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Review on enzymatic synthesis of value added products of glycerol, a by-product derived from biodiesel production

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ABSTRACT

Crude glycerol is produced as a by-product from biodiesel production via trans-esterification with methanol and this process accounts for 10% (w/w) of the total biodiesel produced worldwide. The glycerol glut created can be utilized to increase biodiesel profitability since disposal can pose a threat to the environment. The need is to transform this surplus crude glycerol into added-value products. Biological based conversions are efficient in providing products that are drop-in replacements for petro-chemicals and offer functionality advantage, commanding higher price with the potential to increase bio-refinery revenue. Glycerol is a stable and multifunctional compound used as a building block in fine chemical synthesis like bio-polymers, polyunsaturated fatty acids, ethanol, hydrogen, *n*-butanol, glycerol carbonate, glycerol acetyl esters etc. Bio-catalysts add higher value to bio based products by catalyzing not only their selective modification, but also their synthesis under controlled and mild conditions. This article focuses on different bioconversion technologies of crude-glycerol to value added industrial products – obtained as waste from current bio-diesel production. We abridge the recent relevant approach for the production of various platform chemicals from bio-glycerol over enzyme and chemical catalysts.

1. Introduction

Petroleum derivatives are fuels that allow existence of fast, efficient ways of transportation and industrialization [1–3]. However it is likely that they will not last longer than few decades due to their finite reserves, energy security and environmental concerns [4–7]. Researchers are now focusing on bio-energy and value added chemicals that are derived from biomass of renewable sources which emit less greenhouse gases than fossil fuels. Studies show edible plants, ligno-cellulosic biomass, microalgae, animal/vegetable oil etc. being commonly used for biodiesel production by transesterification in the recent past and glycerol, a by-product, amounts to 10% of bio-diesel production (Fig. 1) [8–10]. The EU is still the world's largest biodiesel producer with production capacity of 24.9 billion liters in 2016 and is expected to increase to 25.5 billion liters by 2017 [11]. Some of the major biodiesel producing countries include the US, Brazil, Germany, France, Argentina, Netherlands and Indonesia. India ranked 13th with the production of 0.1 billion liters in the year 2015 [12]. Though the production of bio-diesel globally is still in its nascent stages, the market price of glycerol has dropped rapidly and is available in excess [13–16]. The classical use of glycerol has been in pharmaceutical, food and cosmetic industries [17,18]. However, crude glycerol from biodiesel industry needs further purification in order to be industrially applicable since it contains various impurities. Application of different downstream steps and the costing make its utilization economically un-viable [19–22]. Thus, the valorization of glycerol can potentially improve the profitability of biodiesel in a broader bio-refinery scenario [23]. With biochemical research, we may be in a position to mitigate environmental impact of fossil fuel based products within the realms of technological innovations that can enhance production of bio-based monomers from renewable carbon, on an industrial scale [24–27]. These next generation bio-based chemicals may not only address their sustainability, but also compete in terms of superior technological and functional properties [28]. Bio-catalysis goes a step further by accentuating the production of structured, functionalized and biodegradable products through highly selective and novel synthetic processes. Also, biocatalysts enable targeted hydrolyses and modification that are not possible with conventional strategies. In this review, gist of some recent developments in conver-

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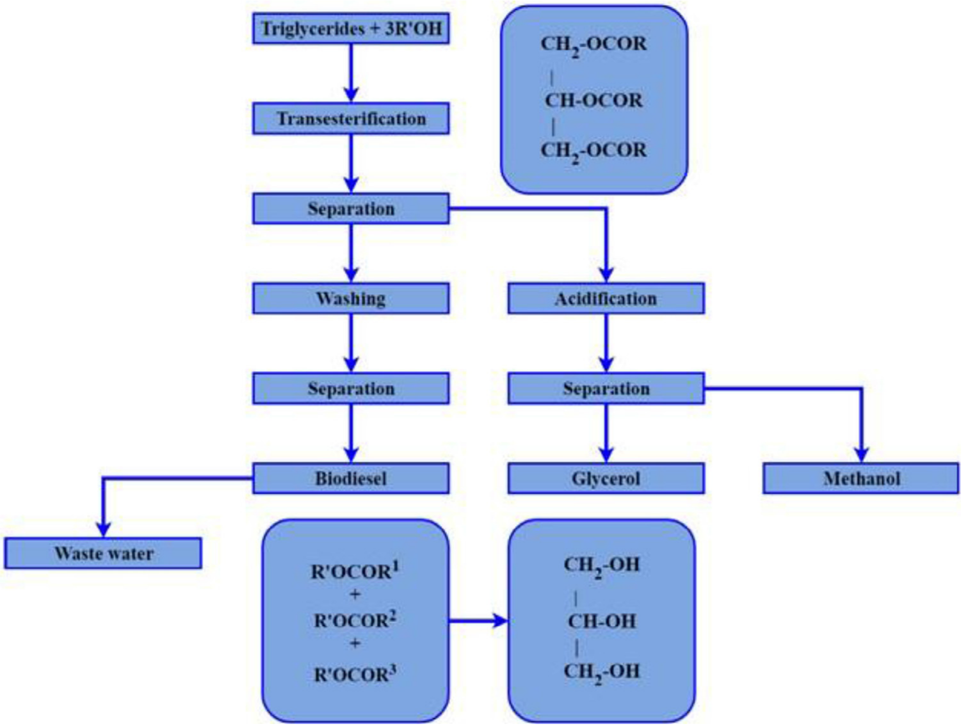

Fig. 1. Schematic representation of general transesterification process; R^1, R^2 and R^3 are alkyl chains.

sion of bio-glycerol to added-value products is provided [29,30]. The examples mentioned below demonstrate various alternatives that promise conversion of abundantly available crude glycerol toward betterment of bio-refinery.

2. Glycerol

Glycerol (1.2.3-propanetriol), $C_3H_8O_3$ [31–33], is a highly hygroscopic polyalcohol with clear and colorless texture, odorless, highly viscous, hygroscopic, sweet to taste and non toxic to both human and environment. The boiling point, flash point and melting point are 290 °C, 177 °C and 18 °C respectively with negligible vapor. Glycerol has a molecular weight of 92.09 g mol^{-1}, viscosity of 1.5 Pa-s and density of 1.261 g cm^{-3} under normal atmospheric pressure [34–38]. It is a stable compound that consists of three hydroxyl functional groups, which render this compound with hydrophilic and hygroscopic properties. Its molecular structure and physiochemical properties make it a highly functional and versatile compound that can be readily esterified, reduced, halogenated, oxidized, etherified etc. to obtain alternative green chemicals [39–42]. Pure glycerol finds application in industries such as food, cosmetics, textile, pharmaceuticals, feedstock etc. In contrast, usage of crude glycerol from biodiesel industry is very limited because of its composition, which includes spent catalysts, residual methanol, heavy metals, free fatty acids etc. Its disposal is also difficult as the methanol content deems it as hazardous waste. The purity of glycerol is a major concern [43–51] and hence conversion of (crude) glycerol to various highly valuable products by the means of chemical and/or microbial technology is of great importance. As far as enzyme technology is concerned, in the recent years, only limited editions of scientific papers on valorization of crude glycerol are published. Several technologies for synthesis of alternatives have been reported in the literature and a significant number of platform molecules have been synthesized and are found to be highly potential in replacing petroleum based products [52–54]. Fig. 2 summarizes the findings of several studies on upgrading routes and their products.

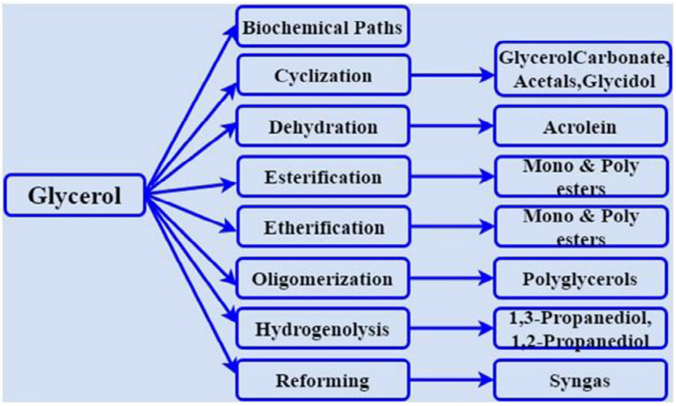

Fig. 2. Different pathways for possible glycerol derivatives.

3. Crude glycerol utilization in microbial fermentation

Recent research is focused on producing green chemicals via microbial fermentation with crude glycerol as carbon source [55,56]. The end products of such bioconversions have found applications in production of various platform chemicals and their derivatives. Glycerol represents a great substrate for the growth of microorganisms, both aerobically and anaerobically to produce products such as 1,3-propanediol, 1,2-proanediol, dihydroxyacetone (DHA), docosahexaenoic acid (DHA), citric acid, lactic acid, fuel additives, single cell oil, hydrogen, ethanol etc. [57,58]. Some widely applicable glycerol consuming species include *Clostridium*, *Klebsiella*, *Lactobacillus*, *Rhodosporidium*, *Lipomyces*, *Escherichia*, *Candida* etc. [59–61]. More recently, engineering microbial co-cultures is emerging as a promising approach for bulk production [62]. The potentiality of these organisms to produce at an industrial level could be limited due to various reasons such as pathogenicity,

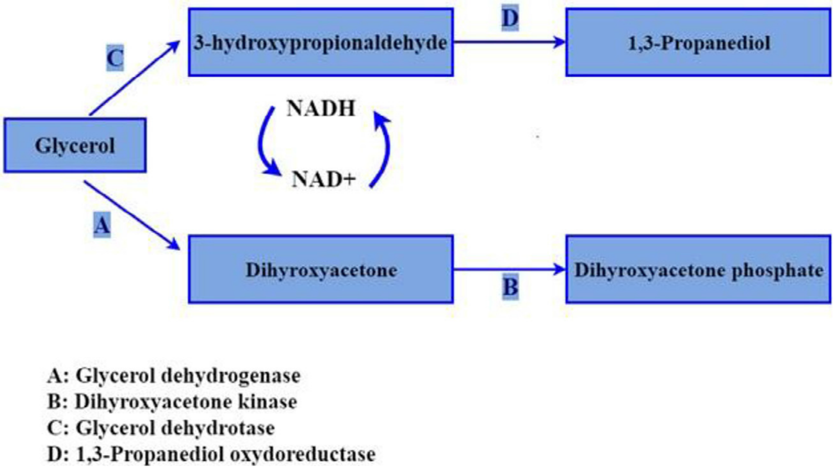

Fig. 3. Potential pathway for the microbial production of 1,3-propanediol.
Source: Modified from Jiang et al. [78].

strict anaerobic conditions and due to impurities present in the substrate that may affect their growth and conversion rates.

3.1. Glycerol to 1,3-propanediol

1,3-Propanediol is of great interest as it can be used to produce polymers with special properties such as polyesters, poly-ethers, and polyurethanes; in production of paints, lubricants, antifreeze and as solvents. Chemical production is generally through two different routes – hydration of acrolein and the hydro-formulation of ethylene oxide. Chemical synthesis requires expensive catalysts, high pressure conditions and this process often results in production of toxic intermediates that are environmentally unsafe [63–65]. Production of bio-based 1,3-propanediol from renewable biomass is gaining wide interest as they are environmental friendly and microorganisms such as *Klebsiella*, *Enterobacter*, *Citrobacter*, *Clostridium*, and *Lactobacillus* are natural producers [66,67]. Literature on fermentation pathway with glycerol and mixed cultures including *Clostridium pasteurianum* dates back to the nineteenth century, as identified by Freund in 1881 [68]. Since then, various cultivation techniques either naturally or genetically, immobilized or free, mono or multi- culture, batch or continuous, have been employed for microbial production of 1,3-propanediol under anaerobic conditions [69–72]. Glycerol is assimilated via two metabolic pathways, oxidative and reductive along with the production of alcohols and organic acids [73]. Most commonly employed are *Klebsiella pneumonia*, *Clostridium butyricum*, *Citrobacter freundii*, *C. pasteurianum*, *Lactobacillus diolivorans* etc. [74–77]. Glycerol assimilation follows two different coupled pathways as shown in Fig. 3. Under oxidative pathway glycerol is transformed into pyruvate through dihydroxyacetone (DHA) and phosphoenolpyruvate, releasing succinic acid to recover NAD accompanied with the production of ATP. Pyruvate is then converted to formic acid, lactic acid, 2,3-butanediol and acetyl-CoA which is further oxidized into ethanol and acetic acid to further generate NAD and ATP. Glycerol is then dehydrated through the reductive pathway to 3-hydroxypropionaldehyde by the enzyme glycerol dehydratase and subsequently reduced to PDO by 1,3-propanediol dehydrogenase. The activity of the enzymes depends on the presence of co-factors, coenzyme-B_{12} and NADH + H^+ [63–66,78,79]. Experimental work with strain *Lactobacillus brevis N1E9.3.3* reported yield of 0.89 $g_{1,3\text{-PDO}}/g_{Gly}$ and productivity of 0.78 $g_{1,3\text{-PDO}}\,L^{-1}\,h^{-1}$ under strict anaerobic conditions at a pH of 8.5 [80]. To reduce production costs, mixed cultures have also been applied under non sterile conditions and reported yields between 0.52 and 0.64 $mol_{1,3\text{-PDO}}\,mol^{-1}{}_{gly}$ [65,68]. *Shimwellia blattae* ATCC 33430 is also found capable of producing 1.3-propanediol with a yield of 0.45 $g\,g^{-1}$ and a productivity of 1.19 $g\,L^{-1}\,h^{-1}$ [64]. Tabah et al. [81] reported the use of fungal strain *Saccharomyces cerevisiae* under optimal reaction conditions of aerobic fermentation at 25 °C with the yield of 42.3%. Wang et al. in their approach combined bio and chemo catalytic method for the conversion of bio-renewable alcohols in a single reaction, limiting unnecessary energy consumption and waste formation. Bacteria were employed to convert crude glycerol from bio-refinery in the production of 1,3-propanediol which is selectively extracted from the broth as propionaldehyde by ionic solvents which initiate hydrogen transfer dehydration – catalyzed by $Cp^{*}IrCl_2(NHC)$ complex [82]. Catalytic glycerol hydrogenolysis is a sustainable pathway where a bimetallic Pt–Cu catalysis supported on H-mordenite synthesized with copper loadings showed 1.3-PD selectivity of 58.5% [83]. Table 1 shows 1,3-propanediol produced by different micro-organisms at relatively high concentrations and operational conditions that accounted for such conversions.

3.2. Glycerol to bio-ethanol

In recent years, ethanol has emerged as an important and sustainable bio-fuel. Bioconversion of crude glycerol to ethanol can be produced via fermentation process by microbes. Of the many microorganisms used for microbiological and metabolic applications, *Escherichia coli*, *Enterobacter aerogenes*, *S. cerevisiae*, and *Ogataea polymorpha* are best suited for glycerol utilization in a pH dependent manner – either aerobically or anaerobically [84,85]. The fermentation is by the conversion of DHAP mediated pathways: The oxidative pathway is catalyzed by glycerol dehydrogenase and dihydroxyacetone kinase enzyme and the reductive pathway is catalyzed by glycerol 3-phosphate dehydrogenase and kinase [86,87]. A non pathogenic strain of *E. coli* (ATCC 11505) under anaerobic condition is capable of withstanding high concentration of glycerol and resists glycerol inhibition [88]. Strains of *Pachysolen* species of yeast are also capable of producing ethanol under aerobic conditions immobilized in polycryogel that resulted in 90% yield [89]. Several yeasts such as *Candida diddensiae*, *Candida tropicalis*, *Pichia ciferrii*, *Williopsis saturnus*, *Candida boidinii*, and *Candida oleophila* were known to assimilate glucose and produced ethanol but could not convert glycerol into ethanol [90]. Pachapur et al. studied the impact of nitrogen (N_2) sparging on the co-culture system of *E. aerogenes* and *C. butyricum* in the production of bio-hydrogen from crude glycerol. With the production of hydrogen, ethanol is also

Table 1
Micro-organisms that produce 1,3-propanediol at relatively high concentrations and operational conditions that accounted for such conversions.

Compound	Microorganisms	Operating conditions			Yield (g g^{-1})	Productivity (g L^{-1} h^{-1})	Reference
		Process	Glycerol	Temperature (°C)			
1,3-propanediol	*C. beijerinckii* DSM 791	Batch mode, anaerobic	CG	37	0.55	0.99	[63]
	L. brevis N1E9.3.3	Batch mode, anaerobic	CG	36	0.89	0.78	[80]
	C. pasteurianum DSM 525	Batch mode, anaerobic	CG	35		0.14	[66]
	S. blattae ATCC 33430	Batch mode, aerobic	CG	37	0.45	1.19	[64]
	Mixed cultures *(Clostridiaceae, Enterobacteriaceae*)	Batch mode, microaerobic	CG	37	0.52–0.64	–	[65]

produced – this is a process based improvement, resulting in shift of metabolic pathway with increased production [91]. Production of ethanol is regulated by several factors such as carbon source, pH, transportation of metabolites within and outside the cell, temperature etc. Despite high yields from glycerol fermentation, the slow consumption rates of glycerol and unfavorable productivities are major drawbacks that are unsuitable for industrialization. Nevertheless, microorganisms such as *E. coli* can be easily manipulated genetically for large scale application through metabolic engineering [92]. Mutations that have growth and production advantages can be achieved by adaptive evolution that subjects organisms to serial or continuous cultivation for many generations to select fit variants. Some of the improved strains of *E. coli* include HW2, frdC, HW1 [93] (Table 2). Martin et al. optimized a process that uses algae in production of ethanol. This process includes growing algae, oil extraction, liquefaction, saccharification, transesterification and fermentation using Duran and Grossmann's model that resulted in ethanol production by 50% [98].

3.3. Glycerol to lactic acid

Lactic acid (2-hydroxy propionic acid) is a bi-functional molecule containing carboxylic acid group and hydroxyl group, making it versatile for wide range of industrial application [99]. As a monomer it is used for the production of biodegradable polymers and non toxic esters [100]. Lactic acid is one among the top 12 bio-based platform chemicals and it serves as a starting commodity for a wide range of chemicals such as acrylic acid, poly lactic acid, ethyl lactate etc. 2,3-Pentanedione can be derived from lactic acid and is extensively used in food, cosmetic and pharmaceutical industries [101]. Lactic acid has a chiral center and therefore exists as one of the two stereo isomers, L-lactic acid and D-lactic acid, and the chemical synthesis always produces racemic mixture. Commercially LA is produced mainly from sugar alcohols and sugars by fermentation followed by downstream processing steps such as purification, distillation and hydrolysis, resulting in high production cost, sustainability and waste disposal concerns. Literature on base catalyzed synthesis of lactic acid by hydrothermal conversion is available reporting various yields. Shen et al. studied the effect of alkaline catalysts such as hydroxides of alkali metals, aluminum and alkaline – earth metals and alkali-metal hydroxides were found to be more effective with a yield of 90% at 300 °C [102]. Kishida et al. experimented on hydrothermal decomposition of glycerin with an alkali by first forming an intermediate pyruvaldehyde, eliminating hydrogen by H$^-$ sift to the adjacent hydrogen, which is then converted to lactic acid ion by benzylic acid [103]. Other catalysts that have been used for alkaline hydrothermal conversion of glycerol to LA include MgO$^-$, ZrO$_2^-$, hydroxyapatite and their combinations [104]. Selective oxidation of glycerol in the presence of AlCl$_3$ and AuPd/TiO$_2$ as catalyst led to predominant production of lactic acid with the possible pathway of glycerol being converted to glyceraldehydes and dihydroxyacetone with eventual formation of lactic acid [105]. Studies on continuous production of lactic acid by hydrothermal transformation using copper as catalyst under alkaline condition were investigated by Moreira et al. and showed high conversion rate with selectivity and yield of 90 and 80% respectively. This reaction was carried out at 240 °C, 35 atm [106]. Oxidehydration of glycerol to pyruvaldehyde in comparison to dihydroxyacetone as an intermediate is known to provide better conversion to lactic acid. In an alternative two step process best conversion was achieved by Ag/Al$_2$O$_3$ nano-particles with a yield of 80% [107]. Monometallic Pt nanoparticles supported by Ketjenblack proved to be effective catalyst with chemo-selectivity of 95% [108]. Iridium catalyst also shows high selectivity and reactivity toward production of lactic acid from crude glycerol [109]. In a one-pot conversion of glycerol to lactic acid in water, Pt nano-particles and TiO$_2$ were highly active catalyst with yield of 63% and a conversion rate of 99% at 100 °C for 18 h. It is inferred that Pt nano-particles on TiO$_2$ selectively oxidized glycerol to aldehydes, ketones and TiO$_2$ smoothly promoted dehydration and rehydration of intermediates to produce lactic acid [110]. The above processes indicate that Lewis acid sites play an important role by accelerating the process for LA production and much work is done in developing such sites on combined catalysts that are active and durable. Recently, a simple cascade catalytic approach was found effective using multifunctional catalysts in combination with oxidative and acidic catalytic sites. Such reactions are carried out to maximize temporal and spatial productivity with minimum resources. Phosphomolybdic acid (H$_3$PMo$_{12}$O$_{40}$) was found to be highly efficient giving 90% conversion at 60 °C for 5 h with yield of 79% [111]. Tao et al. in their recent experimental work synthesized silver-exchanged phosphomolybdic acid catalysts Ag$_x$PMo$_{12}$O$_{40}$ with Ag acting as Lewis metal enhancing red-ox potential for phosphomolybdic acid catalysts to be suitable for oxidation of crude glycerol to DHA and PAL intermediates, then the Lewis site further favors dehydration pathway for lactic acid production achieving yield of 92%, a base free process [112]. Heterogeneous catalysts can be employed to produce racemic resolution which can be transformed to D-LA, that is difficult to produce by fermentation. Sharninghausen et al. demonstrated that a family of iridium complexes used as homogeneous catalysts has higher activity and selectivity (>95%) and can be performed at milder conditions without a solvent, obtaining hydrogen as by-product [113]. Enzymatic method of product production is superior when compared to chemical method due to low energy consumption, high product quality and selectivity. Glycerol as a carbon source (substrate) was explored extensively for lactic acid production. Microorganisms such as *E. coli*, *K. pneumonia*, *Lactobacillus panis*, *Lactobacillus rhamnosus*, *Lactobacillus delbrueckii*, *Enterococcus faecalis*, and Rhizopus oryzae have surprisingly generated D-lactic acid in high concentration [114–116]. Hong et al. were able to screen eight bacterial strains that could effectively convert crude glycerol to lactic acid of which *E. coli* AC-521 synthesized higher concentration under optimal conditions of 42 °C, pH 6.5, productivity of 0.97 g L^{-1} h^{-1}, yield of 0.9 mol/mol$_{gly}$ and product concentration of 85.5 g L^{-1} [117]. Electro-fermentation – merging fermenta-

Table 2
Summary of some of the works undertaken in converting crude glycerol to bio-ethanol.

Compound	Microorganisms	Operating conditions			Yield	Productivity	Reference
		Process	Glycerol	Temperature (°C)			
Bio- ethanol	*E. coli* MG1655	Batch mode, anaerobic	CG	37	–	$7.58 \pm 1.52\,g\,L^{-1}\,h^{-1}$	[92]
	P. tannophilus Y-475	Batch /continuous mode	CG	36	–	$0.65\,g\,L^{-1}\,h^{-1}$	[89]
	O. polymorpha	Batch mode	CG	45–48	–	$3.1\,g\,L^{-1}\,h^{-1}$	[85]
	E. aerogenes, *C. butyricum*	Batch mode, microaerobic	CG	35	$1.4\,g\,L^{-1}$		[91]
	Enterobacter and *Klebsiella*	Batch/Fed Batch	CG	35	$0.66–0.81\,mol_{EtOH}/mol_{gly}$	$3.9–11.1\,g\,L^{-1}\,h^{-1}$	[94]
	E. coli (HW2)	Batch anaerobic	CG	37	$2.1 \pm 0.3\,mg\,mg^{-1}$	–	[93]
	E. coli (ATCC 11505) immobilized in chitosan beads -	Batch anaerobic	CG	37	$96.7\,g\,L^{-1}$ – comparative to free cells		[88]
	E. aerogenes	CSTR, semi aerobic conditions	CG	37	$0.75\,mol_{EtOH}/mol_{gly}$		[84]
	Klebsiella sp. (TR17)	Batch, anaerobic	CG	35	$0.63\,mol_{EtOH}/mol_{gly}$	–	[95]
	Klebsiella pneumoniae GEM167	Batch,	CG	35	$21.5\,g\,L^{-1}$	$0.93\,g\,L^{-1}\,h^{-1}$	[96]
	K. cryocrescens S26	Batch, microaerobic	CG	36	$27\,g\,L^{-1}$	$0.61\,g\,L^{-1}\,h^{-1}$	[97]

tion in industrial applications with electro-chemistry – has been tested for improving yields and rates of glycerol conversion where polarized anodes and cathodes employed are able to increase the yields of hydrogen, alcohols and medium chained fatty acids. An electrical field influences the fermentation environment and microbial metabolism either in oxidative or reductive manner [118]. Murakami et al. isolated *E. faecalis* QU11 that produced optically pure L-lactic acid in the presence of acetic acid and further converted acetic acid to ethanol restoring the redox balance by oxidizing excess NADH with a yield of $0.991\,mol_{lactic\ acid}/mol_{gly}$ and production at $55.3\,g\,L^{-1}$ [56]. *R. oryzae* NRRL 395 can use crude glycerol as carbon source, tolerate high impurities, survive on minimum nutrition and simplify downstream product separation as fungal biomass can be easily separated from broth. The optimal crude glycerol concentration for cultivating *R. oryzae* NRRL 395 was $75\,g\,L^{-1}$ with a yield of $3.72\,gg^{-1}$ of lactic acid as reported by Vodnar et al. [119]. Engineered strains of *E. coli* can be used to overexpress genes that correspond to glycolytic intermediates by inactivating fumarate reductase, phosphate acetyltransferase, acetaldehyde dehydrogenase and respiratory D-lactate dehydrogenase [120,121]. Wang et al. addressed the limitations in conversion of crude glycerol due to impurities, by systematic engineering of *E. coli*, eliminating mgsA and other undesired pathways and enhancing glpD-glpK and D-lactate dehydrogenase. This engineered strain enabled production of $105\,g\,L^{-1}$ from $121\,g\,L^{-1}$ crude glycerol at 40 h [122]. Table 3 summarizes few experimental works on conversion of glycerol to lactic acid.

3.4. Glycerol to 1,3-dihydroxyacetone (DHA)

Dihydroxyacetone (DHA) is a specialty chemical and finds several industrial applications in cosmetic, food and pharmaceutical industry. DHA is an important precursor in the synthesis of fine chemicals such as 1,2-propylene glycerol (lactic acid), biodegradable polymers etc. [127]. DHA also finds application as nutrient supplement in neural development, visual acuity and in avoiding cardiac disorder [128]. It usually is produced via organic synthesis or fermentation. Dihydroxyacetone is a downstream metabolite of glycerol and an intermediate in glycolysis [129] produced by selective oxidation of glycerol via catalytic thermal oxidation or an electro oxidation. Several monometallic catalysts such as Au, Pd, Pt and bimetallic catalysts such as Pt–Bi and Pt–Au have been extensively studied. Ning et al. in their experimental work reported selective oxidation of glycerol catalyzed by Pt supported on N-doped carbon nano-tubes. This system showed better performance and a simplified catalyst preparation, undergoes surface modification that facilitates the activation and transformation of secondary hydroxyl group through chelation between Pt–Bi sites and the substrates [130]. Xiao et al. investigated the performance of five different catalysts (Pt–Bi/AC, Pt/MCM-41, Pt–Bi/ZSM-5, Pt–Bi/MCM-41 and Pt/Bi-doped-MCM-41) in their experimental work. Pt–Bi/MCM-41 exhibited highest yield and this is attributed to the presence of Bi located in adatom-like configuration with Pt rather than inside [131]. Electrochemical oxidation of glycerol on Pt electrodes (Pt_{100} and Pt_{111}) in acetic media leads to the formation of glyceraldehydes, glyceric acid and dihydroxyacetone as products at Pt_{111} when compared to only glyceraldehydes at $Pt_{100.}$ This is due to the different bonding modes of dehydrogenated glycerol to the surfaces. At Pt_{111}, intermediates bind to the surface by forming two single Pt-C bonds leading to the formation of another intermediate, a precursor to glyceraldehydes and dihydroxyacetone. At Pt_{100}, the intermediate binds to a single Pt=C bond [132]. In yet another work, nano-particle composite of Pd–Ce/Fe-MIL-101-N=$CH_{Neocuproine}$ was found to be highly effective in selective oxidation conversion of glycerol to dihydroxyacetone [133]. In an aqueous base-free solution N-doped multiwall nano-tube supported Pt

Table 3
Lactic acid produced by microbial fermentation of crude glycerol.

Compound	Microorganisms	Operating conditions			Yield ($g\,g^{-1}$)	Productivity ($g\,L^{-1}$)	Reference
		Process	Glycerol	Temperature (°C)			
Lactic acid	*K. pneumonia*	Batch mode, microaerobic	PG	28	0.82	142.1	[123]
	E. faecalis QU11	Fed-Batch, aerobic	CG	30	0.99	55.3	[56]
	E. coli	Batch, anaerobic	CG	30	0.93	50	[124]
	E. coli LA02	Batch, anaerobic and microaerobic	CG	37	0.85	32	[114]
	E. coli B0013-070	Batch, anaerobic	CG	40	0.72	14.5	[125]
	P. acidipropionici CGMCC 12230	Fed-Batch	CG	–	0.56	0.20	[126]

NPs (N-MWCNT) catalyst improved selective oxidation of glycerol by providing electro rich active sites [134]. In an interesting approach, crude glycerol was oxidized to chemicals including 1,3-dihydroxyacetone, formic acid, glyceraldehyde and hydroxyacetic acid by integrating reduction of nitrobenzene to aniline and transforming glycerol by UV light in the presence of Pd/TiO_2 as catalyst. With water as solvent at ambient temperature, glycerol acts as hydrogen source for nitrobenzene reduction [135]. Electrocatalytic oxidation on a carbon supported platinum, in a saturated bismuth acidic condition and at a potential is capable of oxidizing glycerol with 100% selectivity. The presence of bismuth blocks the active site available for the oxidation of primary alcohols on Pt/C surface resulting in high selectivity toward dihydroxyacetone formation [136]. Microbial conversion is more efficient in terms of economy and safety as various microorganisms occurring naturally and metabolically engineered are capable of utilizing crude glycerol. Bacteria such as *Gluconobacter oxydans* ATCC 621, *Gluconacetobacter xylinus* DSM 46604, *Gluconobacter frateurii*; algae such as *Schizochytrium limacinum* SR21, *Aurantiochytrium limacinum* SR21; fungi such as *Aplanochytrium* sp., *Thraustochytrium* sp./Ira-8, *Pichia membranifaciens* ZJB-0009 were extensively studied and found to utilize crude glycerol as sole carbon source in converting them to DHA [137,138]. *Gluconobacter* strains are the most extensively used microorganisms for the production of DHA by incomplete oxidation catalyzed by the membrane bound glycerol dehydrogenases. The mode of growth of these organisms is aerobic rather than anaerobic and hence demand for oxygen is relatively high. Therefore the configurations of bioreactors, oxygen transfer rate, physiochemical properties of the culture medium, and strains that can effectively increase the oxygen transfer raters are the parameters explored. Leu et al. isolated the strain *G. frateurii* CGMCC 5397 that could convert glycerol to DHA with high productivity and yield. For a fermentation period of 48 h, DHA concentration obtained was $73.1\,g\,L^{-1}$ [139]. Zeng et al. evaluated mass transfer coefficient using *G. frateurii* CGMCC 5397 and inferred that K_La of $52.05\,h^{-1}$ favored glycerol utilization in DHA production of $131.16\,g\,L^{-1}$. In a fed-batch mode, when K_La was set to $82.14\,h^{-1}$, DHA productivity, concentration and yield were $7.96\,g\,L^{-1}$, $175.44\,g\,L^{-1}$ and $0.89\,g\,g^{-1}$ respectively [140]. *G. oxydans* NL71 under compressed oxygen supply was reported to improve the bio transformative production of 1,3-dihydroxyacetone. Zhou et al. reported a concentration of $301.2 \pm 8.2\,g\,L^{-1}$ of DHA after 32 h in compressed oxygen supply-sealed and stirred tank reactor system with a productivity of $9.41 \pm 0.23\,g\,L^{-1}\,h^{-1}$ [141]. An inter-loop airlift bioreactor controlling aeration rate with *G. oxydans* ZJB09113 produced DHA of concentration of $156.3 \pm 7.8\,g\,L^{-1}$, $89.8 \pm 2.4\%$ conversion rate for 72 h at 30 °C [142]. *G. oxydans* ZJB09112 strain in a bubble column with multiple feeding of glycerol of $161.9 \pm 5.9\,g\,L^{-1}$ of DHA was produced at a conversion rate of $88.7 \pm 3.2\%$ [143]. Though microbial productions of DHA provide cost effective and environment friendly solutions when compared to their chemical counterpart, they still cannot be applicable on a broader platform. Enzymes catalyze diverse chemical reactions efficiently in a living cell and have found to work ex-vivo even when isolated under natural and non-natural environmental conditions. Alternatively, glycerol oxidation by isolated enzymes can overcome these limitations. Glycerol dehydrogenases (GlyDH), a metallo-enzyme, plays a crucial role in the pathway of glycerol metabolism. GlyDH is a NAD+ dependent oxido-reductases that dehydrogenates glycerol to dihydroxyacetone [144]. However, even isolated enzymes cannot be extensively realized due to various limitations such as high production cost, expensive red-ox co-factors, stability, solubility issues, reusability, workability in flow processes etc., hence protein immobilization makes it suitable [145]. Benefits of enzyme immobilization are immense; it simplifies downstream processing, improves stability, reusability, enzyme activity, selectivity or inhibition. Many studies on immobilization have been undertaken to enhance DHA productivity. Kumar et al. used magnetically, separable meso-porous silica adsorbed GDH called ADH and glutaraldehyde treated NER (nano-scale enzyme reactors) to stabilize glycerol de-hydrogenase for the production of dihydroxyacetone. NER had maintained 39% of initial activity even after seven cycles of repeated use while residual activity of ADS dropped to 13% of its initial activity only after two recycled use [146]. Martin et al. in their study used recombinant and multimeric GlyDHs from *Citrobacter braakii*, *Cellulomonas* sp. and *Geobacillus stearothermophilus* immobilized on agarose carriers to minimize enzyme product inhibition and maximize enzyme thermal stability. The immobilized GlyDH on agarose retained 100% of its activity at 65 °C, 18 hours of incubation at a neutral pH. Zang et al. exploited use of silica coated magnetic Fe_3O_4 nanoparticles, activated by an amino-silane reagent for immobilization of GlyDH via a glutaraldehyde linkage. The immobilized GlyDH showed enhancement in thermal stability by 3.5 folds, less sensitive to changes in temperatures and pH, thermal stability at 50 °C and 9% loss of enzyme activity even after 10 cycles [147]. Martin et al. in their work on immobilizing systems bio-catalysis, combine three different enzymes on a hetero-functional carrier that allows selective oxidization of glycerol. Co-immobilization allowed in situ recycling of red-ox co-factor and H_2O_2 respectively to produce 9.5 mM DHA [148]. Yang et al. in their study engineered *E. coli* (*E. coli* D4) for dihydroxyacetone production by enhancing the activity of the enzyme by introducing NOX (NADH oxidase) from *E. faecalis*. Under optimum conditions, productivity reached $0.13\,g\,g^{-1}\,h^{-1}$ wet cell mass [149]. Table 4 summarizes some more work undertaken in DHA production.

4. Hydrogen

Hydrogen finds numerous applications in process industries and almost 95% is produced from fossil fuel based raw materials. Hydrogen is also recognized as a potential fuel as it brings a carbon-free solution, sustainable and can be stored for prolonged usage [150]. As a by-product, it is used in chemical industry in the production of compounds like hydrochloric acid, formic acid, cyclohexane, methanol, ammonia, urea, acetic acid etc. Though hydrogen promises to be advantageous for sustainable energy solutions, its production methods are under developmental stages for

Table 4
1,3-Dihydroxyacetone produced by microbial fermentation of crude glycerol.

Compound	Microorganisms	Operating conditions			Concentration ($g L^{-1}$)	Productivity/ Conversion rate ($g L^{-1} h^{-1}$)	Reference
		Process	Glycerol	Hours of incubation			
1,3-dihydroxyacetone	*G. oxydans* NL71	Fed-Batch mode, aerobic	CG	32	301.2 ± 8.2	9.41 ± 0.23	[141]
	G. frateurii CGMCC 5397	Fed Batch mode, aerobic	CG	16	175.44	7.96	[140]
	G. oxydans ZJB09113	Batch, airlift bioreactor	CG	72	156.3 ± 7.81	89.8 ± 2.4%	[142]
	*G. oxydans ZJB*09112	Batch, bubble column reactor	CG	68	161.9 ± 5.9	88.7 ± 3.2%	[143]
	G. oxydans	Batch mode, aerated (COS-SSTR)	CG	36	40.6 ± 1.8	80.6 ± 3.5%	[127]
	G. frateurii CGMCC 5397	Fed-Batch mode aerobic	CG	48	125.8	2.6, 98.5%	[139]

commercial application. Conventional methods of production include water electrolysis [151], thermo-chemical [152–155], thermo-electro-chemical [156,157], solar thermal [158], photo-catalytic water splitting method [159,160] and biological processes. Among all the available processes, biological route is preferable as it involves less expenditure, carried out at ambient temperature and pressure and the reactors can be as simple as waste water or waste biomass [161]. The other methods such water electrolysis, photo-catalytic method etc. are not an economical alternative and can only be applied under special cases. The most widely applied route is the thermo-chemical method where power consumption is inevitable in converting crude glycerol to synthesis gas. Some variations of processes under thermo-chemical reforming of crude glycerol under consideration include supercritical water reforming (SCWR) – low temperature high pressure system (218 atm, 374 °C) and is highly selective and efficient towards H_2 production. Xu et al. conducted experiments of glycerol gasification in supercritical water within a continuous flow tubular reactor operated between temperatures 380 and 500 °C to obtain 60% mole fraction of hydrogen as gaseous product [162]. Greater yields of hydrogen are obtained at high temperatures while at low temperatures, formation of CH_4 is favored and hence the process is economically unattractive [163]. Steam reforming (SR) is also one of the most commonly used chemical method for hydrogen production. In this, water vapor reacts with glycerol in the presence of catalyst producing hydrogen, carbon dioxide and carbon monoxide. Simultaneous removal of hydrogen produced increases the yield of the reaction [164]. The best condition for the production of hydrogen is at 625 °C and at water to glycerol molar ratio of 9:1. Under such conditions, methane production is minimized and carbon formation is inhibited [165]. The catalysts that can be applicable as cited in the literature are those that can cleave C–H, O–H and C–C bonds, such as Pt, Ni, Rh, Pd, Co and Ru with their various supporters and promoters [166]. Partial oxidation reforming (POR) occurs under atmospheric pressure with oxygen quantities below the optimal stoichiometry for complete combustion. The process is exothermic and its efficiency directly depends on the amount of oxygen entering the mixture [167]. The reaction is exothermic and hence the reactor itself supplies the required amount of heat [168]. Auto-thermal reforming (ATR) is similar to POR and differs due to inclusion of water vapor in the combustion process favoring increased production of hydrogen. The compactness and efficiency of this system makes it possible to develop autonomous units for small scale decentralized production [169]. Gasification, liquid phase reforming (LPR) and pyrolysis have been employed as waste management practices in energy and agriculture for combined heat and power generation thus creating a huge potential as circular economy. Crude glycerol, the residual biomass of biodiesel production, can fulfill the energy need of the biodiesel industry and contribute in decreasing the cost of biodiesel production while providing short time solution of waste glycerol disposal [170]. Gasification is a promising technology for utilizing crude glycerol to produce fossil fuel alternatives namely combustible gaseous mixture of syngas consisting of hydrogen, carbon-monoxide, methane and carbon dioxide at temperatures ranging from 800 to 1000 °C [171]. Apart from gasification, other routes include pyrolysis, aqueous phase reforming and catalytic reforming. Aqueous phase reforming (APR) is also of particular interest owing to the low energy cost of the process and the suppressed formation of CO. Crude glycerol supported on metal catalysts (Group VIII) show high activity. Pt and Pt based alloys have been reported beneficial. Several studies indicate that, the support properties play a crucial role in reforming glycerol, such as Pt-catalyzed APR of glycerol with oxides Al_2O_3, MgO, ZrO_2, CeO_2 supported high hydrogen production and low hydrocarbon formation [172]. Remón et al. (2016) [173] in his experimental work established a highly customizable process that can valorize crude glycerol for either gaseous or liquid products and details that high pressure (45 bar) and medium temperature (206 °C) favors production of liquid products such as alcohols, aldehydes, ketones, carboxylic acids and esters. Gas production is favored at high temperature (238 °C) and low pressure (39 bar) and the resulting products are hydrogen, carbon monoxide, methane and carbon dioxide [173]. In yet another study, hydrogen production from crude glycerol was optimized by steam reforming using two novel process steps; initially crude glycerol was purified using acetic acid to remove impurities and the refined glycerol was valorized by catalytic steam reforming to yield gas and liquid phase components. Temperature, glycerol concentration and spatial time were the key parameters that influenced the thermodynamics of the process [174]. Pyrolysis, another sustainable energy technology that is widely practiced in waste management, was explored by Ganesapillai et al. by addition of crude glycerol to lignocellulosic biomass. The microwave pretreated feedstock based pyrolysis showed enriched concentration of Syngas (84.9% v/v) when compared to non-treated feed-stock (79.1% v/v) at 720 °C [175]. In another study, anaerobic digestion using mixed culture was explored for hydrogen production. Pretreatment by five methods such as acids, base, microwave, heat and chloroform were conducted. The heat treatment method showed the highest production across other pretreatment methods mentioned. Heat eliminated H_2 consuming bacteria. The maximum H_2 production obtained at maximum conditions was 29.43 ± 0.71 mmol L^{-1} [176]. Pachapur et al. investigated hydrogen production by co-culture system using *E. aerogenes* NRRL B-407 and *Clostridium butyricum* NRRL B-41122. There was increased hydrogen production, reaching a maximum of 19.46 ± 0.95 mmol-H_2L^{-1} when compared to respective monocultures. In addition other products such as 1,3-propandiol, acetic acid, ethanol and butyric acid were co-produced [177]. The other microorganisms that are capable of producing hydrogen from glycerol are *Citrobacter freundii*, *Bacillus subtilis*, *Enterobacter ludwigii*, *Bacillus licheniformis*, *Shigella sonnei*, *Bacillus amyloliquefaciens*, *Bacillus atrophaeus*, *Alcaligenes faecalis and Staphylococcus warneri* [178]. Particular microbes and their conversion rates are mentioned in Table 5.

Table 5
Hydrogen produced by microbial fermentation of crude glycerol.

Compound	Microorganisms	Operating conditions		Yield	Reference
		Process	Glycerol		
Hydrogen	*Clostridium acetobutylicum* ATCC 824	Batch mode, anaerobic	CG	0.44 mol/mol$_{gly}$	[179]
	E. aerogenes and *C. butyricum*	Batch mode , anaerobic	CG	32.1 ± 0.03 mmol L^{-1}	[180]
	E. coli MG1655	Fed-batch, anaerobic	CG	0.56 mol mol$^{-1}{}_{gly}$	[92]
	Bacillus amyloliquefaciens	Batch mode, anaerobic	CG	0.50 ± 0.20 mol/mol$_{gly}$	[178]
	Klebsiella sp. *TR17* and *Rhodopseudomonas palustris TN1*	Batch, anaerobic	CG	6.42 mmol H_2	[181]
	R. palustris	Batch, anaerobic	CG	37.7 mL·gbiomass^{-1}·hr^{-1}	[182]

5. Glycerol to additives

Oxygenated compounds are employed as fuel additives to reduce gum formation, cloud point, HC, CO and nitrogen oxide emissions, to provide high octane and to improve viscosity and cold flow properties [183,184]. Glycerol can be converted into acetals and ketals and used as fuel additives [185]. Glyceryl triacetate (TAG) also known as triacetin is a valuable bio-additive produced by the catalytic esterification of acetic acid [186]. Triacetin also finds application as a plasticizer of cellulosic polymers such as nitrocellulose, cellulose acetate, vinylidene polymers, etc. Studies on combined ketalization–alkylation process were conducted in a fixed bed flow reactor over a zeolite BEA catalyst [187]. This reaction proved to be a one step process for the qualitative conversion of glycerol to a mixture of ethers under mild conditions. Ilgen et al. in their experimental work converted glycerol to solketal over Amberlyst-46 heterogeneous catalyst. 84% yield was achieved under optimal reaction conditions of 60 °C temperature, 30 min reaction time, 1% (w/w) catalyst. Their blends with oxygenate free gasoline reported improved octane number as compared to unblended gasoline [188]. Swetha et al. in their experimental worked on acetylation of glycerol with acetic anhydride and esterification with acetic acid to produce acetins. They conducted a comparative study using various solid acid catalysts such as cesium phosphotungstate, amberlyst-15, H-beta, sulfated zircon and montmorillonite K-10 under mild reaction conditions. Cesium phosphotungstate showed the highest activity 99.1% for acetylation. Solketal, the ketal produced when glycerol is reacted with acetone, is a potential oxygenated gasoline additive like triacetin and improves the octane number and is easily hydrolyzed in excess water. Triacetin and Solketal are the two major additives among others that can be obtained. Esterification of glycerol with acetic acid yields important oxygenated compounds such as MAG, DAG and TAG. Esterification with levulinic acid generated mono-, di- and tri-glycerides. Acetylation of glycerol with acetone produces Solketal and acetal. Many catalysts to have reported to have enhanced these reactions such as Amberlyst 70, SnO2, Graphene oxide, heteropoly acids, Al-SBA-15, Zeolite beta, PTSAZrO_2 etc., altered rate in obtaining fuel additives. Production of biofuel additive is an emerging field and is still awaiting rationalization [189].

6. Enzymes

Microbiota transformation of crude glycerol to value added products has been cost effective and environment friendly than chemical synthesis [190]. However, long fermentation times, limitations due to oxygen requirement, high energy consumption for sterilization, high concentration of broth product and substrate concentration, inhibitory effects on the cell growth, their pathogenicity etc. prevent broader application. Isolated enzymes can overcome these limitations offer techno-economic and environmental advantages. Enzymes are capable of catalyzing a wide range of chemical transformations with high stereoselectivity, region-selectivity, chemo-selectivity, producing almost exclusively a single major product without undesired by-products [191,192]. The most applicable enzymes available in the literature for glycerol conversions are lipases and glycerol dehydratases. Lipases (triacylglycerol hydrolase, EC3.1.1.3) stand out as the main catalyst for industrial application as they are highly selective and catalyze a wide range of ester reactions, especially those that are insoluble in water. An important industrial application of lipases is the modification of fats and oils to produce biodiesel and other structured lipids [193,194]. Their features such as their chemo, regio, enantioselectivity, substrate specificity and ability to be active in aqueous and organic media makes it more versatile. They work successfully in glycerolysis systems even in the presence of solvents. Lipases are categorized in the subclass of esterase's and are easily extractable in bulk from microorganisms than from plants and animals. Microorganisms that have been used for lipase production include *Aspergillus niger*, *R. oryzae*, *Candida cylindracea*, *Pseudomonas fluorescens*, *Candida rugosa*, *Pseudomonas cepacia*, *Candida antarctica*, and *Chromobacterium viscosum* [195].

6.1. Glycerol dehydratases (GlyDH – EC 1.1.1.6)

Glycerol dehydratase is an important polyol dehydrogenase that is a NAD+ dependent oxido-reductase and converts glycerol into DHA. They catalyze regioselective oxidation of glycerol to yield an important building block in chemical industry called DHA. Microbial sources from which the enzymes are extracted include *C. braakii*, *G. stearothermophilus*, *K. pneumonia*, *Cellulomonas* sp. etc. Polyol dehydrogenases consist of a large family of oxido-reductases that catalyzes the initial step of glycerol oxidation, which is responsible for glycerol utilization with diverse microorganisms [196]. The reductive pathway is regulated by B-12 dependent glycerol dehydratase (GDHt – EC 4.2.1.30) and related diol dehydratases (DDHs – EC 4.2.1.28) converting glycerol to 3-hydroxypropionaldehyde (HPA) and by the coenzyme nicotinamide adenine dinucleotide (NADH) and H^+ dependent enzyme, 1,3-PD and regenerating NAD+. In the oxidative pathway, the NAD+ dependent enzyme glycerol dehydrogenase (GDH – EC 2.7.1.29) catalyzes the conversion of glycerol to DHA, and glycolytic enzyme DHA kinase (EC 2.7.1.29,) phosphorylates the DHA to the latter product, which is then funneled to glycolysis [142–146].

7. Conclusion

Overall production of biodiesel is increasing rapidly. The by-product crude-glycerol 10% wt of total overall biodiesel production possess low value as a result of the presence of impurities. To increase its commercial value, crude glycerol has to be treated and refined through various physico-chemical processes such as filtrations, distillation and chemical additions. This may be a costly affair subjected to the availability of glycerol purification facility and not economically viable for a small and medium scale industry.

This review presents possible processes for the conversion of glycerol into useful commodities. Processes such as oxidation, transesterification, esterification, hydrogenolysis, and carboxylation have been studied extensively on a lab scale in recent years and in most cases, products desired at high conversion rates are still difficult because of extensive functionalization of glycerol molecule, lack of optimal catalysts and unknown reaction conditions. Traditionally, the high price of glycerol limited the economic viability of such transformations and as the price decreases, new products will be increasingly derived from glycerol. Availability, low price and a higher degree of reduction make it extremely versatile and therefore microbes are able to use this reduced carbon source by the process of fermentation. Organisms like *C. pasteurianum*, *K. pneumonia*, *C. butyricum* and *E. coli* have been used to produce several industrially important commodities including lactic acid, DHA, 1,3-PDO, ethanol, hydrogen etc. Although organisms are beneficial, their use on the industrial scale proves difficult due to ignorance on physiological behavior and genetic makeup. Genetic manipulation for improved production is challenging, but with continued interest and advancement in the field of metabolic engineering would alter the portfolio of available compounds. Furthermore, conversion of glycerol is expected to grow as does the need for biofuels. Future advancements in this field could bring great environmental and socioeconomic benefits to the society.

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