h reaction time. Selectivity of 33% towards di-tertiary butyl glycerol was achieved with LiOH, while others gave lower selectivity despite the longer reaction time and was attributed to the exhibition of very high alkalinity in the reaction mixture [131].

The use of SiO₂-supported tungstophosphoric acid ($H_3PO_{40}W_{12}$, HPW) catalyst was excellent, with 97.1% conversion of glycerol with formation of mono, di and tri-ethers at 160 °C and ethanol:glycerol molar ratio of 6:1 compared to other catalysts (H-ZSM5, H- β , tungstophosphoric acid ($H_3PO_{40}W_{12}$, HPW), FeCl₃, AlCl₃, and H_2SO_4) under the same conditions [132]. However, deactivation of the SiO₂-supported HPW was reported due to leaching.

The use of zeolites and sulfonic group containing resin catalysts appear to be more stable and generally more acceptable in view of their performance and ease of separation as exemplified by several research works. When Viswanadham and Saxena [133] compared variously prepared resins (Amberlyst-15 and Amberlyst-35), zeolites (Beta-BEA and USY) and mordenite (MOR)-based catalysts in batch and fixed-bed reactor, it was discovered that the resin catalysts exhibited higher glycerol conversion and ether selectivity at relatively lower reaction temperature (75 °C) than the zeolite-based catalysts (90 to 110 °C). However, the zeolite-based catalysts performed better in terms of stability to produce high amounts of di-tertiary butyl glycerol and TTBG of glycerol. At optimized conditions, nano-beta (N-BEA) zeolite catalyst exhibited above 95% conversion of glycerol with more than 45% and 54% selectivity to di-tertiary butyl glycerol and tri-tertiary butyl ether glycerol in a fixed-bed reactor. This behavior has been attributed to the pore structure of zeolites. Bigger porosity favors large molecule formation. Similarly, Veiga et al. [134] reported the performance of USY, HZSM-5 and H-Beta zeolites after calcination. H-Beta and USY-650-L-2 zeolites showed higher activity with glycerol conversion of up to 74 and 75% with tert-butyl alcohol and 67 and 81% with ethyl alcohol with selectivity towards mono- and di- substituted ethers which was attributed to the fact that these catalysts exhibit higher hydrophobicity (low hydrophilicity). However, the earlier findings of Pinto et al. [135] showed that Amberlyst-15 acid resin exhibited the best performance with 96% of glycerol conversion and 80% selectivity to the ethyl ethers at 180 °C at ethanol:glycerol molar ratio of 3:1 and within the reaction time of 4 h when it was compared with clays and zeolites catalysts which was attributed to higher acid strength of the Amberlyst-15 acid resin catalyst. The catalyst also showed good stability because there was no any significant deactivation noticed after three consecutive reuses.

In another study, Estevez et al. [136] reported the use of silica-based and organosilica-based hybrid materials as catalysts in glycerol etherification with tert-butyl alcohol. Of all the hybrid materials, $S_{50}TS_{50}O$ catalyst performed better than the highly active commercial sulfonic resin (Amberlyst-15) with glycerol conversion of 98% after 24 h reaction time at 75 °C. The high performance was attributed to the high density of acid sites, textural and chemical properties of the catalyst as well as its ability to prevent the effect of water due to silanol groups on the hybrid silicas. Table 9 shows the summary of the performance of some catalysts in the conversion of glycerol to glycerol ethers as recently reported in some literature.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
USY-650-L-2 (741)		GC = 67, ME = 73, DE = 25, TE = 2		
H-Beta (623)	T = 200 °C, Cat = 3.5 wt% G, t = 6 h, Glycerol/Ethyl alcohol (1:9)	GC = 81, ME = 72, DE = 25, TE = 2		
HZSM-5 (337)		GC = 60, ME = 90, DE = 10, TE = 0		[10]
USY-650-L-2 (741)		GC = 74, $ME = 79$, $DE = 21$, $TE = 0$	nd	[134]
H-Beta (623)	T = 90 °C, Cat = 7.6 wt% G, t = 4 h, Glycerol/tert-butyl alcohol (1:4)	GC = 75, ME = 74, DE = 26, TE = 0		
HZSM-5 (337)		GC = 15, $ME = na$, $DE = na$, $TE = na$		
Blank	T = 180 °C, Cat = none, t = 8 h, Glycerol/Ethanol (1:6)	GC = 0, ME = 0, DE = 0, TE = 0	-	
K-10 (260)	T = 180 °C, Cat = 2.1 g, t = 8 h, Glycerol/Ethanol (1:3)	GC = 70, ME = 79, DE = 14, TE = 7	5	
K-10 (260)	T = 180 °C, Cat = 2.1 g, t = 4 h, Glycerol/Ethanol (1:6)	GC = 59, ME = 72, DE = 18, TE = 10	8	
HZSM-5 (408)	$T = 180 \degree C$, Cat = 1.9 g, t = 8 h, Glycerol/Ethanol (1:3)	GC = 61, ME = 94, DE = 4, TE = 2	4	
HZSM-5 (408)	T = 180 °C, Cat = 1.9 g, t = 4 h, Glycerol/Ethanol (1:6)	GC = 40, ME = 95, DE = 3, TE = 2	5	[135]
H-Beta (564)	$T = 180 \degree C$, Cat = 1.1 g, t = 8 h, Glycerol/Ethanol (1:3)	GC = 92, ME = 71, DE = 17, TE = 12	6	
H-Beta (564)	T = 180 °C, Cat = 1.1 g, t = 4 h, Glycerol/Ethanol (1:6)	GC = 89, ME = 75, DE = 14, TE = 10	12	
Amberlyst-15 (53)	T = 180 °C, Cat = 0.32 g, t = 8 h, Glycerol/Ethanol (1:3)	GC = 96, ME = 65, DE = 19, TE = 16	6	
Amberlyst-15 (53)	T = 180 °C, Cat = 0.32 g, t = 4 h, Glycerol/Ethanol (1:6)	GC = 95, ME = 79, DE = 12, TE = 9	12	
S ₉₀ TS ₁₀ O (538)		GC = 27, ME = 92, DE + TE = 2.0		
S ₅₀ TS ₅₀ O (18)		GC = 74, ME = 76, DE + TE = 18.0		
BS ₉₀ TS ₁₀ O (601)	T = 75 °C, Cat = 5 wt% G, t = 17 h, Glycerol/tert-butyl alcohol (1:4)	GC = 6, ME = 97, DE + TE = 0.2	,	[10/]
BS ₅₀ TS ₅₀ O (48)		GC = 32, ME = 87, DE + TE = 4.0	nd	[136]
Amberlyst-15 (39)		GC = 51, ME = 65, DE + TE = 18.0		
S ₅₀ TS ₅₀ O (18)	T = 75 °C, Cat = 5 wt% G, t = 24 h, Glycerol/tert-butyl alcohol (1:4)	GC = 98, ME = 71, DE + TE = 28.0		
Amberlyst-15 (530		GC = 97.8, ME = 94.2, DE = 5.8, TE = na	35	
Amberlyst-35 (50)		GC = 97.7, ME = 94.8, DE = 5.2, TE = na	17	
Zeolite-BEA (450)	$T = 90^{\circ}C$ Cat = 0.38 g t = 4 h Clycorol /tort butyl alcohol (1.4)	GC = 96.7, ME = 81.8, DE = 18.2, TE = na	34	[122]
Mordenite (400)	$1 = 90^{\circ}$ C, Cat = 0.36 g, t = 4 ft, Grycetor/tert-butyr atomot (1.4)	GC = 66.1, ME = 99.4, DE = 10.6, TE = na	24	[155]
Ultra-Stable Y (USY) (614)		GC = 100, ME = 100, DE = -, TE = na	36	
N-BEA (565)		GC = 98.4, ME = 75.6, DE = 21.8, TE = 2.6	35	
Sulfonated sugar cane bagasse (<10)		GC = 81.8, ME = 60.5, DE + TE = 21.8		
Sulfonated coconut husk (<10)	T = 120 °C, Cat = 5 wt% G, t = 4 h, Glycerol/tert-butyl alcohol (1:4)	GC = 61.5, ME = <40, DE + TE = 21.1	nd	[130]
Sulfonated coffee grounds (<10)		GC = 61.5, ME = <40, DE + TE = 14		
LiOH (na)		GC = 100, ME = na, DE = <40, TE = na		
NaOH (na)	$T = 240 \circ C$ P = atm proce Cat = 2 wt% C t = 8 h Character as solvent used	GC = 100, ME = na, DE = <40, TE = na		[121]
KOH (na)	1 - 240 C, $1 - a$ and press., Cat = 2 wt/o G, $t = 0$ ft, Grycerol, no solvent used	GC = 100, ME = na, DE = <20, TE = na	na	[131]
Na ₂ CO ₃ (na)		GC = 100, ME = na, DE = <20, TE = na		

Table 9. Performance of some catalysts in the conversion of glycerol to glycerol ethers as reported in some literature.

Table 9. Cont.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
Blank		GC = 0, ME = na, DE = -, TE = na	-	
HZSM5-20 (na)		GC = 7.3, ME = 80, DE = 7.9, TE = 12.1	2	
HZSM5-100 (na)		GC = 1.1, ME = 100, DE = 0, TE = 0	3	
H-β (na)	T = 160 °C, P = 3.0 MPa N ₂ , Cat = 1 g, t = 20 h, Glycerol/Ethanol (1:6)	GC = 5.7, ME = 100, DE = 0, TE = 0	2	
$H_3PO_{40}W_{12}$ (na)		GC = 68.9, ME = 79, DE = 14.8, TE = 6.2	19	[132]
H_2SO_4 (na)		GC = 70, ME = 78.6, DE = 14.9, TE = 6.5	19	
FeCl ₃ (na)		GC = 19.2, E = 72.4, DE = 16.3, E = 11.3	5	
AlCl ₃ (na)		GC = 10.2, ME = 79.6, DE = 9.4, TE = 11	3	
$H_3PO_{40}W_{12}$ (na)	T = 160 $^{\circ}$ C, Cat = 3.3 g, t = 20 h, Glycerol/Ethanol (1:6)	GC = 97.1, ME = 61.9, DE = 28.1, =10.0	26	

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, ME = Monoglycerolether selectivity, DE = Diglycerolether selectivity, TE = Triglycerolether selectivity, STSO = Sulfonated organosilicas, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.

4.3. Glycerol Formal

Glycerol formal is a mixture of both solketal (4-hydroxymethyl-1,3-dioxolane) and acetal (5-hydroxy-1,3-dioxane) and is synthesized by the condensation of glycerol with aldehydes or ketones over homogeneous and/or heterogeneous catalysts (Scheme 8). The predominant acetal or ketal in the mixture depends on the conditions of the reaction especially the catalyst used [43,115,137].



Scheme 8. Conversion of glycerol to solketal and acetal by acetalization with aldehyde or ketone.

4.3.1. Solketal

Solketal is a colorless and odorless 5-membered ring compound liquid that is completely soluble in water [107]. In addition to reducing particulate emission and improving cold flow properties, solketal can also reduce gum formation, improve oxidation stability and can be used as solvent and plasticizer in a polymer industry [138,139]. Solketal production has also received considerable attention as reported in the literature.

The reaction of glycerol and acetone in a glass reactor was catalyzed with *p*-toluenesulfonic acid under reflux for 12 h. Findings from the experiment showed that with increased acetone to glycerol molar ratio, the conversion toward solketal increased. At the end of 12 h, 1:6 molar ratio gave the highest conversion (82.7%) followed by 1:4 molar ratio (70.9%) and 1:2 molar ratio (54.9%) [140]. Higher yield of over 90% solketal and high selectivity has been previously reported by Vicente et al. [141] using the same catalyst with a high molar ratio of glycerol:acetone of 1:6.

To know the possibility of using other ketones in the condensation, De Torres et al. [142] used several linear, branched and cyclic ketones (acetone, butanone, cyclopentanone, 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone) over several catalysts. Results revealed that on using sulfuric acid as catalyst, the yield was strongly depending on the structure of the starting ketone. Yields above 80% were obtained for ketals using acetone, butanone and cyclopentanone in 1 h. While moderate yield of about 60% were obtained for ketals using 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone due to the steric hindrance caused by isobutyl and tert-butyl groups. However, in the case of 3,3-dimethyl-2-butanone it took a longer reaction time of 4 h. The use of some heterogeneous catalysts has revealed better performance as exhibited by De Torres et al. [142]. Excellent yield of 100% and 81.4% solketal were obtained when fluorosulfonic resins (NR-50 and SAC-13) and K10-montmorillonte were used as catalysts in the condensation of glycerol and cyclopentanone at a molar ratio 1:1, 60 °C in reaction time of 2 h.

Similarly, excellent yield of solketal was also obtained with increase in the molar ratio of acetone/crude glycerol irrespective of the heterogeneous catalysts used in a new continuous-flow process [143]. Among all the solid acid catalysts tested (Amberlyst wet, zeolite, Amberlyst dry, zirconium sulfate, montmorillonite and polymax), the use of Amberlyst Wet produced the maximum solketal yield at 40 °C, 4.1 MPa and weight hour space velocity (WHSV) of 4 h⁻¹ (being 88% at the acetone/crude glycerol molar ratio of 6.0). However, all the catalysts, except polymax, showed a slight decrease in its activity for up to 24 h on-stream, which may be due to the loss of acidity. The above process was further optimized using response surface methodology based on Box-Behnken design at optimal conditions (temperature of 25 °C, acetone/crude glycerol molar ratio of 4 and weight

hour space velocity (WHSV) of 2 h⁻¹) and maximum yield of $94 \pm 2\%$ solketal was obtained [144]. The catalyst, Amberlyst Wet, demonstrated that it could be regenerated and reused for 24 h with little or no sign of deactivation. Furthermore, [145] was able to show the spontaneity of the reaction using thermodynamic and kinetic studies. The authors concluded that the rate of the reaction increased with increase in temperature, quantity of catalyst and acetone:glycerol molar ratio, with the effect of pressure and agitation was negligible.

Molybdenum phosphate catalysts supported on SBA-15 with varying MoPO loadings (5–50 wt%) showed excellent yield [146]. 40 wt% MoPO/SBA-15 catalyst exhibited the best activity with 98% selectivity towards solketal and 100% glycerol conversion within the reaction time of 2 h due to high Bronsted acid sites. However, leaching of the catalyst was observed leading to decreased activity. The authors further reported that the glycerol conversion and selectivity during acetalization strongly depends on catalyst loading, glycerol to acetone molar ratio and the reaction time.

The use of acid-treated zeolite has also shown great performance. Acid (hydrochloric acid, nitric acid and oxalic acid)-treated beta zeolite showed enhanced catalytic activity with the nitric acid-treated beta zeolite exhibiting the highest glycerol conversion with 94.26% and 94.21 wt% solketal yield [147]. The excellent performance of the nitric acid-treated beta zeolite was attributed to the higher specific surface area, mesoporosity and strong acidity. Similarly, when ammonium-treated beta zeolites catalysts (H-Beta-1 small crystallite size) were tested and compared with other zeolites (H-Beta-2, H-ZSM-5 H-Y and H-Mordenite) and other catalysts (Amberlyst-15, K-10, CsHPW and MoO₃), 5 wt% H-Beta-1 zeolite catalyst was the most active with 86% glycerol conversion and 98.5% selectivity towards solketal [148]. The catalysts were reusable without any significant loss in their activities. The excellent performance was attributed to the presence of high number of strong acid site on small crystal of the zeolites (H-Beta-1).

Metal, bimetals and trimetals supported catalysts have also shown good potentials in solketal production as reported by Khayoon and Hameed [149], de Carvalho et al. [150], Rodrigues et al. [151] and Kapkowski et al. [152] with low to high glycerol conversion (33–100%) and high solketal selectivity (98–100%).

4.3.2. Acetal

Glycerol acetal is a viscous six-membered ring liquid. In addition to being used as fuel additive, it is also used as solvent in paint and pesticide industries. Acetalization of glycerol to predominant product of acetal has been reported in the literature.

Acetalization of glycerol with benzaldehyde was carried out using solid catalyst, mesoporous MoO₃/SiO₂ with varying MoO₃ loadings (1–20 mol%) [153]. Results indicate that 20 mol% MoO₃ loading was found to be the most active catalyst at 100 °C for 8 h with a maximum conversion of benzaldehyde to be 72% and 60% selectivity towards the six-membered acetal. Further studies of using various aldehydes (p-tert-butylbenzaldehyde, 2-hydroxy,5-nitrobenzaldehyde, anisaldehyde, o-chlorobenzaldehyde, benzaldehyde n-heptaldehyde, n-butyraldehyde, trans-cinnamaldehyde and phenylacetaldehyde) by the same authors revealed that with substituted benzaldehydes under the same reaction conditions, the conversion of aldehydes decreased with increase in selectivity to acetal. They concluded that aliphatic aldehydes gave comparatively higher conversions when compared to aromatic aldehydes which were attributed to the level of unsaturation. However, Da Silva et al. [3] reported higher yield (95%) with 70% selectivity towards 6-membered ring when zeolites were used as catalyst. Zeolite beta was found to be the most active within a shorter reaction time of 1 h compared to the foregoing. Furthermore, a shorter reaction time of 30 min was enough to achieve good performance when solid acid metal oxides supported catalysts were used as reported below. Sudarsanam et al. [154] investigated the use of ZrO₂, TiO₂-ZrO₂, MoO_x/ZrO₂ and MoO_x/TiO₂-ZrO₂ catalysts using benzaldehyde and its mono substituted derivatives (o-chloro benzaldehyde, p-chloro benzaldehyde, p-anisaldehyde, o-nitrobenzaldehyde and p-nitrobenzaldehyde). The MoO_x/TiO_2-ZrO_2 catalyst exhibited the highest glycerol conversion (74%) with 51% selectivity towards1,3-dioxane product

within the reaction time of 30 min with benzaldehyde attributable to the presence of a greater number of acidic sites. Lower conversion of glycerol and high selectivity towards 1,3-dioxane were reported with the mono substituted derivatives of benzaldehyde due to steric hindrance. However, temperature (60–100 °C) exhibited significant effect on the glycerol conversion when compared with the use of solvents (aldehydes listed above).

The use of supported iron oxide nanoparticle system of a mesoporous aluminosilicate heterogeneous catalyst (Fe/Al-SBA-15) in acetalization of glycerol with paraformaldehyde, benzaldehyde, furfural and acetone was investigated at 100 °C [121]. All the reactions gave very good conversion and selectivity to glycerol formal. With paraformaldehyde, up to 90% conversion was achieved with dioxane and dioxolane selectivity of 66 and 34% within 8 h reaction time. However, when the glycerol:paraformaldehyde molar ratio increased to 1:2, the glycerol conversion increased up to 100% with increase in dioxane selectivity (76%). The catalyst, Fe/Al-SBA-15, was found to be highly active, stable and reusable despite the long hours of reaction which was attributed to the large number of active sites.

Chen et al. [155] reported the use of different heterogeneous acid functionalized catalysts (mesoporous organosilicas (PMOs), zeolite ZSM-5, heteropoly compound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Amberlyst-15) in the acetalization of glycerol with aqueous formaldehyde to glycerol formal. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ exhibited the best performance with glycerol conversion of 70% within 1 h of reaction time. The authors also reported that catalyst load, glycerol to formaldehyde molar ratio and temperature play critical roles in the distribution of the two isomers of acetal (5- and 6-membered rings). Table 10 shows the summary of the performance of some catalysts in the conversion of glycerol to solketal and acetal as recently reported in some literature.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
β-Zeolite (467.4)		GC = 70.13, SK = 64.65, AT = 5.48		
HCl-treated β-Zeolite (597.15)	$T = 60 \degree C$. Cat = 10 wt% G, t = 4 h. Bioglycerol / Acetone (1:6)	GC = 86.32, SK = 83.71, AT = 2.61	nd	[147]
HNO ₃ -treated β -Zeolite (607.22)		GC = 94.26, SK = 94.21, AT = 0.05	na	[11/]
Oxalic acid-treated β -Zeolite (527.09)		GC = 92.45, SK = 89.60, AT = 2.85		
Blank		GC = 0.3, SK = 100, AT = 0, OT = 0	-	
SiO_2 (na)		GC = 0.6, SK = 100, AT = na, OT = 0	** 0	
Mo (na)	T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/butanone (1:10), under N ₂ flow	GC = 0.3, SK = 100, AT = na, OT = 0	** 0	[152]
$1\% \text{ Re/SiO}_2$ (na)		GC = 92.6, $SK = 94.6$, $AT = na$, $T = 5.4$	** 124	
1% Ru/Mo (na)		GC = 67.1, $SK = 93.4$, $AT = na$, $OT = 6.6$	** 67.4	
Titanate nanotubes (HTNT-72) (182)	T = 50 °C, Cat = 130 mg, t = 6 h, 150 rpm, Glycerol/Acetone (1:1) under N ₂ flow	GC = 45.5, SK = 83, AT = 15, OT = 2		[150]
	T = 50 °C, Cat = 130 mg, t = 6 h, 150 rpm, Glycerol/Acetone (1:4) under N ₂ flow	GC = 65.5, SK = 35, AT = 0, OT = 65	nd	
	T = 50 °C, Cat = 130 mg, t = 6 h, 150 rpm, Glycerol/Acetone (1:8) under N ₂ flow	GC = 85.4, $SK = 10$, $AT = 0$, $OT = 90$		
1:1 Nb-Al (182)	T = Room temp., Cat = $2.7 \text{ wt}\%$ G, t = 6 h, Glycerol/Acetone (1:4), 600 rpm	GC = 36, SK = 80, AT = 20	24	
1:0.05 Nb-Al (<10)		GC = 73, SK = 93, AT = 7	48	
1:1 Nb-Al (182)	$T = 50 \degree C$. Cat = 2.7 wt% G, t = 6 h, Glycerol/Acetone (1:4), 600 rpm	GC = 62, SK = 94, AT = 6	41	[151]
1:0.05 Nb-Al (<10)		GC = 84, SK = 98, AT = 2	56	
1:1 Nb-Al (182)	$T = 80 \degree C$, Cat = 2.7 wt% G, t = 6 h, Glycerol/Acetone (1:4), 600 rpm	GC = 78, SK = 97, AT = 3	52	
1:0.05 Nb-Al (<10)		GC = 77, SK = 97, AT = 3	51	
10 wt% MoPO/SBA-15 (573)		GC = 75, $SK = 98$, $AT = na$, $OT = na$	75	
40 wt% MoPO/SBA-15 (164)	T = room temp., P = atm. press., Cat = 50 mg, t = 2 h, Glycerol/Acetone (1:3)	GC = 100, SK = 98, AT = na, OT = na	100	[146]
100 wt% MoPO/SBA-15 (na)		GC = 64, SK = 97, AT = na, OT = na	64	
Amberlyst-15 (na)		GC = 73, SK = 91, AT = -	197	
K-10 Clay (na)		GC = 27.3, SK = 89, AT = -	74	
CsHPW (na)		GC = 67.3, SK = 99, AT = -	182	
MoO_3/SiO_2 (na)	T = room temp. (28 °C). Cat = 5 wt% G, t = 1 h. Glycerol / Acetone (1:2)	GC = 46.8, SK = 90, AT = -	126	[148]
HZSM-5 Zeolite (na)		GC = 19.5, SK = 88, AT = -	53	
H-mordenite Zeolite (na)		GC = 8, SK = 85.5, AT = -	22	
H-Y Zeolite (na)		GC = 74.2, SK = 98.2, AT = -	200	
H-Beta-1 Zeolite (na)		GC = 86, SK = 98.5, AT = -	232	
Amberlyst-35 Dry (35)		$GC = 71 \pm 2$, $SK = 70 \pm 1$, $AT = na$, $OT = na$	3547	
Amberlyst-35 Wet (35)		$GC = 71 \pm 3$, $SK = 71 \pm 3$, $AT = na$, $OT = na$	3547	
Zeolite (480)	$T = 40 \degree C$ P = 4.1 MPa WHSV = 4/h Glycerol/Acetone (1.2)	$GC = 73 \pm 3$, $SK = 72 \pm 2$, $AT = na$, $OT = na$	3646	[143]
Montmorillonite (264)	$1 = 10^{\circ} \text{ C}/1 = 1.11111 \text{ a}/11107 = 1/11, \text{ Grycerol/ rectore (1.2)}$	$GC = 60 \pm 4$, $SK = 60 \pm 1$, $AT = na$, $OT = na$	2997	
Polymax (na)		GC = 51 \pm 3, SK = 50 \pm 1, AT = na, OT = na	2548	
Zirconium Sulphate (na)		$GC = 66 \pm 1$, $SK = 65 \pm 3$, $AT = na$, $OT = na$	3297	

Table 10. Performance of some catalysts in the conversion of glycerol to solketal and acetal as reported in some literature.

Tab	le	10.	Cont.
	_		

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
Amberlyst-35 Dry (35)		$GC = 88 \pm 3$, $SK = 86 \pm 3$, $AT = na$, $OT = na$	4396	
Amberlyst-35 Wet (35)		$GC = 89 \pm 3$, $SK = 88 \pm 4$, $AT = na$, $OT = na$	4446	
Zeolite (480)	T = 40 °C $P = 4.1$ MPa WHEV = 4 /b Chromol / A actors (1.6)	$GC = 85 \pm 2$, $SK = 84 \pm 2$, $AT = na$, $OT = na$	4246	
Montmorillonite (264)	$1 = 40^{\circ}$ C, $r = 4.1$ MF a, $W115V = 4/11$, Glycerol/Acetolie (1.0)	$GC = 69 \pm 1$, $SK = 68 \pm 1$, $AT = na$, $OT = na$	3447	
Polymax (na)		$GC = 61 \pm 2$, $SK = 60 \pm 2$, $AT = na$, $OT = na$	3047	
Zirconium Sulphate (na)		GC = 79 \pm 2, SK = 77 \pm 2, AT = na, OT = na	3946	
ZrO_{2} (42)		GC = 58, SK = 47, AT = 53	252	
TiO_2 - ZrO_2 (30)	T = 100 °C Cat = 5 wt% t = 30 min Clycerol/Benzaldehyde (1.1)	GC = 64, SK = 47, AT = 53	278	[154]
10 wt% MoO _x /ZrO ₂ (94)	1 = 100 C, Cat = 5 wt/6, t = 50 min, Gryceror/ Benzaldenyde (1.1)	GC = 70, SK = 47, AT = 53	304	[134]
$10 \text{ wt\% MoO}_{x}/\text{TiO}_{2}\text{-ZrO}_{2}$ (7)		GC = 74, SK = 49, AT = 51	321	
Blank	T = 45 °C, Cat = Nil, t = 3 h, Glycerol/Acetone (1:8), 530 rpm, under N ₂ flow	GC = 28, SK = 75, AT = 6, OT = 25	-	
Activated Carbon (AC) (780)		GC = 33, SK = 81, AT = 0, OT = 19	30	
1% Ni/AC (na)		GC = 65, SK = 91, AT = 3, OT = 6	59	
3% Ni/AC (na)		GC = 83, SK = 62, AT = 26, OT = 12	75	[1/19]
5% Ni/AC (582)	T = 45 °C, Cat = 0.2g, t = 3 h, Glycerol/Acetone (1:8), 530 rpm, under N ₂ flow	GC = 98, SK = 86, AT = 10, OT = 4	89	
1% Zr/AC (799)		GC = 54, SK = 77, AT = 23, OT = 0	49	
3% Zr/AC (na)		GC = 57, SK = 68, AT = 32, OT = 0	51	
5% Zr/AC (na)		GC = 67, SK = 63, AT = 37, OT = 0	61	
5% Ni-1% Zr/AC (612)		GC = 100, SK = 74, AT = 26, OT = 0	90	
1% Ni-5% Zr/AC (74.9)		GC = 74, SK = 61, AT = 39, OT = 0	67	

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, SK = Solketal selectivity, AT = Acetal selectivity, OT = Other product(s), TOF (mmol g^{-1} cat. h^{-1}) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.

5. Other Precursor Bio-Based Chemicals from Glycerol

5.1. Acrolein

Acrolein, also known as propenal, is the simplest unsaturated aldehyde, and it is a versatile intermediate compound obtained via the dehydration of glycerol (Scheme 9). This intermediate is usually manipulated via suitable catalyst and reaction conditions to yield polymers, acrylic acid esters, super absorbers, adhesive and detergents [34].



Scheme 9. Conversion of glycerol to acrolein by dehydration.

In acrolein selectivity, the choice of catalyst is critical and research have shown over the years that the presence of Bronsted acid sites favors high acrolein production [156]. So many catalysts have been employed in acrolein production over the years. Some of these catalysts include sulfuric acid, niobic acid, alumina, silica, metal oxides on different support materials, zeolites, heteropoly acids, hydrotalcite-type compounds, organic acids, etc. Some of these research works are reviewed below.

Sulfuric acid has been used as catalyst to convert glycerol in hot compressed water to acrolein. Rajan et al. [157] obtained up to 74% selectivity to acrolein under supercritical conditions with the sulfuric acid catalyst within reaction time of 12 s. TiO_2 and WO_3/TiO_2 in supercritical water at 400 °C and 33 MPa was examined using a fixed-bed flow reactor [158]. It was observed that the supercritical condition changed the structure of TiO_2 from anatase to rutile type. However, the rate of reaction was found to increase with increase in WO_3 content of the catalyst, which was attributed to higher surface area and stronger acidity of WO_3/TiO_2 catalysts. The use of supercritical conditions was attributed to the fact that at lower temperatures other products such as acetaldehyde, propionaldehyde, methanol, allyl alcohol, carbon monoxide, carbon dioxide, hydrogen, etc. were also formed [158].

Gu et al. [159] used supported nickel sulfate catalyst prepared at lower calcination temperature (350 °C) and moderate loading (17NiSO₄-350). More than 90% glycerol conversion was obtained with acrolein selectivity higher than 70 mol% even after 10 h of reaction. However, it was noticed that the catalyst became deactivated due to oxidation and loss of sulfur. Several catalysts and support materials (dodecatungstophosphoric acid (DTP) supported on hexagonal mesoporous silica (HMS), K-10 clay and octahedral molecular sieves (OMS)) were investigated [160]. Results showed that HMS acted as a better support material for acrolein selectivity compared to K-10 clay and OMS. 20% w/w DTP/HMS catalyst resulted in 94% of glycerol conversion and 80% of acrolein selectivity at 225 °C. The catalyst deactivation was not reported after six times reuse. However, subsequently the catalyst suffered deactivation due to coke deposition. In a similar vein, using the deactivation data obtained from the 20% w/w DTP/HMS catalyst above, a new robust one, MUICat-5 catalyst (W-Zr-Al/HMS composition) was synthesized and on testing, gave 86% glycerol conversion and 60% selectivity to acrolein. Unlike the DTP/HMS catalyst, the MUICat-5 was not deactivated even after reuse up to six times and did not affect the glycerol conversion and acrolein selectivity.

The use of Cs heteropoly salt as the catalyst at 275 °C and 1bar gave excellent results [161]. 100% glycerol conversion and 98% selectivity of acrolein were achieved. However, when Wells–Dawson and Keggin-type phosphotungstic acids supported on MCM-41 catalysts ($H_3PW_{12}O_{40}/MCM$ -41 and $H_6P_2W_{18}O_{62}/MCM$ -41) were synthesized and used in the gas phase dehydration of glycerol to acrolein, not much was achieved [162]. $H_6P_2W_{18}O_{62}/MCM$ -41 catalyst gave 51.3% while $H_3PW_{12}O_{40}/MCM$ -41 gave 43.8% acrolein respectively. The low catalytic activity was attributed to the leaching of heteropolyacids (HPW) and coke deposition.

The use of supported copper catalysts in glycerol conversion into acrolein has also been reported. Dar et al. [163] prepared and compared the activities of CuO/CeO_2 , CuO/CeO_2 -ZrO₂, CuO/CeO_2 -SiO₂. All the catalysts prepared were found to be active and acrolein was obtained as the major product. The range of glycerol conversion was observed to be 12–70% with selectivity to acrolein in the range of 14–57%. On investigating the effect of various supports materials on the catalyst, CuO/CeO_2 :ZrO₂ showed the best activity and selectivity followed by Cu/Cs and then Cu/Ce. The decrease in the activity of the catalysts after 5 cycles with time was negligible. The method of preparing catalysts also plays a great role in acrolein production.

The use of zeolite-based catalysts has also shown great potential in acrolein production from glycerol. The use of nanocrystalline HZSM-5 catalyst with a Si/Al ratio of 65 was compared with the bulk HZSM-5 catalyst [164]. The nanocrystalline HZSM-5 catalyst showed enhanced catalytic performance in glycerol dehydration even at very high space velocity (GHSV) of 1438 h^{-1} with excellent glycerol conversion and selectivity even with crude glycerol. When glycerol was dehydrated over ZSM-5 zeolite treated with NaOH, oxalic acid or HCl and later impregnated with vanadium oxides (V₂O₅), over 65% glycerol conversion was achieved with high selectivity towards acrolein [165]. The catalyst performance was attributed to it micro-mesoporous nature with high pore volume as well as the presence of redox-active sites.

Glycerol conversion of 54.2% and acrolein yield of 44.9 wt% were achieved over the montmorillonite catalyst activated by aqueous sulfuric acid (10 wt%) at optimum conditions of 320 °C, liquid hourly space velocity (LHSV) of 18.5 h^{-1} and 10 wt% glycerol solution [166]. Table 11 shows a summary of the performance of some catalysts in the conversion of glycerol to acrolein as recently reported in some literature.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
H ₃ PW ₁₂ O ₄₀ /MCM-41 (615)	T = 320 °C, P = atm. press., t = 1–5 h, Cat = 0.5 g,	GC = >95, S = 43.8	** 103.7	[1(0]
$H_6P_2W_{18}O_{62}/MCM-41$ (601)	10 wt% glycerol solution, FFR = 3 mL/h,	GC = >93, S = 51.3	** 184.2	[162]
ZSM-5 (na)	under 10 mL/min N ₂ flow	GC = 90, S = ≈33	900	
ZSM-5 (NaOH-treated) (na)		$GC = 89, S = \approx 24$	890	
ZSM-5 ($H_2C_2O_4$ -treated) (na)	$T = 200 \degree C B = atm mass t = 1 h Cat = 100 m c$	$GC = 100, S = \approx 29$	1000	
ZSM-5 (HCl-treated) (na)	I = 500 C, $F = atm. press., t = 1 m, Cat = 100 mg,10 wte/ glycorol solution EEP = 0.05 mJ /min$	$GC = 100, S = \approx 35$	1000	[165]
10 wt% V ₂ O ₅ /ZSM-5 (na)	under 30 mL /min N- flow	$GC = 100, S = \approx 26$	1000	[105]
10 wt% V ₂ O ₅ /ZSM-5	under 50 mL/ mm N ₂ now	$CC = 89$ $S = \approx 35$	890	
(NaOH-treated) (na)		GC = 07,0 = 1000	070	
10 wt% V ₂ O ₅ /ZSM-5		$GC = 93$, $S = \approx 33$	930	
$(H_2C_2O_4$ -treated) (na)		GC = 90,0 = 1000	200	
10 wt% V ₂ O ₅ /ZSM-5		$GC = 100, S = \approx 30$	1000	
(HCI-treated) (na)			_	
17NiSO ₄ -350		GC = >90, S = >70	nd	
29NiSO ₄ -350	T = 340 °C, P = atm. press., Cat = 1 g, GHSV = 8/3/h,	GC = >85, S = >70		[159]
17NiSO ₄ -550	20 wt% glycerol solution, FFR = 0.13 mL/min , t = >10 h	GC = <85, 5 = <60		
$29N_{1}SO_{4}-550$		GC = >89.2, S = >62.1		
20% w/w DIP/K-10 (na)	T = 225 °C, P = atm. press., Cat = 1 g, WHSV = 10.74/h,	GC = 89, S = 50	46	
20% w/w DTP/HMS (299.6)	20 wt% glycerol solution, FFR = 10.2 mL/h , t = 4 h,	GC = 94, S = 80	47	
20% w/w DIP/OMS (na)	under 1.5 L/min N ₂ flow	GC = 62, S = 45	31	[1(0]
Sulfuric acid	T 075 % C D ater server Cat 1 a MULEN 10.74 /h	GC = 60, S = 28	3	[160]
Presedent Privis (na)	I = 2/5 °C, P = atm. press., Cat = 1 g, WHSV = 10.74/n,		24	
Chlorosulfonic	20 Wt% giveroi solution, FFK = 10.2 mL/n ,	GC = 68, S = 38	34	
chlorosunonic	under 1.5 L/min N_2 flow, t = 4 n	GC = 71, S = 29	36	
W-Zr-A1/HMS (143.9)		GC = 86.S = 60	43	
$10 \text{ wt}\% \text{ CuO/CeO}_2(\text{na})$		GC = 12.21, $S = 14.42$	15	
$10 \text{ wt}\% \text{ CuO/CeO}_2\text{-ZrO}_2$ (na)	T = 320 °C, P = atm. press., Cat = 0.5 g,	GC = 69.96, $S = 56.92$	35	[163]
$10 \text{ wt\% CuO/CeO}_2-\text{SiO}_2$ (na)	30 mL/min H_2 flow, t = 5 h, 30 wt % glycerol solution	GC = 44.68, S = 43.14	22	[]
	$T = 320 \degree C$, $P = atm$, press., $Cat = 0.5 g$,			
SO_3H -Activated Montmorillonito (46.9)	10 wt% glycerol solution, FFR = 0.3 mL/min,	GC = 54.2, S = 83	nd	[166]
(40.7)	under 10 mL/min N ₂ flow, LHSV = $18.5/h$.			

Table 11. Performance of some catalysts in the conversion of glycerol to acrolein as reported in some literature.

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, W/GHSV = Water/Gas Hourly Space Velocity, FFR = Feed Flow Rate, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, nd = not determined.

5.2. Glycerol Carbonate

Glycerol carbonate (GC), also named as 4-hydroxymethyl-2-oxo-1,3-dioxolane, is a liquid compound that has huge applications in the polymer and chemical industries to produce polyurethanes, polyesters, polycarbonates and polyamides. Generally, GC is considered to be a green substitute for important petro-derivative compounds such as ethylene carbonate or propylene carbonate. It is used as solvent in the paint, battery and detergent industries as well as in the synthesis of very valuable intermediates such as glycidol, which is used in textile, plastics, pharmaceutical and cosmetics industries [167].

GC is prepared by reacting glycerol with urea or dimethyl carbonate or by directly reacting it with carbon dioxide under supercritical conditions (Schemes 10–12). In view of the versatile applications of glycerol for the production of GC via catalysis, it has generated a lot of interest over the years as reviewed below.



Scheme 10. Conversion of glycerol to glycerol carbonate via glycerolysis with urea.



Scheme 11. Conversion of glycerol to glycerol carbonate via transesterification with dimethyl carbonate.



Scheme 12. Conversion of glycerol to glycerol carbonate by direct carboxylation with carbon dioxide.

The use of oxides as catalyst proved to be excellent. The transesterification reaction of glycerol with ethylene carbonate over basic oxides (MgO and CaO) and mixed oxides (Al/Mg, Al/Li) derived from hydrotalcites were studied [168]. Results showed that calcined Al/Ca-mixed oxide (AlCaMO) was the optimum catalyst in terms of activity and selectivity due to its strong basic character. The advantage of this catalyst is that low reaction temperature (35 °C) and low catalyst loading (0.5 wt%) was able to give high glycerol conversion with 98% selectivity to GC.

The use of copper (II) complexes as catalysts in the synthesis of glycerol carbonate via oxidative carbonylation was reported with above 92% glycerol conversion and over 93% selectivity towards GC

within 4 h reaction time [169]. The best reaction condition was found to be CuCl₂:pyridine in a 1:0.5 molar ratio catalyst in DMA as the solvent, at 130 °C and 4 MPa of CO:O₂ (5:1 as molar ratio). However, the use of nanoparticle-sized Cu/La₂O₃ catalysts could not give as much GC as expected, despite the use of moderate temperature and pressure conditions. The glycerol conversion and selectivity to GC of 33.4 and 45.5% were obtained at 150 °C, 7.0 MPa and 12 h reaction time [170]. The authors also

Zuhaimi et al. [171] reported the use of both calcined and uncalcined gypsum (CaSO₄) as catalysts. The calcined β -CaSO₄ phase showed the highest activity with 92.8% glycerol conversion, 90.1% selectivity and 83.6% yield of GC. The catalyst was found to be stable and easily recoverable. The performance of the calcined catalyst was attributed to the presence of Lewis acid sites (Ca²⁺) and conjugate base sites (SO₄²⁻).

reported that monoacetin was formed during the reaction with selectivity of 52.9%.

The catalyst preparation method was taken into consideration and good glycerol conversion and selectivity towards GC were obtained. Wu et al. [172] prepared 0.2CeNiO-400 by co-precipitation method and when used in the transesterification of glycerol with diethyl carbonate at optimum conditions (5 wt% catalyst loading, 85 °C, glycerol:diethyl carbonate molar ratio of 1:3 and 8 h), 94.14% glycerol conversion and 90.95% GC selectivity were achieved. The catalyst demonstrated high potential when reused up to three times without deactivation or decreased GC yield. The performance was attributed to the presence of strong basic sites and a well dispersed NiO species.

Zeolites are known to be inactive in the carbonation of glycerol. However, when they were impregnated with metals, the resultant catalysts were seen to be active and produced some quantity of GC. This was reported by Ozorio et al. [173], where AgY, ZnY and SnY zeolite catalysts were synthesized and tested in the direct carbonation of glycerol with CO_2 at 180 °C, 100 bar in 3 h. All of the catalysts produced some quantity of GC as against the parent zeolite (NaY). The ZnY yield was the highest with about 5.8% GC. The activity exhibited by the metal-impregnated zeolites was attributed to the presence of large volume of active metal oxide phase.

When waste boiler ash was used as catalyst in the direct synthesis of GC from glycerol and urea, it exhibited high-activity 93.6 \pm 0.4% glycerol conversion with GC selectivity and yield of 90.1 \pm 1.0% and 84.3 \pm 1.1% [174].

The use of organocatalyst in the production of GC has been explored, with good glycerol conversion and selectivity being obtained. Naik et al. [175] obtained as much as 93% GC after 5 h with a low catalyst loading of 5 mol% 1-n-butyl-3-methylimidazolium-2-carboxylate. The interesting thing about this catalyst was that no byproduct was formed, and catalyst loading as low as 1% was sufficient to yield quantitative conversions. The catalyst performance was found to strongly contrast the K₂CO₃ catalyst commonly used, which requires pure glycerol. Similarly, when selected ammonium and imidazolium-based ionic liquids were used as catalysts in the transesterification reaction, 1-ethyl-3-methylimidazolium acetate recorded the highest activity, with glycerol conversion of 93.5%, selectivity 94.9% and GC yield of 88.7% at optimum conditions of 120 °C, 0.5 mol% catalyst loading, diethyl carbonate/glycerol molar ratio of 2 and reaction time of 2 h [176]. There was no significant deactivation even when the catalyst was used three times, which was attributed to excellent interaction between the ionic liquid and the reactant. Table 12 shows a summary of the performance of some catalysts in the conversion of glycerol to GC as recently reported in some literature.

Table 12. Performance of some catalysts in the conversion of glycerol to glycerol carbonate as reported in some literature.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
NiO-400 (56.07) 0.2CeNiO-400 (30.49) 0.6CeNiO-400 (41.10) 1.0CeNiO-400 (71.80)	T = 80 °C, P = na, t = 6 h, Cat = 5 wt% G, Glycerol/DEC (≈1:3)	GC = 17.3, S = 100 GC = 76.95, S = 100 $GC = \approx 75, S = 100$ GC = 66.51, S = 100	6 28 27 24	[172]

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
Methylammonium nitrate Ethylammonium nitrate 2-hydrozyethylammonium formate 1-ethyl-3-methylimidazolium dimethyl phosphate 1-butyl-3-methylimidazolium dicyanamide 1-butyl-3-methylimidazolium chloride 1-butyl-3-methylimidazolium tetrafluoroborate	T = 120 °C, P = na, t = 2 h, Cat = 0.5 mol%, Glycerol/DEC (≈1:2)	GC = <10, Y = <10 GC = <10, Y = <10 GC = 24.08, Y = 24.00 GC = 22.20, Y = 22 GC = 45, Y = 45 GC = <10, Y = <10 GC = <5, Y = <5 GC = <5, Y = <5, Y = <5 GC = <5	nd	[176]
I-ethyl-3-methylimidazolium acetate Gypsum (CaSO ₄ .2H ₂ O) (10.8) Gypsum-150 (2.6) Gypsum-800 (1.4) Gypsum-30% H ₂ O ₂ Blank	T = 150 °C, P = na, t = 4 h, Cat = 0.25 g, 340 rpm, Glycerol/Urea (1:1.5)	GC = 93.5, Y = 88.7 GC = 92.5, S = 64.8, Y = 59.9 GC = 92.8, S = 90.1, Y = 83.6 GC = 89.1, S = 82.8, Y = 73.8 GC = 91.0, S = 43.8, Y = 39.8 GC = 78.7, S = 32.8, Y = 25.8	** 89.7 ** 110.5 ** 125.4 ** 59.6	[171]
Waste boiler ash-110 (8.05) Waste boiler ash-700 (na) Waste boiler ash-900 (2.00) Waste boiler ash-1100 (na) Blank	T = 150 °C, P = na, t = 4 h, Cat = 0.25 g, 340 rpm, Glycerol/Urea (1:1.5)	GC = 91.1, S = 83.5, Y = 76.2 GC = 94.1, S = 88.6, Y = 83.4 GC = 93.6, S = 90.1, Y = 84.3 GC = 89.8, S = 85.6, Y = 77.0 GC = 78.7, S = 32.8, Y = 25.8 CC = 0.8, S = 6.3, Y = 0.05	** 136.7 ** 141.2 ** 140.4 ** 134.7	[174]
$\begin{array}{c} La_{2}O_{3}\left(21\right)\\ 0.7\%\ Cu/La_{2}O_{3}\left(21\right)\\ 2.3\%\ Cu/La_{2}O_{3}\left(20\right)\\ 4.6\%\ Cu/La_{2}O_{3}\left(20\right)\\ 13.4\%\ Cu/La_{2}O_{3}\left(na\right)\\ Blank\end{array}$	T = 150 °C, P = 7 MPa, t = 12 h, Cat = 0.23 g, Glycerol/CH ₃ CN/CO ₂	$ \begin{array}{l} GC = 0.3, S = 0.3, 1 = 0.03 \\ GC = 19.3, S = 47.7, Y = 9.2 \\ GC = 33.4, S = 45.4, Y = 15.2 \\ GC = 30.6, S = 44.2, Y = 13.5 \\ GC = 1.7, S = 35.3, Y = 0.6 \\ GC = 0.4, S = 5.0, Y = 0.02 \end{array} $	4 6 6 0.3	[170]
NaY-Zeolite (760) 5.9 wt% AgY-Zeolite (289) 6.0 wt% ZnY-Zeolite (407) 10.3 wt% SnY-Zeolite (442) AgNO ₃ (na) Zn (NO ₃) ₂ (na) SnCl ₂ (na)	T = $180 \circ C$, P = 10 MPa, t = 3 h, Cat = 0.5 g , Glycerol/CO ₂	GC = na, Y = 0.0, S = na GC = na, Y = 5.6, S = na GC = na, Y = 5.8, S = na GC = na, Y = 5.1, S = na GC = na, Y = 3.5, S = na GC = na, Y = 2.7, S = na GC = na, Y = 2.6, S = na	0 10 11 9 6 5 5 5	[173]
$\begin{array}{l} CuCl_2 \ (na)) \\ CuBr_2 \ (na)) \\ CuJ_2 \ (na)) \\ CuSO_4 \ (na)) \\ Cu \ (OAc)_2 \ (na)) \\ Cu \ (OAc)_2 \ (na)) \\ Cu \ (OTf)_2 \ (na)) \\ Cu \ (ClO_{4)2} \ (na)) \end{array}$	$T = 130 \ ^{\circ}C, P = 4 \ MPa,$ t = 4 h, Cat = 0.6 mmol, Glycerol/DMA/CO:O ₂ (5:1), Pyridine = 0.3 mmol	$\begin{array}{l} GC = 93, S = 91 \\ GC = 51, S = 89 \\ GC = 69, S = 94 \\ GC = 75, S = 95 \\ GC = 10, S = 40 \\ GC = 72, S = 60 \\ GC = 41, S = 40 \end{array}$	nd	[169]

Table 12. Cont.

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, Y = Yield, S = Selectivity, DEC = Diethylcarbonate, DMA = Dimethylcarbonate, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.

5.3. 1,3–Propanediol

1,3-propanediol (1,3-PD) is an important chemical compound considered to be a monomer in the production of polyesters, polyethers and polyurethanes [3]. It is also used as an intermediate in the production of cosmetics, lubricants, engine coolants, water-based inks, adhesives, wood paints, coatings, antifreeze, and heterocyclic compounds [177,178]. The versatility of 1,3-PD was tremendously enhanced with the development of new biodegradable polyester, polytrimethylene terephthalate (PTT) because of its great potential in carpet, fiber and textile industries [179]. 1,3-PD is obtained via hydrogenolysis of the secondary OH of glycerol with the type of catalyst and conditions of the reaction playing critical roles (Scheme 13).



Scheme 13. Conversion of glycerol to 1,3-propanediol by hydrogenolysis.

Several catalysts involving noble metals have been employed in 1,3-PD synthesis in the presence of hydrogen. Due to alcohol's resistance to hydrogenation, modified metals supported by different materials have been employed as catalysts in hydrogenolysis of glycerol with low to moderate product yields as reviewed below.

Qin et al. [180] reported the hydrogenolysis of glycerol over $Pt/WO_3/ZrO_2$ as catalyst in a fixed-bed continuous-flow reactor at 130 °C under 4.0 MPa. 70% glycerol conversion with 32% yield and 46% selectivity towards 1,3-PD was attained after 24 h reaction time. In another report, silica supported catalyst, $Pt/WO_3/TiO_2/SiO_2$ in several solvents and in a batch reactor was found to be effective and selective in the conversion of glycerol to 1,3-PD when compared to $Pt/WO_3/TiO_2$ catalyst. The authors concluded that the reaction was influenced by the type of solvent, catalyst loading, temperature and hydrogen pressure [181]. At slightly higher temperature and pressure of 220 °C and 4.5 MPa, higher selectivity to 1,3-PD was obtained (38.5%) when alumina was used as support, $Pt/WO_x/Al_2O_3$, after a reaction time of 16 h [182]. Similarly, under the same conditions, but with a longer reaction time of 24 h, glycerol conversion and selectivity towards 1,3-PD increased to 51.9% and 53.1% with 9 $Pt/8WO_x/Al_2O_3$ catalyst [183]. This great improvement was attributed to the highly dispersed polytungstate species responsible for Bronsted acidity, the closeness of platinum oxide and tungsten oxide as well as the electronic interactions between the acid and metallic sites.

In other to further improve 1,3-PD yield, selectivity and glycerol conversion, mesoporous catalysts were deployed in the hydrogenolysis. Longjie et al. [184] compared the hydrogenolysis of glycerol to 1,3-PD over the prepared mesoporous tungsten trioxide (m-WO₃) catalyst with the commercial WO₃ catalyst. The Pt/m-WO₃ catalyst performed better with 18.0% glycerol conversion and 39.2% selectivity under the reaction conditions of 180 °C, 5.5 MPa H₂, and within a reaction time of 12 h. The Pt/m-WO₃ catalyst activity was attributed to the presence of a larger surface area and the highly dispersed Pt particles on the support.

Good improvement was noticed when alkaline metals (Li, K, Rb and Cs) were added to Pt–H₄SiW₁₂O₄₀/ZrO₂ catalysts (heteropolyacids). The addition was found to greatly enhance the catalysts' acidic property (both in terms of Bronsted acid sites and Lewis acid sites), thereby improving glycerol hydrogenolysis [185]. The Pt–Li H₄SiW₁₂O₄₀/ZrO₂ catalyst promoted the reactivity most pronouncedly with 43.5% glycerol conversion and selectivity of 53.6% towards 1,3-PD at 180 °C and 5 MPa. In a comparative study using zirconia supported bifunctional catalysts containing Pt and heteropoly acids (H₄SiW₁₂O₄₀, H₃PW₁₂O₄₀ and H₃PMo₁₂O₄₀) as active compounds; the results indicate that heteropoly acids modified Pt/ZrO₂ catalysts were effective due to the enhanced acidity [186]. The Pt-H₄SiW₁₂O₄₀/ZrO₂ catalyst, which exhibited the highest selectivity towards 1,3-PD (48.1%), also showed the highest Bronsted acid sites and thermal stability. Zhu et al. [186] also revealed that independent of the heteropolyacid type used, the concentration of Bronsted acid sites guide the glycerol hydrogenolysis to 1,3-PD, while the concentration of Lewis acid sites direct to the formation of 1,2-PD.

To further improve 1,3-PD selectivity, SiO_2 modified $Pt-WO_x/ZrO_2$ catalysts prepared via deposition–precipitation method were employed in the hydrogenolysis of glycerol [187]. The SiO₂ doping greatly improved Pt dispersion and acidity, which led to improved activity as well as 1,3-PDO selectivity. The highest glycerol conversion of 54.3% and the best selectivity of 52% were achieved with 5 wt% Pt-WO_x/ZrO₂-SiO₂. However, it was noticed that the excessive introduction of SiO₂ led to decline in the glycerol conversion and 1,3-PD selectivity.

Deng et al. [188] employed a series of synthesized different particle sizes of Pt-Re/carbon nano tube (CNT) catalysts and found that smaller particle sizes were better in hydrogenolysis due to increase in the surface acidic areas. However, sizes below 1.5 nm suffered severe coking, leading to decreased activity.

The use of Pt and Ru supported on ZrO_2 and WO_3/ZrO_2 as catalyst in the hydrogenolysis of glycerol did not improve its conversion nor selectivity to 1,3-PD as such [189]. Maximum selectivity achieved were 30.6% for Pt/ZrW and 9.5% for Ru/ZrW after 18 h of reaction time, while the glycerol conversion was 10.4%. The wide difference in the activity of the catalyst was traced to the fact that the metals exhibited different electron density on ZrO_2 .

The use of zeolite as support material was explored in hydrogenolysis. Single and bimetals of Zr, Ni, Cu, and Zn supported on H-beta zeolite were prepared by wet impregnation method and used in the hydrogenolysis of glycerol under aqueous conditions at different reaction temperatures

(150–250 °C), times (5–15 h) and H₂ pressures (2.1–8.3 MPa) [190]. Zr-Ni/H-beta catalyst (bimetallic) showed high activity with 77% glycerol conversion and 14% selectivity towards 1,3-PD, which was associated with its strong Bronsted acidity. Furthermore, the authors also reported that longer reaction time, higher temperature, and higher H₂ pressure had positive effects on the efficiency of glycerol hydrogenolysis. However, propanol and 1,2-PD were also obtained in reasonable quantity.

The production of 1,3-PD remains a challenge in view of the difficulties to high selectivity towards the CO cleavage of the secondary hydroxyl group in glycerol. So many researchers over the years have also explored, and are still exploring, the use of biocatalysts, usually from microorganisms, in 1,3-PD production.

It has been reported that bacteria, namely *Bacillus*, *Lactobacillus*, *Klebsiella*, *Citrobacter*, *Ilyobacter*, *Enterobacter* and *Clostridium*, have been used in the fermentation of glycerol to 1,3-PD using batch and/or continuous operation system [58]. The use of these organisms in 1,3-PD production is beyond the scope of this review. Table 13 shows the summary of the performance of some catalysts in the conversion of glycerol to 1,3-PD as recently reported in some literature.

Table 13. Performance of some catalysts in the conversion of glycerol to 1,3-Propanediol as reported in some literature.

Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
H-beta (484)		GC = 85, S = 0.2, Y = 0.2	85	
5 wt% Zr/H-beta (445)	$T = 200 \circ C$ $P = 4.1 MP_2 H_1 + 10 h$	GC = 70, S = 8, Y = 5.6	7	
10 wt% Zr/H-beta (434)	$I = 200$ C, $F = 4.1$ MFa H_2 , $I = 10$ R,	GC = 69, S = 7, Y = 4.8	69	[100]
5 wt% Ni-Zr/H-beta (407)	Cat = 0.5 g, 600 rpm,	GC = 77, S = 14, Y = 10.8	77	[190]
5 wt% Cu-Zr/H-beta (417)	50 wt /8 gryceror solution	GC = 70, S = 9, Y= 6.3	7	
5 wt% Zn-Zr/H-beta (420)		GC = 68, S = 9.3, Y = 6.3	68	
2 wt% Pt/ZrO ₂ (34.2)	$T = 180 \circ C$ $P = 8 MP_{2} + 18 h$	GC = 13.7, S = 4.8	0.3	
2 wt% Pt/ZrO ₂ -WO ₃ (76.3)	1 = 100 C, $1 = 0$ Wi a, $t = 10$ I, Cat = 1 g 1000 rpm 10 wt% glycorol	GC = 10.4, S = 30.6	0.3	[180]
2 wt% Ru/ZrO ₂ (34.4)	cal = 1 g, 1000 rpm, 10 wt/8 gryceror solution (in 40 mL H_{-} O)	GC = 100, S = 0.3	2.4	[109]
2 wt% Ru/ZrO ₂ -WO ₃ (81.5)	solution (in 40 mil 1120)	GC = 12.0, S = 9.5	0.3	
9 wt% Pt-8 wt% WO ₃ /Al ₂ O ₃ (95)		GC = 80.3, S = 38.5	7	[182]
1 wt% Pt-1 wt% WO ₃ /Al ₂ O ₃ (128)	T = 220 °C, P = 4.5 MPa H ₂ , t = 16 h,	GC = 25.6, S = 0	2	
1 wt% Pt-9 wt% WO ₃ /Al ₂ O ₃ (104)	Cat = 0.35 g, 550 rpm under H ₂ atm.	GC = 16.7, S = 16.4	2	[192]
4 wt% Pt-8 wt% WO ₃ /Al ₂ O ₃ (na)	5 wt% glycerol solution	GC = 42,1, S = 27.8	4	[105]
9 wt% Pt-8 wt% WO ₃ /Al ₂ O ₃ (81)		GC = 60.3, S = 31.2	6	
	T = 200 $^{\circ}$ C, P = 4.5 MPa H ₂ , t = 24 h,			
9 wt% Pt-8 wt% WO ₃ /Al ₂ O ₃ (81)	Cat = 0.35 g, 550 rpm,	GC = 53.1, S = 51.9	3	
	5 wt% glycerol solution			
2 wt% Pt-15 wt% WO ₃ /ZrO ₂ (35.1)		GC = 30, S = 44.3		
2 wt% Pt-15 wt% WO ₃ /ZrO ₂ -2.5 wt% SiO ₂ (101.2)	T = 180 °C, P = 5 MPa, Cat = 3 g,	GC = 41.5, S = 46.3		
2 wt% Pt-15 wt% WO ₃ /ZrO ₂ -5 wt% SiO ₂ (113.3)	WHSV = 1.0 g/g cat/h ,	GC = 54.3, S = 52	nd	[187]
2 wt% Pt-15 wt% WO ₃ /ZrO ₂ -7.5 wt% SiO ₂ (121.2)	10 wt% glycerol solution	GC = 40.1, S = 46.7		
2 wt% Pt-15 wt% WO ₃ /ZrO ₂ -10 wt% SiO ₂ (152.4)		GC = 32.1, S = 47.1		
1 wt% Pt-20 wt% HSiWO _X /ZrO ₂ (46.9)		GC = 26.7, S = 38.9		
$1 \text{ wt\% Pt-LiSiWO}_{\chi}/\text{ZrO}_{2} (50.5)$	T = 180 °C, P = 5 MPa, Cat = 2 g,	GC = 43.5, S = 53.6		
1 wt% Pt–KSiWO _X /ZrO ₂ (51.8)	WHSV = 0.09/h,	GC = 24.0, S = 36.8	nd	[185]
$1 \text{ wt\% Pt-RbSiWO}_{\chi}/\text{ZrO}_{2}$ (53.3)	10 wt% glycerol solution	GC = 16.6, S = 31.6		
1 wt% Pt-CsSiWO _X /ZrO ₂ (53.8)		GC = 41.2, S = 40.2		
2 wt% Pt/ZrO ₂ (61.0)	$T = 180 \circ C$, $P = 5 MPa$, $Cat = 2 \circ$	GC = 18.7, S = 3.9		
2 wt% Pt-15 wt% HSiW/ZrO ₂ (54.8)	WHSV = 0.09/h	GC = 24.1, S = 48.1	nd	[186]
2 wt% Pt-15 wt% HPW/ZrO ₂ (57.0)	10 wt% glycerol solution	GC = 25.5, S = 32.9	na	[100]
2 wt% Pt-15 wt% HPMo/ZrO ₂ (55.3)		GC = 27.1, S = 7.8		
Pt/mesoporous-WO ₃ (22)	T = 180 °C, P = 5.5 MPa H_2 , t = 12 h,	GC = 18.0, S = 39.3	1.5	[184]
$Pt/commercial-WO_3$ (9.0)	Cat = 1 g, 10 wt% glycerol solution	GC = 4.5, S = 29.9	0.3	[104]

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, WHSV = Water Hourly Space Velocity, GC = Glycerol Conversion, S = Selectivity, TOF (mmol g^{-1} cat. h^{-1}) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.

5.4. Polyglycerol (Oligomers)

Polyglycerol (PG) is simply the coming together of more than one glycerol, which is also known as oligomerization. PG is classified as an ether in view of its C-O-C bond formation and may be linear, branched or cyclic [191]. PG has numerous applications in the cosmetic, pharmaceutical, food and detergent industries [42,192].

PG can also be diglycerol, triglycerol, tetraglycerol, hexaglycerol and decaglycerol depending on the number of glycerol and the hydroxyl group of the glycerol (primary or secondary) involved in



Scheme 14. Conversion of glycerol to polyglycerol by self-condensation.

Several catalytic conversions of glycerol to PG have been undertaken, with the big challenge of controlling the oligomerization to the desired oligomer, and so more and more research is being undertaken in the area of catalysis with a view to improving yield and selectivity [193].

Researchers have shown that the use of homogeneous catalyst such as sulfuric acid results in high quantities of PG with preference to linear and/or cyclic oligomers. However, several disadvantages are associated with these catalysts, some of which include lack of effective selectivity in the oligomerization and difficulty in separating the catalyst from the product, as well as the burden involved in purification of the process. These foregoing reasons made scientists shift attention to solid heterogeneous catalysts, finding that they are more selective and easier to separate, but the quantity is not as great as their homogeneous counterpart. Heterogeneous catalysts yield more branched oligomers [192].

Different alkaline earth metal oxides (MgO, CaO, SrO, and BaO) were tested as potential heterogeneous catalysts [194]. Results showed that the glycerol conversion increased with increasing catalyst basicity in the order: MgO<CaO<SrO<BaO. The best selectivity values for di- and triglycerol (>90% at 60% conversion) were obtained over CaO, SrO, and BaO. Further study also showed that catalysts activity depends on the strength of both basic and Lewis acid sites.

The catalyst preparation method also improves glycerol conversion and product yield. García-Sancho et al. [195] investigated the use of MgAl mixed oxides as base catalysts (prepared by coprecipitation and urea hydrolysis) at 220 °C in a batch reactor. The catalyst prepared by coprecipitation exhibited the highest glycerol conversion of 50.7% with full selectivity to diglycerol with 43% yield and was attributed to highest specific surface area.

Hydrotalcite catalysts prepared using combustion method was investigated [196]. The catalyst showed 12.3% glycerol conversion at 450 °C with high selectivity to diglycerol (97.7%). However, with calcination of the catalyst at 650 °C in 16 h, the catalyst activity increased with glycerol conversion of 77.7% after 16 h. However, at higher temperature of 850 °C, the catalyst was affected, thereby affecting the conversion.

When acid-treated montmorillonite K-10 (Clay MK-10) was modified with LiOH (Clay Li/MK-10) and used as catalyst at 240 °C, high glycerol conversion of 98% and selectivity of 53% towards diglycerol were achieved after 12 h of reaction time [197].

Recent research has also shown the etherification of glycerol in a solventless process. Heterogeneous mesoporous basic catalysts were synthesized by wet impregnation of MCM-41 with calcium nitrate and lanthanum nitrate and used in the solventless etherification of glycerol to produce diglycerol at 250 °C for 8 h [198]. Results showed that 20% Ca_{1.6}La_{0.6}/MCM-41 catalyst resulted in the highest glycerol conversion of 91%, with diglycerol yield of 43%. However, leaching of the metal was reported. It was also previously reported that metal oxide composite catalyst ($Ca_{1+x}Al_{1-x}La_xO_3$) calcined at 560 °C with La:Ca ratio of 1:2.7 produced 91% glycerol conversion and 53.2% diglycerol selectivity after 8 h reaction at 250 °C and catalyst loading of 2 wt% [199]. The catalytic performance was attributed to synergetic mixed oxide complex resulting from the interaction between La, Ca, and Al oxides. Similarly, Guerrero-Urbaneja et al. [200] prepared MgFe mixed oxides with a molar ratio ranging from 1 to 4, which were tested in a batch reactor at 220 °C. All the catalysts performed well without solvent, but the selectivity was lower than previously reported by [199]. The catalyst with Mg/Fe molar ratio of 4 produced the highest glycerol conversion of 41% with >90% selectivity to diglycerol. This was attributed to the excellent textural properties, with specific surface areas close to $200 \text{ m}^2 \text{ g}^{-1}$ of the catalyst. However, in addition to diglycerol, triglycerol was also detected after 24 h of the reaction. While the use of lithium-exchanged zeolite Y (Li-ZeY) catalyst at 240 °C was found to be highly active and thermally stable, with glycerol conversion of 99% after 8 h of reaction, which was much higher than homogenous LiOH catalyst [201].

The use of crude glycerol via microwave irradiation was explored in PG synthesis and interestingly 94.94% was obtained at 250 $^{\circ}$ C in 1 h despite soap content of 12.5% [46].

In the optimization reaction (temperature of 270 °C, catalyst concentration of 3 wt%, and reaction time of 1.0 h) of etherification of glycerol to PG without solvent using Na_2CO_3 as catalyst and microwaves as a source of heat yield 93%, 70%, and 7% diglycerol, triglycerol and tetraglycerol respectively [202]. The values obtained correlated with the predicted values of 84%, 63%, and 9%. The authors also reported that increased in the parameters studied (temperature, catalyst concentration and reaction time) led to higher amount of the product.

In other to improve the etherification reaction of glycerol towards di- to pentaglycerol (lower glycerols), Pérez-Barrado et al. [203] prepared several MgAl and CaAl layered double hydroxides (LDH) catalysts and tested them after calcinations at 450 °C. Results showed that catalysts with lower acidity resulted in lower glycerol conversion (24% for calcined MgAl-LDH and 40% for calcined CaAl-LDH) but showed higher selectivity (100% and 64%) towards di- and triglycerol. While higher-acidity catalysts exhibited higher glycerol conversion (96% for calcined MgAl-LDH and 75% for calcined CaAl-LDH) as well as higher selectivity towards other undesired products (88% for calcined MgAl-LDH and 58% for a calcined CaAl-LDH) with acrolein been the major contributor. The authors also reported that as the calcination temperature increased, the acidity decreased and the number of strong basic sites increased, resulting in higher selectivity to triglycerol (20%), tetraglycerol (15%) and pentaglycerol (6%) and decreased formation of acrolein.

Up to 75% PG yield and about 80% glycerol conversion were obtained with Aquivion[®] PFSA PW98 catalyst (solid super acid, perfluoro polymer with in cooperated sulfonic acid (-SO₃H) [204]. The catalyst was so stable that it was recycled 10 times without apparent decrease in activity or selectivity and makes it ahead of other conventional solid acid catalysts such as Nafion NR 50 and Amberlyst-70.

Galy et al. [205] reported the use of K_2CO_3 catalyst in a continuous flow reactor improved the formation of glycerol dimer with 20 wt%, glycerol trimer 21 wt%, glycerol tetramer 16 wt% and glycerol pentamer 11 wt%.

A novel idea of using eggshell waste (raw and calcined) as catalyst was investigated in glycerol etherification and under optimal reaction conditions of 2 wt% catalyst loading, 220 °C temperature and reaction time of 24 h gave 85% glycerol conversion with 43% oligomers (di-and triglycerol) yield [206]. However, the catalyst was not stable because it leached into the reaction medium. Table 14 shows the summary of the performance of some catalysts in the conversion of glycerol to PG as recently reported in some literature.

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Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
Calcined Eggshell (29)	T = 245 °C, Cat = 2 wt% G, t = 6 h, under N ₂ flow T = 220 °C, Cat = 2 wt% G, t = 24 h, under N ₂ flow	GC = 80, DG = 40, TG = 2.5, Oth = 57.5 GC = 85, DG = 35, TG = 8, Oth = 57	72 19	[206]
K_2CO_3 (na)	T = 250 °C, Cat = 18 g, 4.69 mol glycerol (in 50 mL H_2O)	G = 59.9 \pm 2.7, DG = 18.8 \pm 0.2, CDG = 1.5 \pm 0.4, TG = 8.4 \pm 1.2, CTG = 1.0 \pm 0.2, TtG = 4.4 \pm 1.0, PG = 3.1 \pm 0.1, HG = 1.0 \pm 0.5		[205]
Aquivion PW 98 (na) Amberlyst 70 (na) Nafion NR 50 (na)	T = 150 °C, Cat = 0.45 mmol, t = 6 h	$ \begin{array}{l} GC = 82, Y_{DG} = 21, Y_{TG} = 17, Y_{>TtG} = 33, S_{O} = 87 \\ GC = 76, Y_{DG} = 31, Y_{TG} = 15, Y_{>TtG} = 16, S_{O} = 81 \\ GC = 78, Y_{DG} = 14, Y_{TG} = 21, Y_{>TtG} = 24, S_{O} = 75 \end{array} $	nd	[204]
Aquivion PW 98 (na) Na ₂ CO ₃ (na)	T = 150 °C, Cat = 0.45 mmol, t = 7 h T = 270 °C, P = atm. press., Cat = 1 wt% G, t = 1 h T = 270 °C, P = atm. press., Cat = 1 wt% G, t = 2 h	$ \begin{array}{l} GC = 95, Y_{DG} = 13, Y_{TG} = 15, Y_{>TtG} = 47, S_{O} = 79 \\ GC = 85.26, Y_{(DG+TG+tTtG)} = 59.13, S_{PG} = 11.44, S_{CDG} = 7.18 \\ GC = 96.03, Y_{(DG+TG+tTtG)} = 66.83, S_{PG} = 12.50, S_{CDG} = 12.94 \end{array} $		[202]
	T = 270 °C, P = atm. press., Cat = 1 wt% G, t = 3 h T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 1 h T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 2 h T = 270 °C, P = atm. press. Cat = 3 wt% G, t = 3 h	$GC = 96.12, Y_{(DG+TG+tTtG)} = 47.33, S_{PG} = 37.53, S_{CDG} = 8.33$ $GC = 92.83, Y_{(DG+TG+tTtG)} = 70.13, S_{PG} = 9.06, S_{CDG} = 6.50$ $GC = 96.20, Y_{(DG+TG+tTtG)} = 53.30, S_{PG} = 13.33, S_{CDG} = 12.63$ $GC = 87.18, Y_{PG} = 76, 76, 96, 75, 77, S_{PG} = 0.00, S_{PG} = 35.60$	nd	
MgAl-LDH ₁ -723K (237)	$1 = 270^{\circ}$ C, $1 = 400^{\circ}$ press., Cat = 5 wt/8 G, $t = 50^{\circ}$	$GC = 96, S_{DG} = 9, S_{TG} = 3, S_{Oth} = 88, Y_O = 12$	22	
MgAl-LDH ₂ -723K (188) CaAl-LDH ₁ -723K (15) CaAl-LDH ₄ -723K (3) CaAl-LDH ₄ -923K (5)	T = 235 °C, Cat = 2 wt% G, t = 24 h, under N ₂ flow	$ GC = 24, S_{DG} = 89, S_{TG} = 11, S_{Oth} = 0, Y_O = 24 \\ GC = 75, S_{DG} = 36, S_{TG} = 6, S_{Oth} = 58, Y_O = 32 \\ GC = 60, S_{DG} = 44, S_{TG} = 11, S_{Oth} = 45\%, Y = 33 \\ GC = 59, S_D = 38, S_{TG} = 13, S_{Oth} = 49, Y_O = 35 $	5 17 14 13	[203]
CaAl-LDH ₄ -1073K (3) Blank MCM-41 (938) CaO (14) La ₂ O ₃ (na) Ca _{1.8} La _{0.8} O ₂ (20)	T = 250 °C, Cat = 2 wt% G, t = 8 h	$ \begin{array}{l} GC = 84, S_{DG} = 29, S_{TG} = 20, S_{Oth} = 51\%, Y_O = 59 \\ GC = 2, S_{DG} = 3, Y_{DG} = 0, S_{TG} = 0, Y_{TG} = 0, S_{Oth} = 97, Y = 2. \\ GC = 2, S_{DG} = 4, Y_{DG} = 0, S_{TG} = 0, Y_{TG} = 0, S_{Oth} = 96, Y = 2. \\ GC = 72, S_{DG} = 27, Y_{DG} = 20, S_{TG} = 10, Y_{TG} = 7, S_{Oth} = 63, Y = 46. \\ GC = 54, S_{DG} = 32, Y_{DG} = 17, S_{TG} = 11, Y_{TG} = 6, S_{Oth} = 57, Y = 30. \\ GC = 76, S_{DG} = 30, Y_{DG} = 23, S_{TG} = 15, Y_{TG} = 12, S_{Oth} = 55, Y = 42. \end{array} $	19 - 1 49 37 52	[198]
30% Ca/MCM-41 (na) 30% La/MCM-41 (na) 30% Ca _{1.6} La _{0.6} /MCM-41 (128) LiOH (na) Zeolite-Y (690)	T = 240 °C, P = atm. press. Cat = 2 wt% G, t = 8 h, under	$ \begin{array}{l} GC = 69, S_{DG} = 33, Y_{DG} = 22, S_{TG} = 24, Y_{TG} = 17, S_{Oth} = 43, Y = 30. \\ GC = 74, S_{DG} = 25, Y_{DG} = 19, S_{TG} = 18, Y_{TG} = 14, S_{Oth} = 56, Y = 42. \\ GC = 85, S_{DG} = 22, Y_{DG} = 19, S_{TG} = 14, Y_{TG} = 12, S_{Oth} = 64, Y = 55. \\ GC = 99, S_{DG} = 18, S_{TG} = 21, S_{TtG} = 13, S_{PG} = 52, Y = 51.5, Oth S = 48. \\ GC = 15, S_{DG} = 2, S_{TG} = 7, S_{TtG} = 4, S_{PG} = 13, Y = 2, S_{Oth} = 67. \end{array} $	47 50 57 67 10	[201]
Li-ZeY (531)	1N2 110W	$GC = 98$, $S_{DC} = 21$, $S_{TC} = 32$, $S_{TtC} = 19$, $S_{PC} = 72$, $Y = 70.5$, $S_{Oth} = 28$.	67	

Table 14. Performance of some catalysts in the conversion of glycerol to polyglycerol as reported in some literature.

A = Surface area (m^2/g) , T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, S = Selectivity, Y = Yield, O = Oligomers, DG = Diglycerol, TG = Triglycerol, TtG = Tetraglycerol, PG = Pentaglycerol, HG = Hexaglycerol, Oth = Others, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined, na = not available.

5.5. Olefins

Olefin, simply referred to as alkene, is a verse class of unsaturated hydrocarbons with at least a carbon-to-carbon double bond (-C = C-). Lower olefins have short chains with 2 to 4 carbon atoms. The higher olefins have chains of up to 20 or more [207]. In view of the presence of the double bond, olefins are very reactive; hence, their ability to form many derivatives.

The light olefins such as ethylene, propylene, butadiene and their derivatives are considered to be the most sought after because of their industrial applications, which include production of plastics and industrial solvents [208].

Research into the conversion of glycerol into olefins is still in its infancy. The possibility of reducing cost via the use of glycerol against the current method of production, thermal cracking of natural gas and crude oil, is being investigated using heterogeneous catalysts [207,209].

Catalyst screening of various metals (Cr, Ca, Cu, Ni and Al)-impregnated ZSM-5 (zeolite) for catalytic conversion of glycerol to olefins in a fixed-bed reactor was investigated by Zakaria et al. [206]. Results showed that metal-doped ZSM-5 increased its activity and olefin yield. CuZSM-5 exhibited the best result with 17.76% glycerol conversion and 3.55% olefin yield. The authors also indicated that methanol and other unidentified compounds were also produced. Similarly, Zakaria et al. [210] modified ZSM-5 into HZSM-5, Al/ZSM-5, Ca/ZSM-5, Cr/ZSM-5, Cu/ZSM-5, Li/ZSM-5, Mg/ZSM-5 and Ni/ZSM-5, and these were tested as catalysts for the conversion of glycerol to light olefins at 600 °C. Results revealed that olefin and paraffin were produced by all the catalysts, with olefin being the superior product. The turnover frequencies (TOF) for Cu/ZSM-5 and Cr/ZSM-5 catalysts were significantly high, which possibly informed the high yield, with up to a 15% improvement in olefin production. It could also be attributed to the synergistic effect of the physico-chemical properties between the parent ZSM-5 and the metals. In terms of olefin product, ethylene is the most produced (2.61–18.62%), followed by propylene (0.07–2.60%) and butylene (0.56–0.96%). Of the paraffin, methane (4.74–9.63%) was produced by all the catalysts.

Blass et al. [211] also explored the conversion of glycerol to olefins in a reactor using different catalyst at different stages of dehydration and hydrogenation. In the first step, glycerol, co-fed with H₂ over HZSM-5 catalyst at 400 °C, was dehydrated to mixture of acetaldehyde, acrolein, and hydroxypropanone. In the second step, acrolein was hydrogenated to propanal over Pd/ α -Al₂O₃ catalyst, and in the third step, propanal was converted to light olefins over HBEA at 500 °C with minimal CO production, but with catalyst deactivation occurring, leading to a decrease in propanal conversion with time on stream. The authors further showed that varying degrees of olefins can be produced by varying the temperature and the zeolite pore size. Product distribution was shifted to C_{2-3} olefins at higher temperatures and C_{4-5} olefins at lower temperatures. C_{6-9} products were formed when the zeolite pore size increased from 10-MR in HZSM-5 to 12-MR in HBEA due to the fact that larger pores can accommodate larger products.

Using the Gibbs free energy minimization method, the thermodynamic equilibrium analysis of glycerol steam reforming to light olefins was investigated at temperature range (300–1000 $^{\circ}$ C), glycerol/water ratio (1:12–2:1) and pressure (0.1–1.2 MPa). Results revealed that light olefins formation was not spontaneous but experimental work involving catalyst proved that ethylene selectivity could be improved on in a heterogeneous reaction. The amount of ethylene produced was very small, but improved at higher pressure and temperatures between 600 and 750 $^{\circ}$ C. Results further revealed that coking depends on the glycerol/water ratio and temperature [212]. Table 15 shows the summary of the performance of some catalysts in the conversion of glycerol to olefins as recently reported in some literature.

Table 15. Performance of some catalysts in the c	onversion of glycerol to olefins a	s reported in some literature.
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Catalyst (A)	Operation Parameters	Performance (%)	TOF	Reference
HZSM-5 (≈400)	-	Ethene S = 7.94 Y = 3.99, Propene S = 0.35 Y = 0.18, Butene S = 0.00 Y = 0.00, Methane S = 4.75, Y = 2.38.		
30%Al/ZSM-5 (≈350)	T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na	Ethene S = 6.45 Y = 5.26 , Propene S = 0.07 Y = 0.06 , Butene S = 0.00 Y = 0.00 , Methane S = 9.63 , Y = 7.85 .		
30%Ca/ZSM-5 (>215)		Ethene S = 3.95 Y = 1.93 , Propene S = 0.83 Y = 0.41 , Butene S = 0.00 Y = 0.00 , Methane S = 5.95 , Y = 2.90 .	nd	[210]
30%Cr/ZSM-5 (>230)		Ethene S = 15.20 Y = 14.82 , Propene S = 2.60 Y = 2.53 , Butene S = 0.96 Y = 0.93 , Methane S = 8.16 , Y = 7.96 .		
30%Cu/ZSM-5 (≈260)		Ethene S = 18.62 Y = 14.97 , Propene S = 1.06 Y = 0.86 , Butene S = 0.56 Y = 0.45 , Methane S = 5.60 , Y = 4.50 .		
30%Li/ZSM-5 (≈230)		Ethene S = $2.61 \text{ Y} = 0.90$, Propene S = $1.76 \text{ Y} = 0.61$, Butene S = $0.96 \text{ Y} = 0.33$, Methane S = 6.04 , Y = 2.10 .		
30%Mg/ZSM-5 (≈250)		Ethene S = 6.142 Y = 4.19 , Propene S = 0.271 Y = 0.19 , Butene S = 0.00 Y = 0.00 , Methane S = 5.457 , Y = 3.72 .		
30%Ni-ZSM-5 (≈270)		Ethene $S = 3.27$ Y = 3.20, Propene $S = 0.5$ Y = 0.5, Butene $S = 0.00$ Y = 0.00, Methane $S = 7.21$, Y = 7.05.		
HZSM-5 10 wt% Cr-ZSM-5 (na)		GC = 11.62, Olefin S = 1.20 GC = 10.85, Olefin S = 0.63		
10 wt% Al-ZSM-5 (na) 10 wt% Ca-ZSM-5 (na)	T = 700 °C, P = 0.1 MPa, LSV = 20–80 s, Cat = 0.2 g	GC = 10.44, Olefin S = 1.09 GC = 15.02, Olefin S = 1.34	nd	[207]
10 wt% CuZSM-5 (na) 10 wt% Ni-ZSM-5 (na)		GC = 17.72, Olefin S = 3.55 GC = 16.07, Olefin S = 1.84		

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, W/LHSV = Water/Liquid Hourly Space Velocity, FFR = Feed Flow Rate, t = time, GC = Glycerol Conversion, S = Selectivity, Y = Yield, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.

Though it must be stated that there are scanty literature available in this area of conversion of glycerol to olefin, which can be attributed to the fact the area is relatively new hence the need for more research in this direction.

6. Prospects and Conclusions

As the environmental impact of petroleum-based fuels and chemicals continues to tear the world apart, research into the alternatives is growing at an interesting rate, to the extent that some the products have already been commercialized. Today, many countries in the world are already, interestingly, using biodiesel as fuel or as a fuel additive. The major byproduct in biodiesel production, glycerol, has grown to the extent that ways of valorization are not only being contemplated, but are necessary and already underway. This is to guard against immediate and future consequences of the byproduct, as well as to ameliorate the cost of biodiesel production. Glycerol is being converted into many value-added products via several reactions. These products include fuels, fuel additives and other precursor chemicals.

Though some of the reactions leading to the production of the above products have been patented, only a few of the products have reached commercial production stage. Specifically, epichlorohydrin obtained from glycerol-based dichloropropanol is already being produced at commercial level by the Solvay, Dow and Shandong Chemical Companies of Belgium, United States and China, respectively, and have been found to be economically and environmentally friendlier than the usual conventional method which is based on petroleum oil. Similarly, DuPont company developed the production of 1,3-PD through fermentation of glycerol with recombinant *Escherichia coli*, with the process saving 40% of the energy expended by its petroleum-based counterpart. Polyglycerols also has been commercialized by Sakamoto Company in Japan, along with very few others. However, a lot of research efforts are ongoing to overcome some of the challenges hindering commercialization of other products, as well as exploring new frontiers in order to discover new products.

Some of the challenges include overcoming catalyst selectivity to some of the products, deactivation of catalyst occasioned by reuse, the use of harsh conditions such as high temperature and/or pressure, as well as difficulty in separation of catalyst from the desired products, long hours of reaction and low product yields. Overcoming impurities in crude glycerol, if it must be used directly, is also a big challenge for industry.

To address some of the above challenges, scientists, technologists and engineers must explore new process technologies, integrated process systems, highly tolerant and novel catalysts, improved activation methods, improved reactor systems, synergizing chemical and biological catalysis to improve certain inherent weaknesses associated with each of the catalyst.

Finally, if some of these barriers are broken, biodiesel production and usage will become cost effective and sustainable, and glycerol will, no doubt, become a great feedstock that will replace most petroleum-based chemicals.

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