Chapter

Catalysis for Glycerol Production and Its Applications

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Abstract

Globally, there is a climate change due to greenhouse gases, hence the production processes for chemicals should comply with green chemistry principles to decrease the impact it has on the climate. This book chapter focuses on the catalytic production of glycerol, which is a platform chemical that is widely used in the manufacture of various industrially important chemicals and derivatives, namely 2,3-dihydroxy-propanal, glycerol ether, glycerol ester, acrolein, 1,2-propanediol and glycidol. The literature reviewed compares the production of glycerol using homogeneous and heterogeneous catalysts, to determine efficient and environmentally benign glycerol catalysts and to study glycerol as a platform chemical and its value in application.

Keywords: catalysis, homogenous catalysts, heterogeneous catalysts, value-added compounds, glycerol production

1. Introduction

The enormous growth in demand for fuels, along with growing environmental concerns and limited raw oil sources has increased the use of renewable energy. Biodiesel is one of the potential alternatives, and renewable fuels, has gained popularity in recent years, and their production capacity have grown significantly.

It is produced through various methods such as the transesterification of non-edible and waste vegetable oils with methanol and efforts are also being made to utilise the glycerol by-product to compensate the production cost of biodiesel to make it commercially viable, yielding quite significant percentage of a glycerol by-product which lowers the production cost and makes it commercially available. For every 4 litres of biodiesel generated [1].

Around 500 grams of glycerol is made, this equates to approximately 11,500 tons of 99.9% pure glycerine produced by a plant with a capacity of 113,562,354 million litres per year. The resulting oversupply of raw glycerol from biodiesel production can influence the purified glycerol market significantly as glycerol is a high-value and commercial chemical with thousands of applications [2].

Although extensive research has been carried out on the use of glycerol for various industrial applications, however, a compilation review on different approaches of glycerol production using homogenous and heterogeneous catalysts is scarce. The

present chapter focuses on compiling different state-of-the-art in glycerol manufacturing techniques with a special emphasis on homogeneous and heterogeneous catalysis approaches. Moreover, an attempt has also been made to review the application of glycerol in the production of various platform chemicals preferably using microbial pathways. A section has been dedicated on reviewing the application of glycerol in animal feed.

2. Glycerol production

Glycerol can be manufactured using a variety of chemical synthesis feedstocks. It can be produced, for example, by propylene synthesis by several methods [3], such as oil hydrolysis, or transesterification of fatty acids or oils. The following sections describe briefly about different glycerol production processes.

2.1 Glycerol production by propylene

As previously stated, several methods for producing glycerol from propylene can be used [4, 5]. In **Figure 1**, one of the major processes is shown, which includes the use of chlorination (Cl_2) [6].

2.1.1 Glycerol production via chlorination process

Propylene chlorination (**Figures 1** and **2**) produces allyl chloride at a temperature of 510°C in the presence of hypochlorous acid at 38°C. Glycerine dichlorohydrin is formed when allyl chloride reacts. The glycerol dichlorohydrin is then hydrolysed by sodium carbon oxide in a 6% sodium carbonate solution at 96°C or directly to glycerine, the epichlorohydrin being removed as an overhead in a stripping column. Finally, the epichlorohydrin is hydrated to glycerine using sodium hydroxide [4], resulting in a final glycerol yield of around 90% [6].

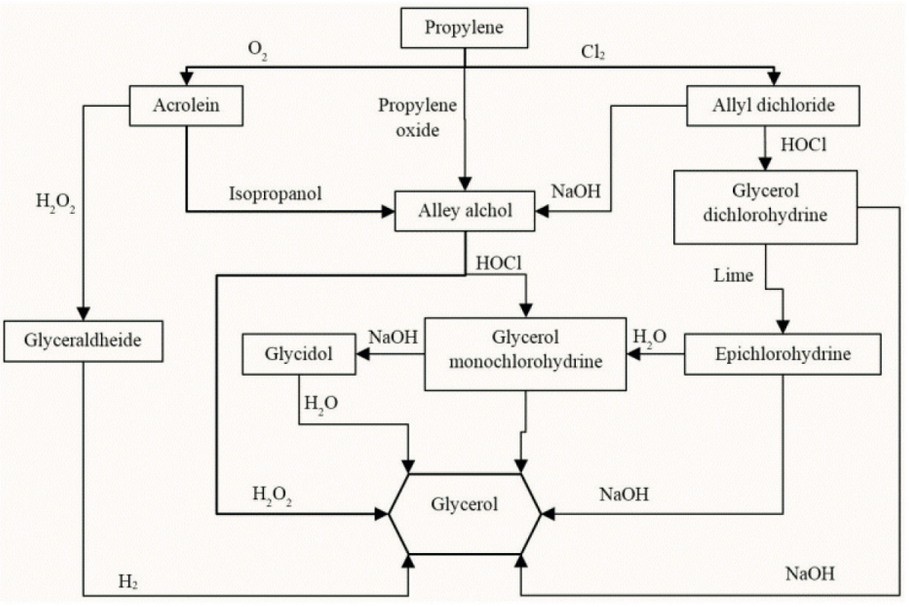

Figure 1.
Flow diagram illustrating the production of glycerol from propylene [6].

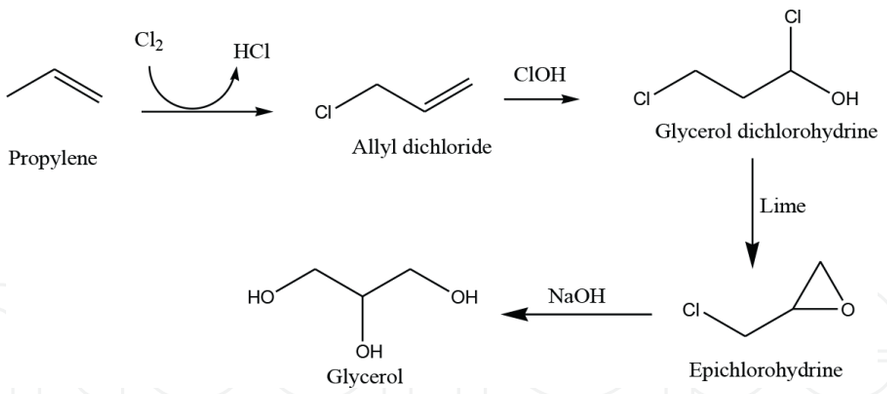

Figure 2.
Reaction of the propylene chlorination process.

2.1.2 Glycerol production via oxygenation process

Figure 3 illustrates two paths to produce glycerol from propylene via oxygenation. Oxygen (O_2) reacts with propylene to produce acrolein, adding an aldehyde (HC=O). Acrolein can be converted to allyl alcohol with a reducing agent sodium borohydride ($NaBH_4$) in a presence of isopropanol as a solvent; peroxide is added to allyl alcohol to produce glycerol. In the other reactions, peroxide is added to acrolein which results in the formation of glyceraldehyde; the glyceraldehyde reacts with hydrogen to produce glycerol.

2.2 Saponification

In this reaction, sodium hydroxide (base) reacts with triglyceride as an ester to form glycerol and soap molecules. This method has been employed since 2800, and the first industrial factory was developed in 1860 [7]. As demonstrated in **Figure 4**, this reaction occurs between triglyceride and sodium hydroxide (caustic soda), producing glycerol and soap [6, 8].

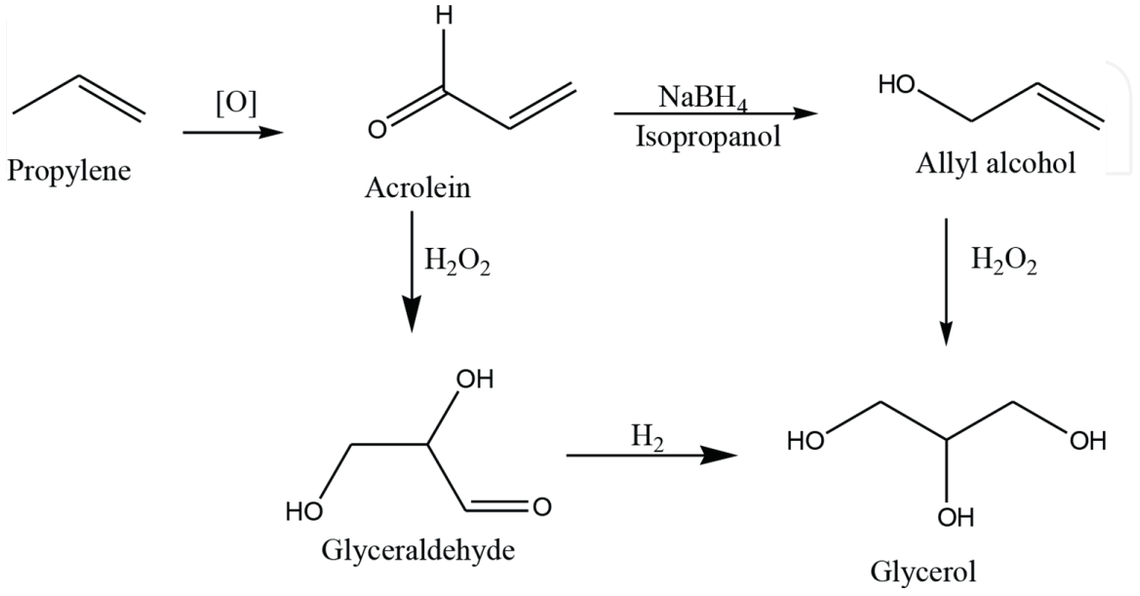

Figure 3.
Production of glycerol from propylene oxygenation reaction.

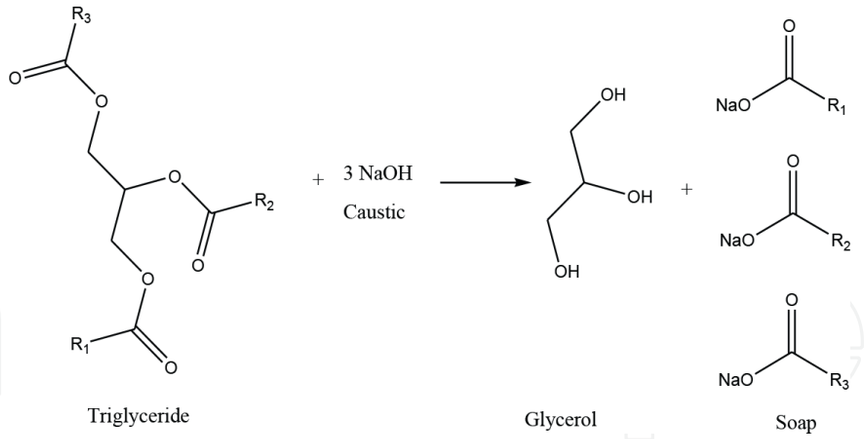

Figure 4.
Illustrates the saponification reaction between triglyceride and sodium hydroxide (caustic soda) for the glycerol production [6].

2.3 Transesterification of the beaver oil

The transesterification reaction of beaver oil with ethanol to produce glycerol was carried out in 1864 [9, 10]. **Figure 5** shows the reaction in which methyl-esters from triglycerides (oils) and methanol (alcohol) combine to form glycerol and fatty esters (or biodiesel) [5, 6, 11, 12].

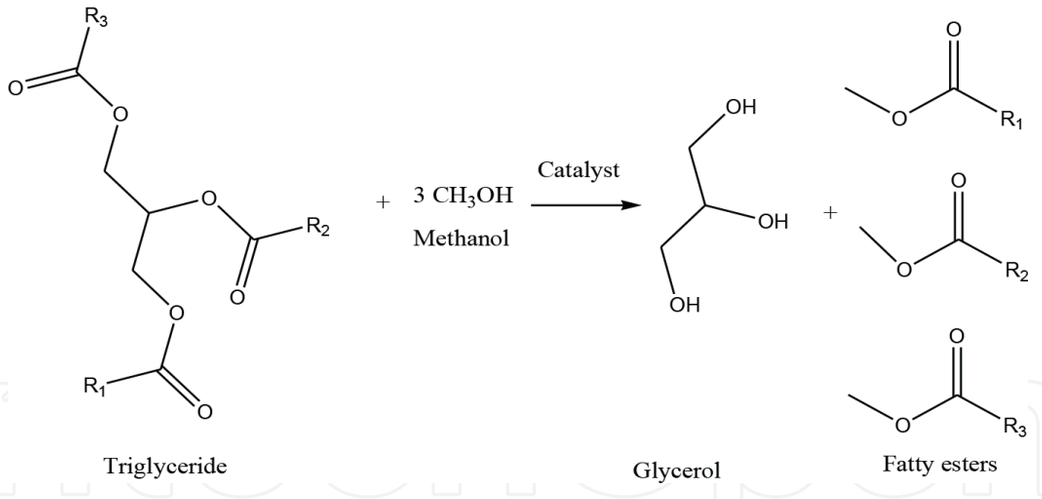

Figure 5.
Glycerol production by a transesterification reaction [6].

Feedstock	Glycerol concentration (w/w %)	Methanol concentration (w/w %)	Soap concentration (w/w %)	Impurities (w/w %)	Ref.
Palm oil waste	87	—	—	6	[13]
Oil of Jatropha	19–22	14.5	29	11–21	[14]
Soybean oil	63	6.2	—	—	[15]
Soybean oil	22	10.9	26.2	23.5	[15]

Feedstock	Glycerol concentration (w/w %)	Methanol concentration (w/w %)	Soap concentration (w/w %)	Impurities (w/w %)	Ref.
Soybean oil	33	12.6	26.1	22.3	[15]
Vegetable oil waste	28	9	21	39	[15]
Palm oil	81	1	—	2.0	[16]
Seed oils	63–77	—	—	—	[17]
Used frying oil	85	—	—	15	[18]

Table 1.
Different glycerol streams depending on initial feedstocks and production reactions.

Interestingly, the glycerol yield from transesterification was not only found to be dependent on different types of processes but also on the different type of oil feedstocks (**Table 1**) [13–18].

3. Glycerol catalysis

Transesterification of oil is accomplished using both homogenous as well as heterogeneous catalysts. **Table 2** depicts glycerol production advantages and disadvantages of using different type of catalysts.

Moreover, depending on the type of catalyst used, the transesterification process can be categorised as homogeneous and heterogeneous catalysis to make biodiesel and subsequently glycerol.

Catalysts group	Type of catalyst	Advantages	Disadvantages
Homogeneous base catalyst	NaOH/KOH	• Fast reaction rate, mild condition and less energy intensity. • Catalysts are widely available and economical.	• If the usage limit for oil is less than 0.5 wt. % free fatty acid. Soap formation occurs as well if the free fatty acid content in the oil is more than 2 wt. %. • Excessive soap formation reduces the glycerol yield and causes problems during product purification.
Heterogeneous base catalyst	CaO/MgO	• Reaction conditions are mild and less energy-intensive, reuse and regenerating of a catalyst. • Mild reaction condition and less energy intensive.	• Sensitive to free fatty acid content in the oil due to its basicity property. • Excessive soap formation decreases the glycerol yield and causes problems during product refining.
Homogenous Acid catalyst	H_2SO_4/HCl	• Affordable than base catalysed process.	• Very slow reaction rate. Not easy to separate the catalyst from products.

Table 2.
Advantages and disadvantages of glycerol catalysts [19].

3.1 Homogeneous catalysis

During homogenous catalysis, the first stage comprises the reaction of vegetable oils with methanol in the presence of a catalyst, and then the separation of glycerol from the resultant mixture using a settler unit follows. The remaining flow is sent to a chamber that uses mineral acids to remove the catalytic component, resulting in two paths: a glycerol recovery chamber and an evaporator that separates biodiesel from the other products. The unit for purifying comprises three output units: the first with 80–95% glycerol; the second one with water, dissolved salts and unreacted methanol (it is then recycled back to the reactor); and one with fatty esters [12]. **Figure 6** depicts the glycerol manufacturing process employing homogeneous catalysts (namely, sodium hydroxide or sodium methylate) [6, 20, 21].

3.2 Heterogeneous catalysis

This type of catalysis procedure envisions two reaction phases to improve vegetable oil conversion; reactor 1 is supplied by vegetable oil and methanol. The product stream is sent through a heat exchanger to evaporate some of the residual methanol, and the remaining stream is directed to a decanter to separate polar and non-polar components such as glycerol and mainly vegetable oil and biodiesel, respectively. While, in reactor 2, the non-polar stream is reacted for the second time to boost biodiesel synthesis and recover methanol. The product stream travels through the heat exchanger, which takes out all unreacted methanol, and the decanter, which separates the biodiesel from polar components.

The polar streams from the first and second polar decanters are directed to another heat exchanger to recover the remaining methanol in the mixture, while the leftover fraction is delivered to a final decanter to separate vegetable oil and residual glycerol. **Figure 7** is a flowchart of triglyceride transesterification using heterogeneous catalysts such as aluminium and zinc oxide [6].

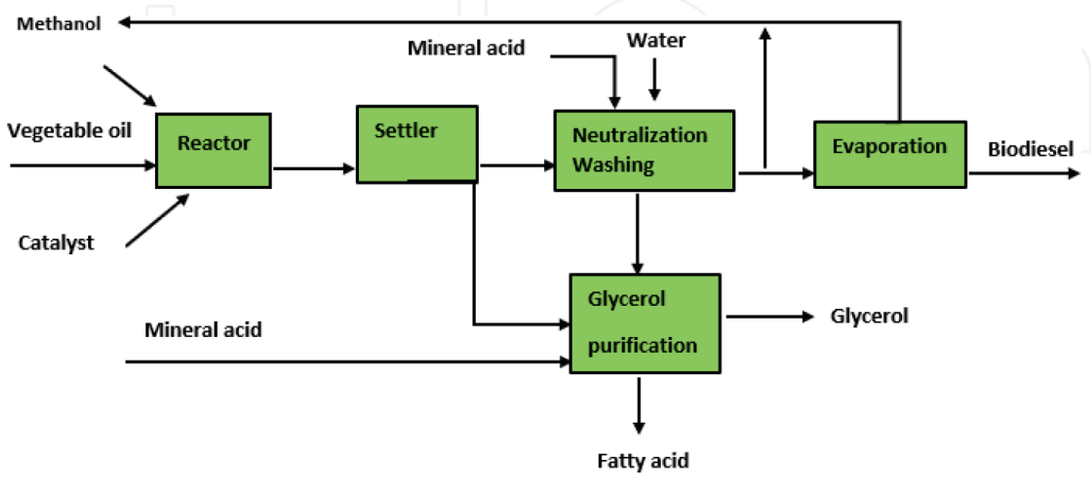

Figure 6.
The production plant for biodiesel is based on a homogenous catalyst.

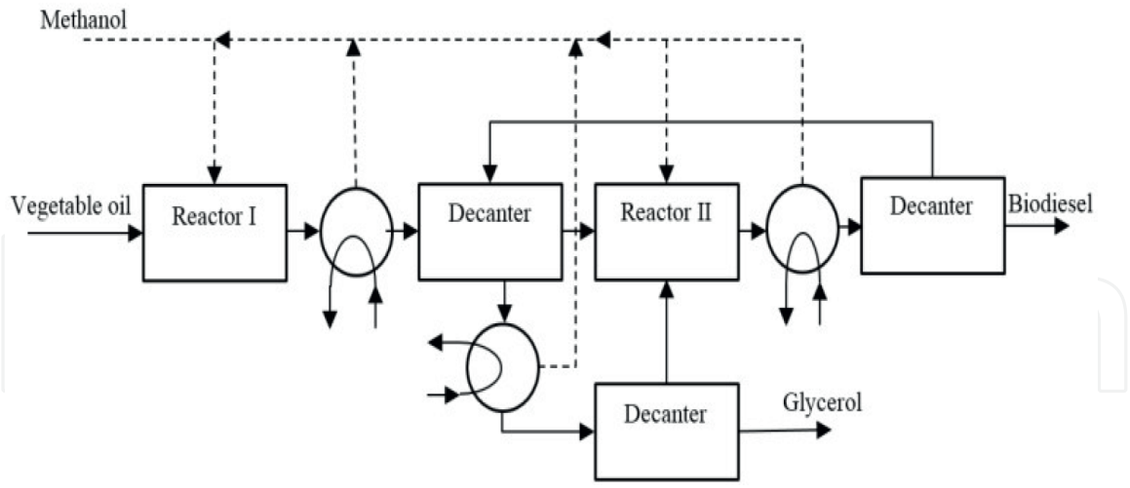

Figure 7.
A heterogeneous catalysis-based production plant flowchart [6].

4. Glycerol: a platform chemical

Synthesis of glycerol following microbial route has been known for over a century, however, new improvements in the biodiesel business have resulted in the production of large amounts of glycerol. During the biodiesel production process, approximately

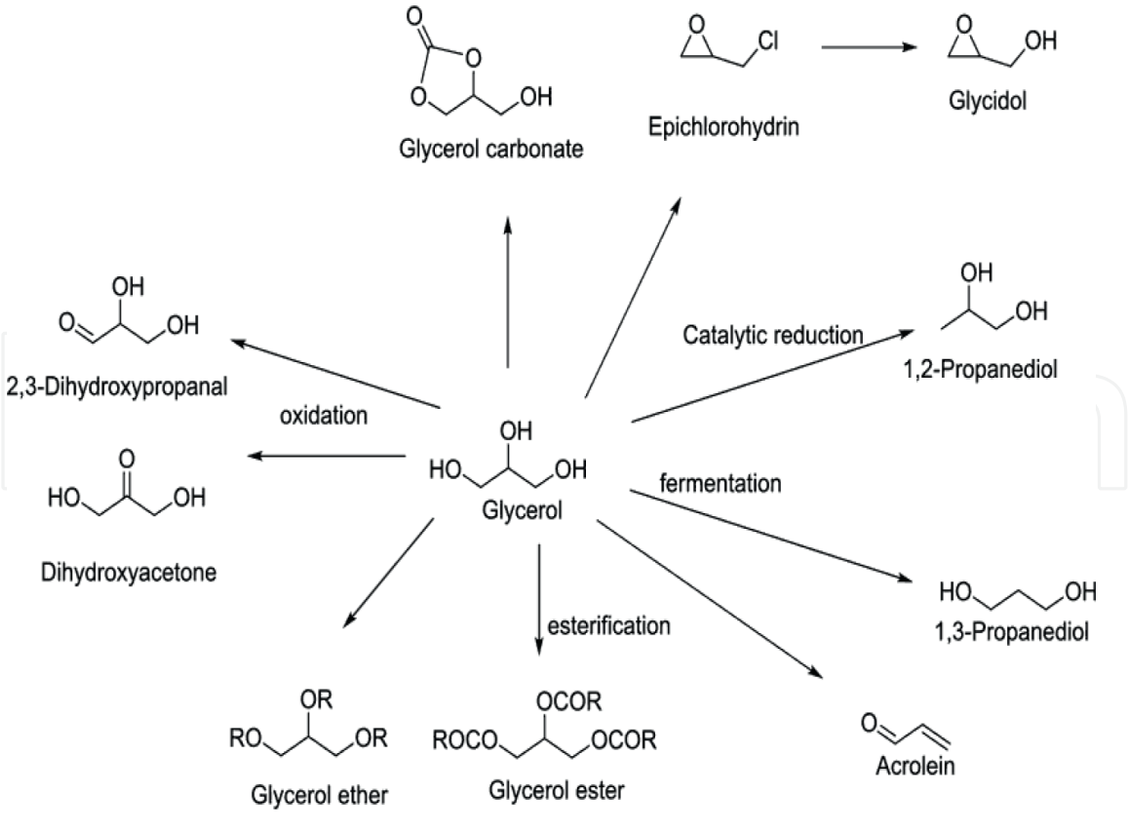

Figure 8.
Glycerol as a platform chemical.

10% of glycerol is produced, accounting for about 90% of total glycerol produced [22]. Glycerol has gathered substantial interest in its conversion to higher value-added compounds due to its availability and potential to operate as a key building block in a biorefinery (**Figure 8**) [23].

Glycerol oxidation produces a wide range of compounds, such as glyceric acid dihydroxyacetone, glyceraldehyde, hydroxy-pyruvic acid, glycolic acid and others. Controlling reaction selectivity is a critical challenge in obtaining the desired molecules.

For example, glyceric acid is a crucial intermediary for more extensively oxidised compounds such as tartronic acid and mesoxalic acid. The catalytic aerobic oxidation of glycerol in a basic media has been extensively studied using monometallic or bimetallic catalysts such as Au, Pt and Pd.

Table 3 lists some of the most prominent catalysts used in this field [24–27, 30, 38–40]. Another approach for producing value-added compounds from glycerol is the reduction process. Lactic acid is produced by a reduction of glycerol in the presence of hydroxide bases [41]. This reaction is frequently carried out at medium to high pressures and temperatures ranging from 100 to 240°C using Cu- and Zn-based catalysts enhanced by sulphide Ru [28].

Glycerol carbonate is another derivative of glycerol that is formed by reaction between glycerol and urea, ethylene or propylene carbonate [22] or carbon dioxide [42]. It is also used in the commercial manufacture of epichlorohydrin. Epichlorohydrin is produced in a similar manner by Solvay and Dow Chemical Company [43]. When the principal hydroxyl groups in glycerol are selectively oxidised, the economically valuable chemicals glyceraldehyde [44], glyceric acid [45] and tartronic acid [46] are formed. Dihydroxyacetone (DHA) is produced by oxidation of the secondary hydroxyl group, whereas ketomalonic acid is produced by oxidation of all three hydroxyl groups [47].

Another glycerol derivative, glycidol, offers immense potential for the synthesis of industrially useful compounds such as epoxy resins, polyurethanes and polyglycerol esters. A bio-based technique for producing glycidol from glycerol was recently published [48]. The manufacture of acrolein from glycerol is an innovative, eco-friendly technology that has several advantages, such as less oil extraction and a minimal environmental impact [31]. In general, acrolein is synthesised from glycerol by acid-catalysed dehydrogenation over synthetic aluminium phosphate ($AlPO_4$), zeolites with varied channel configurations (HY and H-ZSM-5) and SiO_2/Al_2O_3 ratio [31, 49].

A novel synthetic approach for the synthesis of chlorohydrin was proposed, which involved reacting a polyhydroxy aliphatic hydrocarbon with a chlorination agent. Vitiello et al. [33] focused on the activity and selectivity of homologous chlorinated series of catalysts for glycerol halogenation, such as acetic acid, monochloro, dichloro and trichloroacetic acid.

Table 3 also includes information on one of the most significant glycerol conversion processes, esterification with acetic acid, which produces monoacylglycerol, diacylglycerol and glycerol carbonate. These materials are often used in cryogenics, biodegradable polyester and cosmetics [35, 36]. Sulphated-based superacids, heteropoly acid-based catalysts, tin chloride, zeolite, ZrO_2-based solid acids and other significant acid catalysts can be used for glycerol esterification [35–37, 50–52].

Finally, pyrolysis of glycerol to produce syngas is another method of converting glycerol. The pyrolysis of biomass has been extensively studied in the specialist literature, although in most cases, only metal-based catalysts have been used. The microwave-assisted pyrolysis of glycerol over a carbonaceous catalyst is a unique approach

Reaction type	Reactant	Catalyst	Pressure (bar)	Temperature (°C)	Product	Ref.
Glycerol oxidation	O_2	Pd–Ag/C	3	80	Dihydroxyacetone	[24]
	O_2	Pt/NCNT	—	60		[25]
	O_2	Pt/MCN	3	40	Glyceraldehyde	[26]
	O_2	Pt/SiO_2	1	100		[27]
	O_2	Pt/MCN	3	40	Glyceric acid	[26]
	O_2	Pt/SiO_2	1	100		[27]
Glycerol reduction	H_2	Ru/Al_2O_3	25	180	1,2-propanediol	[28]
	H_2	Ru/Al_2O_3	25	200	Ethylene glycol	[29]
	H_2	Ru/ZrO_2	80	240		[30]
Glycerol dehydrogenation	—	$AlPO_4$–450	1	190–230	Acrolein	[31]
	—	HY(5.2)	1	170–230		[31]
	—	12 wt. % V_2O_5, V/P molar ratio of 0.2	1	325		[32]
Glycerol halogenation	HCl	Aspartic acid	4.5	100	1,3-dichloropropanol	[33]
	HCl	Glutamic acid	4.5	100		[33]
Glycerol esterification	Acetic acid	Sb_2O_5	1	80–120	Monoglicerides	[34]
	Palmitic acid	ZrSBA-15	1	160–180	Diacylglicerol	[35]
	Acetic acid	Graphene oxide	1	120		[36]
	Acetic acid	ZSM-5	1	120		[36]
Glycerol pyrolysis	—	Bituminous carbon	1	400–900	Syngas	[37]
	—	Coconut shell	1	400–900		[37]

Table 3.
Compounds derived from traditional glycerol conversion under similar operating conditions.

for syngas generation in which the heating method and operating temperature (between 400 and 900°C) can impact the catalytic action of the activated carbons to optimise syngas production [37]. **Table 3** outlines some of the products derived from glycerol that may be transformed into other compounds with high added value.

5. Value-added products from glycerol via biological conversions

From 2004 to 2008, the global production of crude glycerol from biodiesel conversion increased from 200 thousand tonnes to 1.224 million tonnes [2, 19]. Meanwhile,

in 2005, the global market for purified glycerol was anticipated to be over 900,000 tonnes [53]. This provided a chance for scientists to discover new uses for refined and crude glycerol. Multiple publications on the direct use of crude glycerol from biodiesel synthesis have been published.

5.1 1,3-Propanediol

The most promising alternative for the biological conversion of glycerol in anaerobic fermentative production is 1,3-propanediol [54], which indicates that crude glycerol could be employed directly for the manufacture of 1,3-propanediol in fed-batch cultures of *pneumoniae*.

Raw glycerol composition had less influence on the biological conversion and, therefore, a low fermentation cost could be predicted. However, using a response surface approach, the generation of 1,3-propanediol by *Klebsiella pneumoniae* was optimised. The highest concentration of 1,3-propanediol produced However, statistical optimisation along with genetic engineering approaches may be utilised to improve the 1,3-propanediol production [14, 55]. *K. pneumoniae* ATCC 15380 recently improved the synthesis of 1,3-propanediol from crude glycerol from Jatropha biodiesel. The yield, purity and recovery of 1,3-propanediol obtained were 56 g/L, 99.7% and 34%, respectively [14]. In addition, a hollow fibre membrane was used to produce an integrated bioprocess that linked biodiesel generation by lipase with microbial production of 1,3-propanediol by *K. pneumoniae* [56].

5.2 Citric acid

Citric acid synthesis by *Yarrowia lipolytica* ACA-DC 50109 from raw glycerol was not only comparable to that obtained from sugar-based standard media [57] but also single-cell oil and citric acid were produced simultaneously [58, 59]. When acetate-negative mutants of the *Y. lipolytica* Wratislavia AWG7 strain were employed in a fed-batch fermentation to ferment crude glycerol, the final concentration of citric acid was 131.5 g/L, which was similar to that produced from pure glycerol (139 g/L). Similarly, *Y. lipolytica* LGAM S(7)1 has also shown the ability to convert crude glycerol to citric acid [60]. Interestingly, another strain *Y. lipolytica* N15 could produce large levels of citric acid, namely up to 98 g/L of citric acid and 71 g/L of citric acid from pure glycerol medium and crude glycerol medium, respectively [61].

5.3 Hydrogen and other lower molecule fuels

The photo-fermentative conversion of crude glycerol to hydrogen is one of the most fascinating approach to utilise glycerol. Both crude glycerol and pure glycerol can produce up to 6 moles of H_2 per mole of glycerol, representing 75% of the theoretical value. However, significant technological challenges, such as increasing the efficiency of light use by organisms and building effective photobioreactors, must be overcome before a viable method can be developed [62]. When *Enterobacter aerogenes* HU-101 was used, hydrogen and ethanol were synthesised at high yields and rates. However, in order to improve the rate of glycerol use, the crude glycerol should be diluted with a synthetic medium [63]. While Jitrwung and Yargeau [64] modified several media compositions of the *E. aerogenes* ATCC 35029 fermented crude glycerol procedure to maximise hydrogen generation.

5.4 Polyhydroxyalkanoates (PHB)

As an estimate, a biodiesel facility with a capacity of 10 million gallons per year could produce 20.9 tons of PHB [65]. The feasibility of using crude glycerol for PHB manufacture was investigated using *Paracoccus denitrificans* and *Cupriavidus necator* JMP134, and the resultant polymers were shown to be remarkably comparable to those generated from glucose. However, a high osmotic (sodium chloride-contaminated) crude glycerol was found to have harmful impact on PHB synthesis and needs to be taken care of. One way to handle the issue is combining crude glycerol from various producers to reduce the harmful effect of NaCl contamination [66]. In addition, for a large-scale PHB synthesis, a technique based on the *C. necator* DSM 545 fermentation of crude glycerol was developed [67]. Following this in the presence of NaCl, *Zobellella denitrificans* MW1 could use crude glycerol for growth and PHB synthesis at high concentrations. As a result, it was recommended as an appealing alternative for large-scale PHB manufacturing using crude glycerol [68]. Furthermore, when mixed microbial consortia (MMC) were utilised to produce PHA from crude glycerol, it was shown that methanol in the crude glycerol was converted to PHB by MMC.

5.5 Lipids as the sole carbon source

Crude glycerol might be used to manufacture lipids, which could be utilised to make a sustainable biodiesel feedstock. For example, raw glycerol might be used to culture *Schizochytrium limacinum* SR21 and *Cryptococcus curvatus*. However, the glycerol

Product	Reaction	Yield	Ref.
1,3-Propanediol	Fed-batch cultures of *Klebsiella pneumoniae* strain	1.7 g/L/h	[54]
	Maximum 1,3-propanediol production from *K. pneumonia*	13.8 g/L	[55]
Citric acid	*Yarrowia lipolytica* strain ACA-DC 50109 (process modelling)	NA	[57]
	Acetate mutants of *Y. lipolytica* Wratislavia AWG7 strain; fed-batch operation	139 g/L	[74]
	Y. lipolytica strain LGAM S (7)1	35 g/L	[60]
Hydrogen	Photofermentative conversion process; *Rhodopseudomonas palustris* strain	6 mol/mol glycerol	[62]
	Enterobacter aerogenes strain HU-101; continuous culture; porous ceramics as a support material to fix cells	63 mmol/L/h	[63]
Poly(hydroxyalkanoates) (PHAs)	*Pseudomonas oleovorans* NRRL B-14682 and *P. corrugata* 388 grew and synthesised PHB and mcl-PHA, respectively	NA	[75]
	Producing PHB; *Paracoccus denitrificans* and *Cupriavidus necator* JMP 134 strains	48%	[66]
Lipid	*Schizochytrium limacinum* SR21; batch culture	73.3%	[69]
	Cryptococcus curvatus; two-stage fed-batch process	52%	[76]

Table 4.
Biological conversion of crude glycerol.

Product	Reaction	Yield	Ref.
Acrolein	Fluidised bed, tungsten-doped zirconia catalyst	21%	[77]
Monoglyceride	Two-step process, purification of the monoglyceride produced from glycerolysis of palm stearin	~99% purity	[78]
	Glycerolysis of soybean oil	~42%	[79]
Gaseous products	Steam gasification with in situ CO_2 removal	88 vol.% H_2 purity	[80]
	Hydrothermal reforming of crude glycerol	~90 vol.% H_2 purity	[81]

Table 5.
Conventional catalytic conversions of crude glycerol.

content over a certain threshold may prevent the rapid reproduction of cells. The best glycerol content for batch culturing of crude glycerol obtained from yellow grease were 25 and 35 g/L for untreated and treated crude glycerol, respectively, which may subsequently lead to cellular lipid content of approximately 75%. Methanol residues in crude glycerol may cause damage to the development of *S. limacinum* SR21 [69].

For lipid synthesis in *C. curvatus* yeast, fed-batch was preferable to batch; however, the addition of ammonium sulphate and Tween 20 improved the accumulation of lipids and carotenoids Saenge et al. [70] demonstrated that the oleaginous red yeast *Rhodotorula glutinis* TISTR 5159 generated lipids and carotenoids when grown on crude glycerol. *Chlorella protothecoides* was also capable of converting crude glycerol to lipids.

The lipid yield was 0.31 g lipids/g substrate [71]. Similarly, using *C. protothecoides* and crude glycerol (62% purity), Furthermore, Chatzifragkou et al. [72] did research, to investigate the ability of 15 eukaryotic micro-organisms to change crude glycerol to metabolic products. The results showed that yeast accumulated limited lipids (up to 22 wt.% in the case of Rhodotorula), whereas fungi collected greater levels of lipids in their mycelia (range between 18.1 and 42.6 wt.% of dry biomass). Interestingly, Chen and Walker [73] found that a fed-batch operation yielded a maximum lipid productivity of 3 g/L per day, which was greater than that generated by a batch procedure.

Tables 4 and **5** outline an overview of the conversions of crude glycerol to potential chemical through biological and catalytic conversions.

6. Application of crude glycerol in animal feedstock

Glycerol has been used as an animal feed additive since the 1970s [82]. However, the availability of glycerol has limited its application in diets [83], because of the rising corn prices and the oversupply of crude glycerol, the possibility of using crude glycerol from biodiesel in feeds has recently been examined.

6.1 Crude glycerol in non-ruminant diets

Crude glycerol is an excellent energy source due to its high absorption rates for non-ruminants such as broilers. Once ingested, the enzyme glycerol kinase converts it to glucose for energy generation in the liver of mammals [83]. Its samples from various biodiesel manufacturers were tested as energy sources. The digestible energy (DE) values for 85% of the crude glycerol samples ranged from 14.9 to 15.3 MJ/kg,

with metabolisable energy (ME) values ranging from 13.9 to 14.7 MJ/kg [84]. Overall, the use of crude glycerol derived from biodiesel process as an animal feed component offers significant potential for replacing maize in diets and is gaining popularity. However, the existence of potentially dangerous contaminants in biodiesel crude glycerol needs to be taken into consideration [85].

6.2 Crude glycerol in ruminant diets

Besides, the non-ruminants, crude glycerol may play a very significant role in the diets of ruminant animals as well. However, to improve its edibility, more emphasis should be placed on the crude glycerol produced by small-scale biodiesel plants that employ basic batch distillation or evaporation processes. There are several reports where use of crude glycerol has shown significant improvement in the overall performance of ruminants. Crude glycerol, at up to 15% dry matter in finishing lamb diets, might increase feedlot performance, particularly during the first 14 days, but had little influence on carcass attributes [86]. Diets for meat goats containing up to 5% crude glycerol were shown to be superior to medium-quality hay [87]. Nursing dairy cows can also be fed up to 15% of their dry matter diet without affecting feed intake, milk output or yield [88, 89]. When crude glycerol was added at 8% or less of dry matter in cow-finishing diets, its weight growth and feed efficiency were increased [90].

7. Summary and conclusions

Glycerol may be produced using various techniques and feedstocks, such as propylene synthesis by various routes, hydrolysis of fatty acid triglycerides, or transesterification of fatty acids or oils. The efficient use of crude glycerol is critical to the commercialisation and advancement of biodiesel synthesis. In the long run, using biomass-derived glycerol will not only help to reduce society's reliance on non-renewable resources, but it will also encourage the development of integrated biorefineries. This review focuses on the value-added prospects for crude glycerol derived from biodiesel production, primarily as a feed ingredient for animal feed and as a feedstock for chemicals.

For example, crude glycerol can be converted into 1,3-propanediol, citric acid, poly(hydroxyalkanoates), butanol, hydrogen, docosahexaenoic acid-rich algae, monoglycerides, lipids and syngas. Though many of the processes discussed have already been employed by the industries, they require additional research to minimise the manufacturing cost and be operationally practical for inclusion into biorefineries.

Furthermore, contaminants in crude glycerol can have a noticeable impact on the conversion of glycerol into other products. Pollutants in crude glycerol hinder cell and fungi's rapid reproduction, resulting in less production rates and product yields in many biological conversion processes (compared with pure or commercial glycerol under the same culture conditions). Contaminants, on the other hand, poison the catalysts in traditional catalytic conversions, boosting char generation and affecting product yield.

Many technologies need to be better understood and refined, such as optimising reaction parameters, production yields and fermentation conditions; generating mutant strains and efficient bioreactors for stable cultures and enhancing the activity and selectivity of catalysts.

Researchers have also obtained promising results on utilisation of crude glycerol as animal feed, particularly with non-ruminant animals such as pigs, laying hens and

broilers. But various precautions must be taken before this biomass-derived chemical may be used on a large scale in animal diets. To begin with, animal producers must exercise caution when deciding to incorporate crude glycerol as a component of animal feed diets, since the chemical composition of crude glycerol varies greatly depending on the processes and feedstocks used to manufacture biodiesel. Secondly, contaminants in crude glycerol affect feed performance to some extent. Finally, the amount of crude glycerol in feed formulations must be considered. It is advised that a crude glycerol feed standard be established so that it would be uniform for all producers, the resulting "standard" crude glycerol would have greater value.

There is a need to develop improved processes as well as other important value-added products. For example, among other renewable and bio-derived sources, glycerol has come up as an appealing possibility since it represents a relevant and alternative solution for producing hydrogen via reforming processes that may be carried out in both traditional and novel reactors.

Besides, catalytic process, though it is not yet introduced, the transesterification reaction using supercritical fluids has also gained noticeable attention. As one or two reaction stages are possible in a single-step supercritical fluid transesterification, the reaction occurs only once reactants are heated to critical temperatures and pressures with triglycerides [20, 21]. Triglycerides are initially transformed to free fatty acids and by-products in the hydrolysis reaction during the two-step subcritical-supercritical fluid transesterification. The acquired free fatty acids undergo esterification reaction, yielding fatty acid methyl esters in a supercritical fluid process [91, 92].

Conflict of interest

The authors declare no conflict of interest.

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