



Review

Valorisation of crude glycerol to value-added products: Perspectives of process technology, economics and environmental issues



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ABSTRACT

The enormous production of glycerol, a waste stream from biodiesel industries, as a low-value product has been causing a threat to both the environment and the economy. Therefore, it needs to be transformed effectively and efficiently into valued products for contributing positively towards the biodiesel economy. It can either be converted directly into competent chemicals or can be used as a feedstock/precursor for deriving valuable derivatives. In this review article, a technical evaluation has been stirred up, various factors and technologies used for producing value-added products from crude glycerol, Environmental and economic aspects of different conversion routes, cost factors and challenges of integration of the different routes for biorefinery have been reviewed and elaborated. There are tremendous environmental benefits in the conversion of crude glycerol via the biochemical route, the product and residue become eco-friendly. However, chemical conversions are faster processes, and economically viable if environmental aspects are partially ignored.

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1. Introduction

The raised petroleum prices, fuel crisis due to increasing population and unfavorable effects of emission of hazardous chemicals and greenhouse gases in the environment have stimulated the researcher for searching biofuel(s) as the alternative to fossil fuels [1]. Vegetable oilseed mainly consists of four components, viz. Shell, husk, oil (lipid) and oil-cake of which the nature of the shell and husk is identical to other loose lignocellulosic biomass; oil is a triglyceride in the liquid form while oil-cake is a cellulosic and protein-rich component [2]. The processing of lignocellulosic biomass can be either for direct combustion and power generation, 2G-bioethanol production, while oil-cake can be a feed material for animals and fish or can be used as feedstock for biogas generation. Oil if non-edible, is mostly used for biodiesel production, pharmaceuticals or for other chemical industry applications. Many research articles and reviews are available in the literature for biomass combustion, biogas production from oilcake, and for biodiesel production via transesterification [3–5]. Biodiesel is one such renewable biofuel derived from lipids with easily accessible conditions and chemical reactions [6]. It has the competence to overcome environmental

and ecological disturbances. Biodiesel, popularly termed as fatty acid methyl ester (FAME), is basically derived from the process called transesterification of triglycerides (vegetable oils, animal tallow/fats, waste cooking oils, edible plants, biomass, microalgae) with an alcohol either methanol or ethanol using a suitable basic or acidic catalyst [7–9]. The reaction can be catalyzed either homogeneously or heterogeneously [9]. During this production process, two phases, i.e. upper phase called biodiesel (methyl or ethyl esters) and the lower phase called crude glycerol are formed, which are then separated easily after resting the reaction mixture for a few hours at neutral pH [7]. Different pathways through which crude glycerol can be processed into different valuable products are as shown in Fig. 1.

Jatropha oil in South-East Asian countries, Soybean oil in USA, Rapeseed oil in Europe are the main potential sources for biodiesel production due to their availability [3,10]. The hypothetical concept of biorefinery plant is also linked via biodiesel production [11]. The term “bio-refinery,” supplemented recently to describe for the provision of converting biomass to food, fuel, and valuable chemicals [12]. After transesterification reaction, almost equal volume of biodiesel and about 1/10th volume of glycerol is obtained in a well-set biodiesel industry. However, mostly the glycerol obtained is the crude one which needs further purification for the generation of other value-added chemicals or derivatives. These chemicals are further coupled with the biodiesel industry to potentially realize a biorefinery set up.

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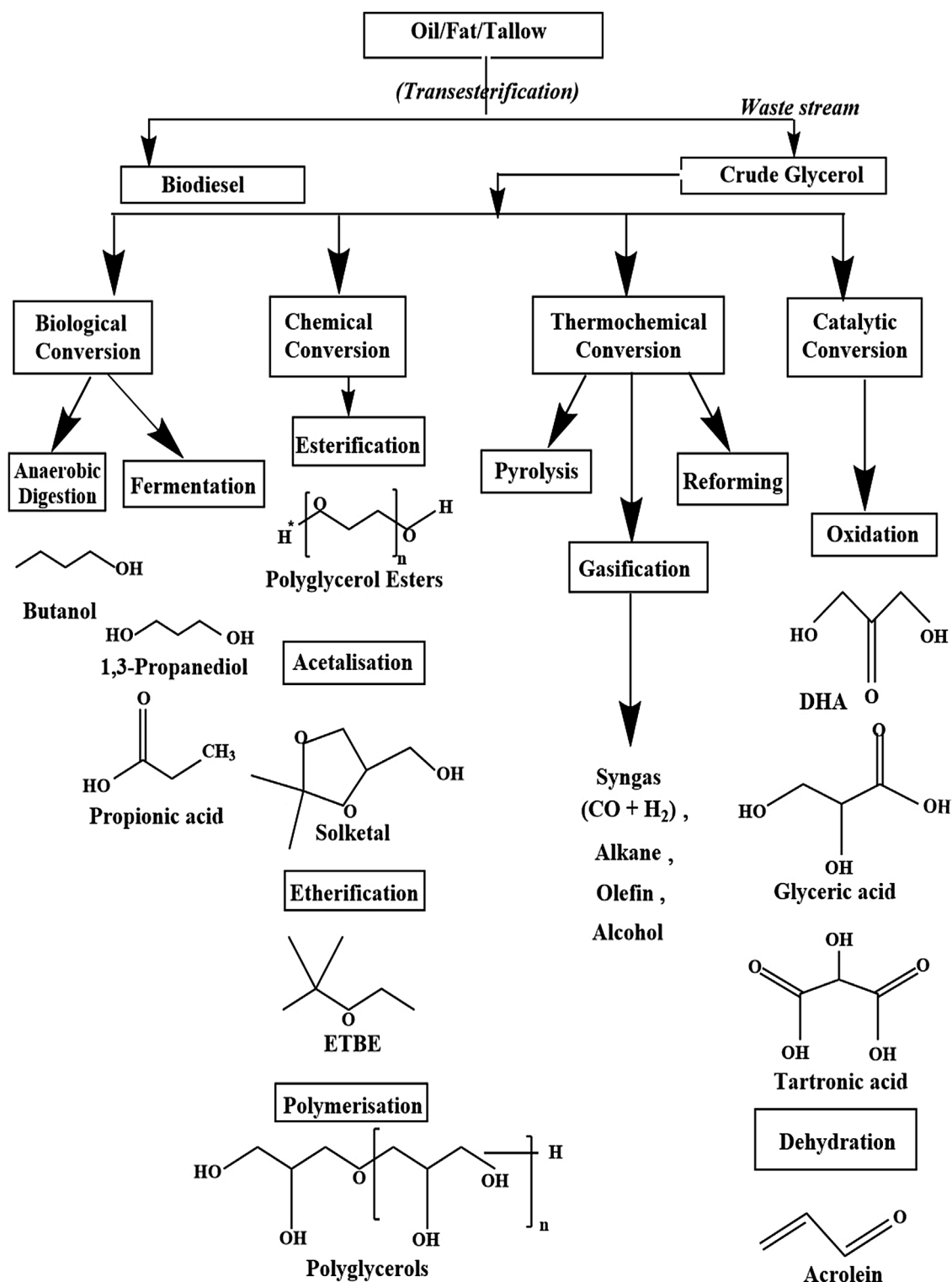


Fig. 1. Derivatives and chemicals produced from glycerol.

Glycerol, also known as 1,2,3-propanetriol, is a compound and a resource of the oleo-chemical industry. Glycerol is commonly called glycerine. It is the primary co-product synthesized from the biodiesel production and its production is about 10 wt. % of the amount of biodiesel produced, i.e. around 0.10 kg of crude glycerol is generated per kg of biodiesel [13]. Also, it can be produced from saponification (soap production) and hydrolysis of fatty acids. In the current scenario, 10 % of glycerol is generated from hydrolysis, 12 % glycerol

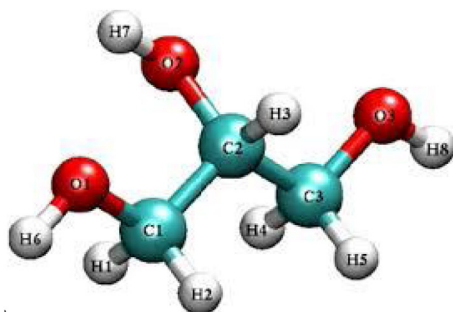
from saponification and 50–80 % glycerol from the transesterification process [13]. Thus, the report states that 66 % of world's glycerol comes only from the biodiesel industry. The world-wide production of glycerol will be approximately 41.9 billion liters [14]. Therefore, utilization of the glycerol as a raw material using sustainable processes is of vital importance. As a means for literature review for conversion of glycerol into value added products, recently published articles in the topic are as listed in Table 1.

Table 1

List and scope of review articles published for glycerol valorisation to value added products.

S. No.	Title of article	Scope and attribute	Authors
1.	Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols	Different approaches and techniques used to obtain glycerol acetals and ketals	Ancuşa Roxana Trifoi, Paul Şerban Agachi, Timea Pap (2016)
2.	Catalytic vaporization of raw glycerol derived from biodiesel: a review	Role of heterogeneous catalyst on the valorisation of glycerol	Sravanthi Veluturla, Narula Archana, D. Subba Rao, N. Hezil, I.S. Indrajya & S. Spoorthi (2017)
3.	Glycerol Production and Transformation: A Critical Review with Particular Emphasis on Glycerol Reforming Reaction for Producing Hydrogen in Conventional and Membrane Reactors	Focus on glycerol reforming reactions, catalysts developed for use, membrane catalytic reactors	Giuseppe Bagnato, Adolfo Iulianelli, Aimaro Sanna and Angelo Basile (2017)
4.	Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: A critical review	Transformation of glycerol into oxygenated fuel additives and discussion of fuel properties and other characteristics	A. Cornejo, I. Barrio, M. Campoy, J. Lázaro, B. Navarrete (2017)
5.	Review on enzymatic synthesis of value added products of glycerol, a by-product derived from biodiesel production	Different bioconversion technologies of crude-glycerol, relevant approach for the production of various chemicals from bio-glycerol over enzyme and chemical catalysts	J. Pradima, M. Rajeswari Kulkarni, Archana (2017)
6.	Continuous Flow Conversion of Glycerol into Chemicals: An Overview	Glycerol valorization in liquid phase continuous flow systems using different types of catalysts and processes	Christophe Len, Frederic Delbecq, Cristobal Cara Corpas, Encarnacion Ruiz Ramos (2017)
7.	Environmental and economical perspectives of a glycerol Biorefinery	Chemical research and process design in the development of CO ₂ - and other biorefineries	Giacomo M. Lari, Giorgio Pastore, Moritz Haus, Yiyu Ding, Stavros Papadokostantakis, Cecilia Mondelli and Javier Pérez-Ramírez (2018)
8.	Techno-Economic Analysis of a Glycerol Biorefinery	Environmental and economic assessment of a glycerol biorefinery by including operating costs	Sebastiano C. D'Angelo, Agostino Dall'Ara, Cecilia Mondelli, Javier Pe'rez-Ramírez and Stavros Papadokostantakis (2018)
9.	A Review on the Catalytic Acetalization of Bio-renewable Glycerol to Fuel Additives	Focus on innovative and potential technologies for sustainable production of solketal	Amin Talebian-Kiakalaieh, Nor Aishah Saidina Amin, Neda Najaafi and Sara Tarighi (2018)
10.	Glycerol from biodiesel production: Technological paths for sustainability	Analysis of patents related to the use of glycerol in the period from 1993 to 2015	Marcos Roberto Monteiro, Cristie Luis Kugelmeier, Rafael Sanaiotte Pinheiro, Mario Otávio Batalha, Aldara da Silva César (2018)
11.	Glycerol valorization under continuous flow conditions-Recent advances	Glycerol valorization to valuable products under liquid phase continuous flow systems using different types of catalysts and processes	Rajender S. Varma, Christophe Len (2018)
12.	Spotlight on biodiversity of microbial cell factories for glycerol conversion	Biodiversity of naturally glycerol consuming Microorganisms - impact and importance	Hannes Russmayer, Michael Egermeier, Denis Kalemasi, Michael Sauer (2019)
13.	Sustainable value-added C ₃ chemicals from glycerol transformations: A mini review for heterogeneous catalytic processes	Progress on sustainable C ₃ chemical production from catalytic glycerol transformations	Yuan Wang, Yang Xiao, Guomin Xiao (2019)

The hygroscopicity and water-soluble nature of glycerol are due to its three-backbone containing carbon atoms along with hydrophilic hydroxyl groups as shown in (Fig. 2) [15]. This unique structure of glycerol is responsible for its properties, making it a prominent material for numerous applications [16]. Glycerol without any chemical treatment and purification is in crude form,

**Fig. 2.** Molecular structure of glycerol.

while after purification it is in pure form. Pure and commercially synthesized glycerol has almost the same qualities because of their applications [17]. The purity of crude glycerol is 60–80 %, while pure or synthesized one has 100 % pure. Crude glycerol obtained contains a lot of impurities such as alcohol, organic and inorganic salts, heavy metals, water, soap, mono, and di-glyceride traces, matter organic non-glycerol (MONG), fatty acid methyl esters (FAME), fatty acid esters (FAE), free fatty acids (FFA), polyol, and ash [13]. Different quality and grades of glycerol are commercially available throughout the globe. Analytical grade glycerol is the highest purity glycerol having >98 % purity without any contaminants. USP (United States Pharmacopeia) grade is 96–99.5 % pure, whose generic use is in food, pharmaceuticals, personal care and cosmetics [18]. A comparison of the physico-chemical properties of crude and pure glycerol is shown in Table 2.

Pure glycerol is commercially the chief feedstock such as for the production of food additives, surfactants, lubricants, beverages, pharmaceuticals, cosmetics, textiles and many more. However, on both small as well as large scale, the purification process of crude glycerol is a very exorbitant [7,20]. In addition to pure/high-quality

Table 2
Comparison of the properties of crude and pure glycerol [19].

Common properties			Uncommon properties		
Property	Crude glycerol	Pure glycerol	Property	Crude glycerol	Pure glycerol
Density (g/cm ³)	1.01 to 1.20	1.31	Odour	-	Odourless
pH	2.0 to 10.8	6.4	Methanol content	6.2–12.6%	-
Viscosity (mPa.s)	1213	930	FFA content	35.7–96.4 %	-
Colour	Dark brown	Colourless	FAME content	5.2–51.6 %	-
Glycerol content	22.9–63 %	> 98.7 %	Soap content	20.5–31.4 %	-
			Water content	1 to 28.7 %	-
			Ash content	2.7 to 5.7 %	-
			Melting point (° C)	-	17.8
			Boiling point (° C)	-	290
			Flash point (° C)	-	>400
			Vapor pressure (mmHg)	-	0.13
			Solubility	-	Miscible in water

glycerol, an abundance of impure glycerol is available in the market at low prices and that can be potentially used as a valued feedstock [21]. Although pure glycerol is a highly valued chemical escorted by numerous uses, but the impurities present in the crude glycerol make the purification techniques costly escalating the price of glycerol [21]. Therefore, current research is a matter of interest that lies in the valorisation of crude glycerol via directly converting it

into value-added products using sustainable production processes. Among the several recently published review articles for valorisation of glycerol as listed in Table 1, none have been found which describes fully the techno economic aspects for optimum yield of product, economic analysis of the processes and products and environmental aspects. Therefore, this review article considers the techno economic aspects of different processes and products for

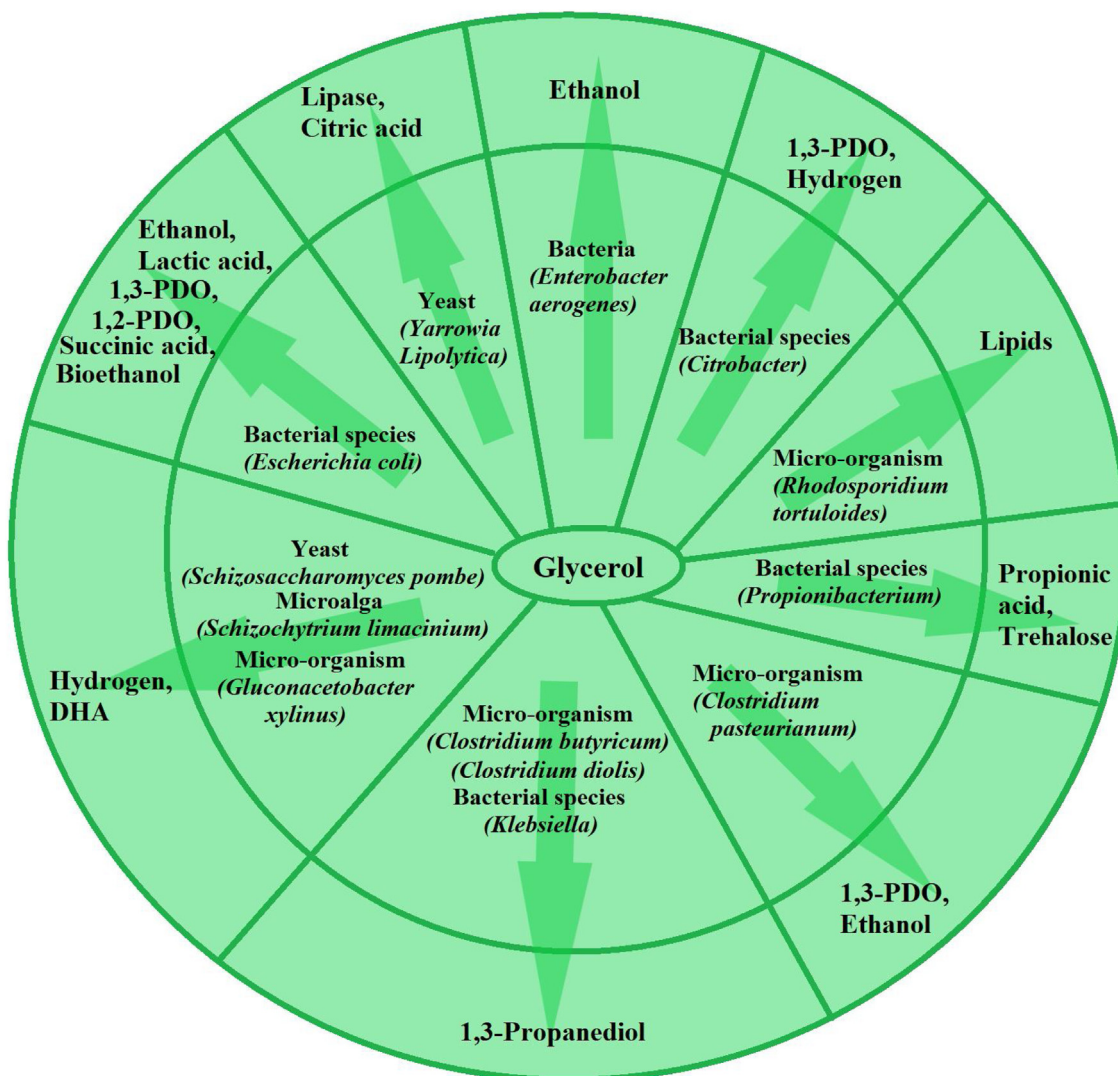


Fig. 3. Bio-catalytic pathways for conversion of crude glycerol to value added products [28–35].

Table 3

Classification of process and products of biological conversion pathways.

S. No	Reactants (Molar ratio)	Pathway	Catalyst	Optimal Reaction Condition(s)	Product (s) -yield	Reference
1.	Glycerol	Fermentation	<i>Escherichia coli</i> AC-521	42 °C, pH-6.5, 88 hour	Lactic acid - 85.8 g/L	[25]
2.	Crude glycerol	Fermentation	<i>G. Oxydans</i> cells immobilised over polyurethane foam	31 °C, glycerol concentration - 20 g/L, pH - 4.7	1,3-Dihydroxyacetone - 17.83 g/L	[26]
3.	Glycerol	Fermentation	<i>Gluconacetobacter xylinus</i> cells	25(w/v), 60 hour, 30 °C, pH - 6	Dihydroxyacetone -6.3 g/L	[30]
4.	Glycerol	Fermentation	<i>Rhodospiridium toruloides</i>	30–60 hour, C/N ratio - 300	Lipids	[32]
5.	Pure and recovered glycerol	Fermentation	<i>Enterobacter aerogenes</i>	Glycerol conc. - 39 g/L, 120 hour, pH - 7	Ethanol - 20 g/L	[33]
6.	Glycerol	Anaerobic batch fermentation	<i>Escherichia coli</i> SS1	37 °C, 96 hour, glycerol conc. - 20 g/L	Bioethanol (ethyl alcohol) - 9.23 g/L	[34]
7.	Crude glycerol and crustacean waste	Fermentation	<i>Yarrowia lipolytica</i>	30 °C, pH - 6	Lipase	[35]
8.	Glycerol	Batch fermentation	<i>Clostridium butyricum</i> DSP1	37 °C, pH- 7, 140 g/L	1,3-propandiol - 67 g/L	[36]
9.	Crude glycerol	Fermentation	<i>Schizochytrium limacinum</i>	19.2 °C, 100 g/L	Docosahexaenoic acid (DHA) - 4.91 /L	[37]

glycerol utilization to value added products including environmental aspects. There are numerous reported techniques for the transformation of crude glycerol into valuable products via biological conversion, catalytic conversion, enzymatic conversion and thermo chemical conversion [22]. Several varieties of important products and chemicals produced by processing glycerol are citric acid, DHA, GTBE, MTBE, esters, biopolymers, lactic acid, hydrogen, synthesis gas, etc.

2. Different technologies for glycerol conversion

The conventional conversion of glycerol mainly includes the reaction between glycerol and another molecule for the production of a new valuable chemical. The catalytic pathways include usage of crude glycerol as a chief feedstock using different types of catalysts which differ in their nature.

2.1. Biological conversion process

Biological routes utilize microorganisms and enzymes for the conversion glycerol either by aerobic or anaerobic metabolism. The conversion of glycerol into useful products with the aid of microbes such as fungi, microalgae, and bacteria is termed as biological conversion [23]. These biological reactions are carried out in a large bio-reactor under aerobic, anaerobic or micro aerobic conditions as per the demand of different microorganism [22]. It is realistically difficult to evaluate the bioconversion of glycerol due to the limited studies and commercial scale unit has not yet been reported, but one can get numerous products by bioconversion [24] and many other organic acids by fermentation as depicted in Fig. 3 and Table 3, respectively. The utility of the end products obtained from such conversion is another important factor that can lead to the commercialization of technology.

The principal utilities are:

- 1,3-propanediol (PDO) - It is an organic chemical obtained via anaerobic fermentation or micro-aerobic fermentation by bacteria. It is used in the solvents and adhesives [1,22].
- Lactic acid (2-Hydroxypropanoic acid) - It is produced by the microbial conversion of the glycerol i.e. via a fermentation process using several microorganisms. Lactic acid along with its salts and esters has the potential to use in the food, cosmetic, pharmaceutical and agricultural industries [25].
- Hydrogen - It is produced using crude glycerol through microbial fermentation. It is an energy carrier in fuel cells [1,26].

- Trehalose - It is a reducing sugar which is used as a stabilizer in therapeutic products [26].
- Glyceric acid (GA) - GA is an organic acid also named as 2,3-dihydroxy propionic acid. It is produced by bioconversion of glycerol. It is a multifunctional monomer [23].
- Citric acid - It is produced by fermentation. This organic acid is weakest in nature among all. It is an intermediate of tricarboxylic acid is widely used as a preservative in the food industry [23].
- Succinic acid - This dicarboxylic acid having four carbon atoms is produced by anaerobic metabolism pathway using different microorganisms. It is used as an intermediate for producing chemicals used in pharmaceutical and food industry [1,23].
- Docosahexaenoic acid (DHA) - Different uses of DHA includes sun tanning agent in cosmetic industry, the feedstock for pharmaceuticals and the main element for producing fine chemicals, synthesis of new biodegradable polymers [27].
- Eicosapentaenoic acid (EPA) - It is produced by fungal fermentation of glycerol [22].
- Polyhydroxyalkanoates (PHA) - PHA is a biopolymer produced by microbial fermentation of glycerol using several bacterial strains. Glycerol is a carbon source used for producing PHA [26].
- Biogas - It is produced by acidogenesis followed by methanogenesis in anaerobic digestion of glycerol [1].

A comparative technical assessment of the different biological conversion processes with respect to initial glycerol concentration, reaction temperature and reaction time leading to maximum yield of end products are depicted in Fig. 4(a), (b), and (c) [25,26,30,32–37]. From the Fig. 4(a), the maximum product concentration is 23.2 g/L corresponding to glycerol concentration of 20 g/L, as evident that higher substrate concentration inhibits the reactivity of organism, (b) maximum product concentration is 43.1 g/L at 42 °C as higher temperatures may not support the growth of organism [24,38] and (c) maximum product concentration is 41 g/L at 40.5 h as with the increase in time, there might be depletion of some factor(s) that adversely affect the reactivity of the enzyme/organism [35,38].

However, crude glycerol has many impurities in it that can have adverse impact on the growth of cell and product formation. They inhibit the metabolism of the organisms [39]. Sometimes, the presence of impurity in excess amount adheres the synthetic pathway of the product [39]. The presence of soap can cause negative effects on cell growth and lipid accumulation. It decreases motility of cells, impacts their orientation and changes their morphology [40]. The presence of methanol in the reaction

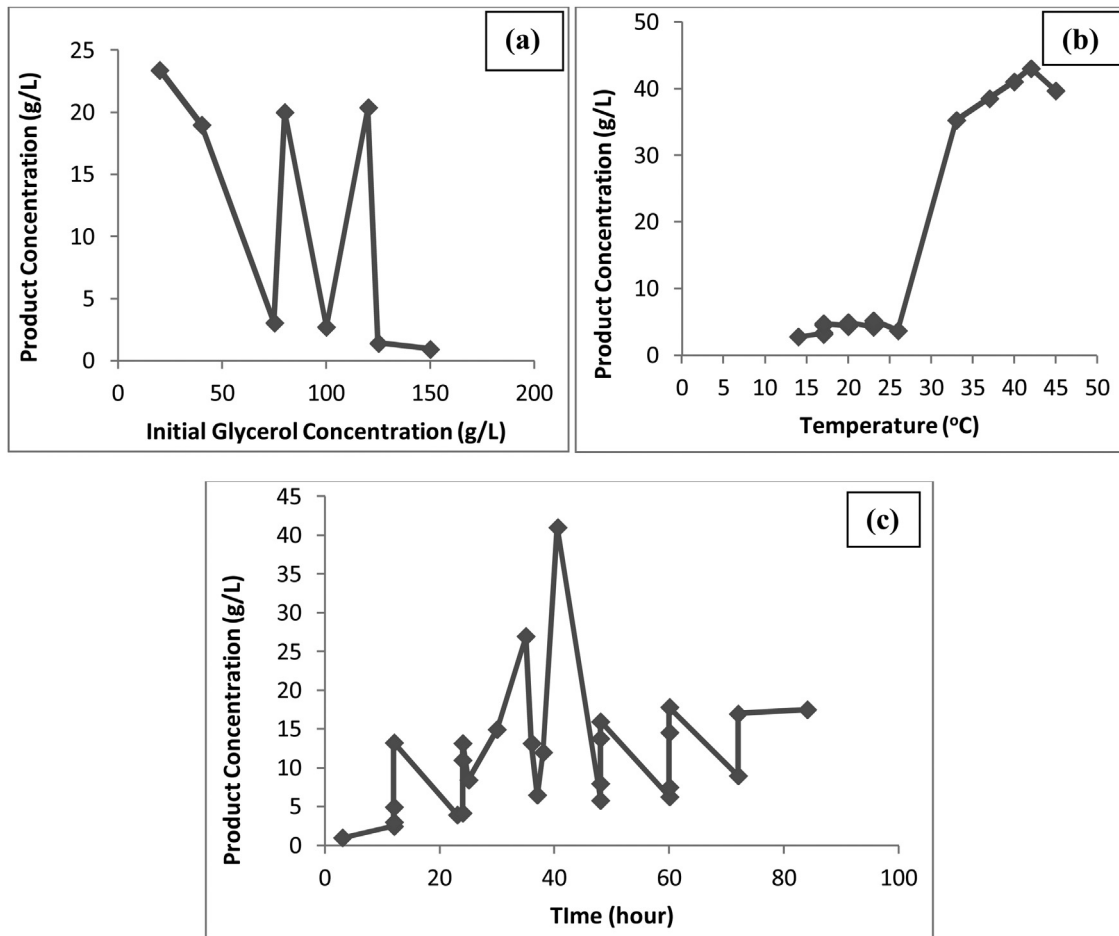


Fig. 4. Effect of (a) Initial Glycerol Concentration, (b) Temperature and (c) Time on bioconversion of glycerol.

mixture in excess amount decreases the lipid concentration due to the change in the membrane fluidity and activity of enzymes [40]. If salts are present in excess, they increase the production of carbohydrates and lipids in the cell [41]. Thus, one should focus on the development of micro-organism that can put up with the impurities present in crude glycerol or remove the impurities of crude glycerol either by evaporation or via acid treatment [40].

2.1.1. Challenges in the crude glycerol valorisation via biochemical routes

Though biochemical pathway is a promising route for the conversion of glycerol, but there are some challenges associated with it. Catalyst selectivity towards some products, the low reusability of the catalyst, harsh conditions for the catalysts, difficulty in separation of catalyst from the products formed and low product yield even after long reaction times are some of the challenges related to catalyst [42]. These are due to the impure nature of the crude glycerol. Therefore, it is a difficult task for industries for using crude glycerol directly along with its impurities. High cost of production and low stability of the enzymes produced are also obstacles that are challenging and feed stock availability [43,44]. Therefore, it is necessary to use the microorganisms that are tolerant to impurities in crude glycerol [45]. Detail aspects has been discussed in the subsequent sections.

2.2. Chemical conversion processes

Chemical conversion is the most common method studied for the conversion of glycerol. Various studies are available for the chemical transformation of glycerol [46–50]. Different useful products obtained from the chemical processes with various industrial applications via different pathways are listed below:

- Polyglycerols - Polymerization of glycerol produces polyglycerols. These are non-ionic surfactants used in the food, detergents and cosmetics industries [46].
- Solketal - Acetalization of glycerol provides solketal. It can also be obtained by condensation of glycerol. It is an effective oxygenated fuel additive, surfactant, and flavoring agent [47].
- Ethers - Etherification of glycerol produces methyl tert-butyl ether (MTBE), di-tert-butyl glycerol ether (DTBG), tri-tert-butyl glycerol ether (TTBG), ethyl tertiary butyl ether (ETBE) [48].
- Esters - Esterification of glycerol gives polyglycerol esters, acylated esters (mono-, di-, tri-acetin), Glyceryl diacetate (DAG), Glyceryl triacetate (TAG). These are used as oxygenated fuel additives [49].
- 1,3-propanediol - It is produced by dehydroxylation of glycerol. It is mainly used for the generation of polytrimethylene terephthalate (PIT) polymer [50]. The global production of 1,3-propanediol already reached to 45,300 tons and has been growing continuously [14].

- Ketals – Ketals are obtained from ketalisation of glycerol that are good ignition accelerators and anti-knock additives in combustion engines [51].
- Malleated glycerides – Malleation of glycerol produces malleated glycerides. These are the renewable precursors used for the production of plastics [22].
- Epichlorohydrin (ECH) - Epicerol process produces ECH. In Epicerol process, glycerol is reacted with a chlorinating agent like HCl. Mainly, epoxy resins are produced from ECH [52].
- Glycerol carbonate (GC) – GC can be synthesized from glycerol from various carboxylation sources. GC is used as an electrolyte and solvent in batteries [53].
- C8 chain ethers - Telomerisation of glycerol produces C8 chain ethers of glycerol, which are used as surfactants [52].

A schematic diagram for the conversion of crude glycerol to value-added products via chemical reaction pathways using different catalysts is depicted in Fig. 5. Some of the important products obtained by chemical conversion and the effect of various parameters on their yield are elaborated looking at the potential for industrial applications.

2.2.1. Epichlorohydrin

1-chloro-2,3-epoxy propane (ECH) is an organochlorine compound and an epoxide. Epoxy resins, elastomers, pesticides, synthetic glycerol, plasticizers, chlorohydrins rubbers, etc. are

some of the products that can be produced via ECH [7]. In the Asia-Pacific region, it is used for the production of wind turbine blades. It helps in the reinforcement of paper which is used for making tea bags. It is produced by the epicerol process. The epicerol process produces epichlorohydrin from the glycerol obtained from the biodiesel industry, while in the conventional process, ECH is produced from the reaction between propylene and chlorine. The reaction conditions reviewed from different literature for epichlorohydrin production from crude glycerol are tabulated in Table 4. The Dow Chemical Company produces ECH globally [7].

The effect of the molar ratio of the reactants used and the temperature of the reaction that affects the optimum yield of epichlorohydrin is presented in Fig. 6 based on literature survey [57–60]. From the Fig. 6(a) the maximum yield 74.6% of ECH is with 1.05 M ratio of reactants, as further increased in molar ratio lowered the yield of the product due to the internal rearrangement/ isomerization reaction of the reactants [59,61] and 6(b) the maximum yield of 73.8% is at 50 °C as further increasing the temperature caused occurrence of side reactions leading to the lower yield of product epichlorohydrin [59].

2.2.2. Glycerol ethers

Glycerol ethers such as MTBE, GTBE are derivatives of crude glycerol, an effective oxygenated fuel and octane promoters. The reaction of crude glycerol and olefins like isobutylene or tert-butyl alcohol along with catalysts is called etherification [62]. GTBE is



Fig. 5. Chemical reaction pathways for conversion of crude glycerol to value added products [[7,18,36,37,53–56].

Table 4
Production of Epichlorohydrin from glycerol.

S. No.	Reactants (Molar ratio)	Catalyst (amount)	Optimal Reaction condition(s)	Product(s)	Reference
1.	Glycerol:HCl gas	Hydrotalcite-derived mixed oxides of Al and Mg (HTIcs)	150 °C, 0.5 hour	ECH	[57]
2.	Glycerol:HCl	Carboxylic acids (8 % by moles)	100 °C, 3 hours,	ECH	[58]
3.	Dichloropropanol:NaOH (1.05:1)	-	50 °C, 15 seconds	ECH	[59]
4.	Glycerol:Hydrogen Chloride	Carboxylic acid (2 wt.%)	200 °C,4 hour	ECH	[60]

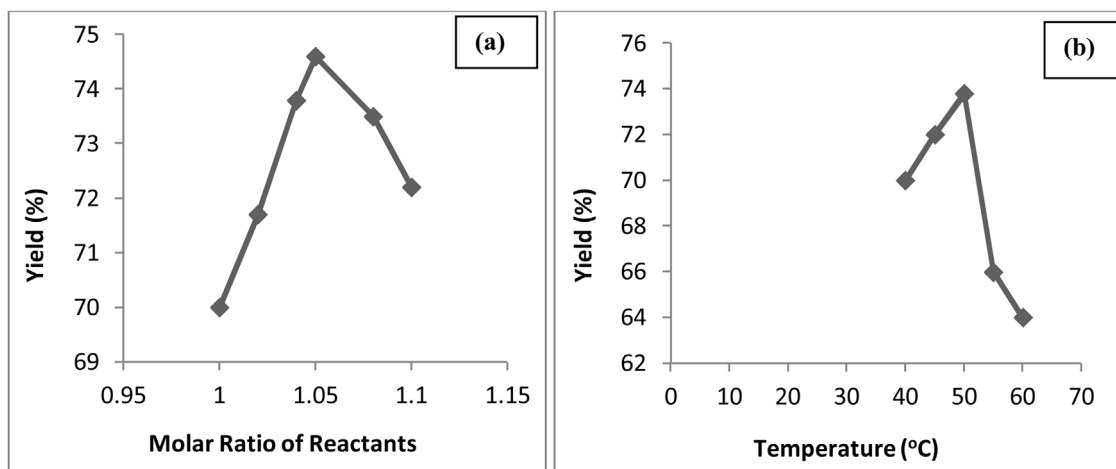


Fig. 6. Effect of (a) Molar ratio of Reactants and (b) Temperature on the production of epichlorohydrin.

Table 5
Different reaction conditions that affect the etherification reaction.

S. No.	Reactants(Molar Ratio)	Catalyst (amount)	Optimal Reaction condition(s)	Product(s)	Reference
1.	Glycerol: 1-Butene (1:4)	Amberlyst-15, S100, S200 (10 wt. %)	100 °C, 24 hours	MPGE, DPGE	[63]
2.	Glycerol: Ethanol (1:8.62)	Acid catalysts – H-beta Zeolite and CER (5 w/v %)	140 °C, 2 hours	Diethyl ether	[64]
3.	Glycerol: <i>tert</i> -Butanol (1:15)	TPA (Tungsto-phosphoric acid) (20 wt. %)	140 °C,120 minutes	ME, DE, TE	[48]
4.	Glycerol:Short chain alkyl alcohols (1:4)	Lewis acid catalyst (6.5 mol %)	150 °C, 24 hours	Monalkyl-glyceryl ethers	[65]
5.	Glycerol: <i>tert</i> -Butanol (1:4)	Amberlyst-36, Amberlyst-15 (5.5 wt. %)	82 °C, 8 hours	Glycerol alkyl ethers	[66]
6.	Glycerol: Isobutene (1:2)	Ambelyst-15 (0.011 wt. %)	92 °C, 480 minutes	GTBE	[67]
7.	Glycerol: <i>tert</i> -Butanol (1:4)	Amberlyst-15, H-BEA (5 wt. %)	90 °C, 180 minutes	Di-ethers	[68]

preferred to use in place of MTBE because MTBE is more toxic than GTBE. These fuel additives reduce the emission of particulates in the atmosphere. These are a group of solvents used in paints and cleaners. Different reaction conditions affecting the etherification reaction have been found out from the extensive literature survey and presented in Table 5.

The technical assessment for the optimum yield of glycerol ethers with varying temperature, catalyst amount, the molar ratio of the reactants and time has been presented in Fig. 7(a), (b), (c) and (d), respectively [63–68]. From Fig. 7(a), maximum 96 % conversion to glycerol ether is at 90 °C, because at lower temperature, catalyst favoured the by-product formation resulting lower yield of ethers [68,69]. In Fig. 7(b) maximum 96 % conversion is achieved using 5 wt. % and 7.5 wt. % catalyst as the amount of by-product appeared to level toward higher catalyst loadings [69]; (c) almost 100 % conversion is achieved using the molar ratio of 4–5 [63] and (d) One can nearly achieve a 100 % conversion as the reaction progresses with time to 72 h.

2.2.3. Polyglycerols

Polyglycerols like diglycerol, triglycerol, tetraglycerol, hexaglycerol, decaglycerol are used in cosmetics, lubricants, additives in polymers and nutritional. These can be produced via either by polymerization of glycerol or etherification of glycerol. Polyglycerols also have different biomedical applications. Different reaction conditions for the production of polyglycerol under different reaction conditions have been reviewed and presented in Table 6.

The technical assessment for optimum yield of polyglycerol using crude glycerol as feedstock have been worked out and presented in Fig. 8 to study the effect of temperature and time with respect to product yield [46,70–73]. From Fig. 8, 100 % conversion is achieved at the 200 °C within 8–9 hours of the reaction [72]. At lower temperatures, the conversion is very less and it again starts decreasing after 200 °C and 9 h. The higher the temperature sustained for the reaction, the more is the reaction conversion resulting in a decrease of hydroxyl groups in reaction products [74].

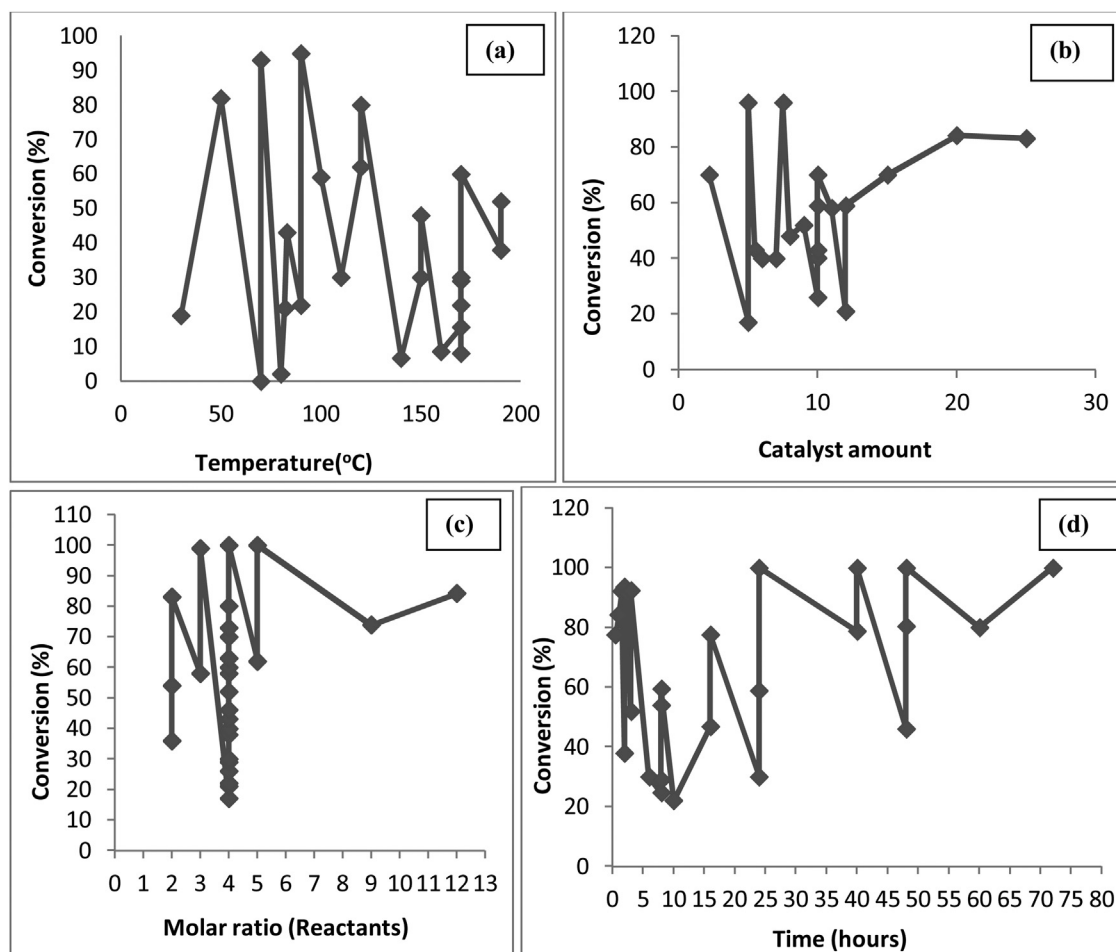


Fig. 7. Effect of (a) Temperature, (b) Catalyst amount, (c) Molar ratio and (d) Time on etherification of glycerol.

Table 6

Different reaction conditions for the production of polyglycerols.

S. No.	Reactants	Catalyst (amount)	Optimal reaction condition(s)	Product(s)	Reference
1.	Crude glycerol	No catalyst	250 °C, 60 min	Polyglycerol(di-, tri-, tetra-, penta-)	[46]
2.	Glycerol	MgAl mixed oxides	220 °C, 24 hour, pH-7.7	Diglycerol, Triglycerol	[70]
3.	Glycerol	LiOH (2 wt.%)	240 °C, 6 hour	Di-, tri-, Tetraglycerol	[71]
4.	Glycerol	mesoporous catalyst- MCM-41 type (2 wt.%)	260 °C	Diglycerol, Triglycerol	[72]
5.	Glycerol	MCM-41 type mesoporous catalysts (2 wt.%)	260 °C	Di-, tri-, Tetraglycerol	[73]

2.2.4. Glycerol esters

Esterification reaction produces glycerol esters in which crude glycerol reacts with carboxylic acid or acetic acid to produce polyglycerol; esters or DAG, TAG; mono-, di- and tri-esters of glycerol acetates. Different catalysts employed in this reaction are homogeneous catalysts (viz. sulfuric acid (H₂SO₄), Hydrochloric acid (HCl), p-toluene sulfonic acid (PTSA), methane sulfonic acid (MSA) and titanate), ion exchange resins, metal oxides (zinc oxide, ferrous oxide and stannous oxide), zeolites, hetero polyacids, mesoporous silica etc. [75]. Triacetin (TAG) is used in plasticizer of cellulosic polymers as a solvent. TAG and DAG are valuable bio-additives for liquid fuels. The commercial supplier of the TAG is to M/s. React Chem. These esters can also be used as emulsifiers. Monoacetin (MA) and Diacetin (DA) are main elements in the preparation of polyesters and cryogenics. The use of Triacetin (TA) is as a fuel additive for improving fuel quality and as a moisturizer in the Cosmetic Industry [76]. Extensive literature has been

reviewed in esterification process and factors affecting the reaction rate viz., reactant molar ratio, catalyst amount and optimal reaction conditions have been tabulated in Table 7.

Technical assessment for optimal glycerol ester production with respect to catalyst amount, temperature, molar ratio and time has been worked out and presented in Fig. 9(a), (b), (c), and (d), respectively [49,75–82]. From Fig. 9, (a) as the catalyst amount increases up to 3 wt.%, conversion increases and reaches to 100 % but using higher amounts of catalyst could lead to soap formation resulting lower concentrations of the product [83], (b) 100 % conversion is achieved at 115 °C and 120 °C as an increase in temperature favours the reaction by providing homogenization to the reaction mixture [75,84], (c) maximum 97 % conversion is achieved using 2 M ratios of the reactant to glycerol as it caused significant change in the reaction rate and excess molar ratio did not affect much on the conversion [85] and (d) 100 % conversion is achieved within 4–5 hours of reaction initiation.

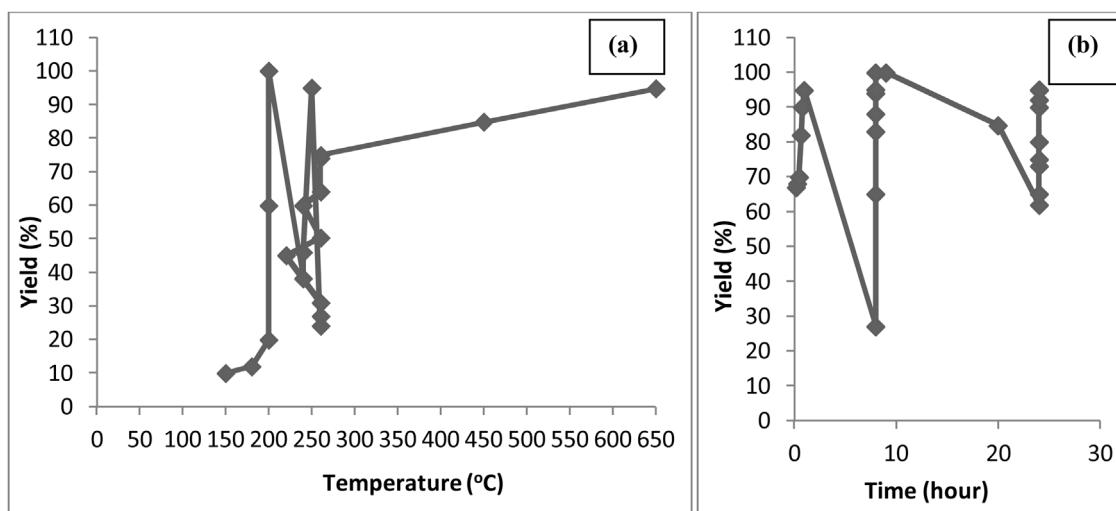


Fig. 8. Effect of (a) Temperature and (b) Time on production of polyglycerols.

Table 7

Different reaction conditions affecting the esterification reaction.

S.No.	Reactants(Molar ratio)	Catalyst (amount)	Optimal reaction condition(s)	Product(s)	Reference
1.	Glycerol:Oleic acid (1:4)	SO ₄ /ZrO ₂ (5 wt. %)	< 180 °C, 3–6 hours	GMO, GDO, GTO	[75]
2.	Glycerol:Palm oil oleic acid (1:1)	MESA (Methyl Ester Sulfonate Acid) (0.5 %)	240 °C, 180 minute	Glycerol ester	[77]
3.	Glycerol:Acetic acid (1:6)	A70, A15, STA/S11, TPS/S11 (5 wt.%)	105 °C, 4 hour	Monoacetin, Diacetin, Triacetin	[78]
4.	Glycerol:FA [mystric acid(tetra-decanoic), stearic acid, Oleic acid, Lauric acid] (1:2)	DMC (Fe-Zn double-metal cyanide) (7 wt.%)	180 °C, 8 hours	Glycerides (MG, DG, TG)	[79]
5.	Glycerol:Acetic acid (1:8)	Double-SO ₃ H functionalized ionic liquids (0.5 wt.%)	100 °C, 30 minutes	Monoacetin, Diacetin, Triacetin	[80]
6.	Glycerol:Olien (1:1)	Zinc oxide, ferrous oxide, stannous oxide (0.4 wt.%)	170 °C, 6 hours	Component for fuel	[81]
7.	Glycerol:Acetic acid (2g:20 ml)	PMo ₃ _NaUSY (dodecamolybdophosphoric acid(PMo) engaged in NaUSY Zeolite) (1.9 wt.%)	3 hour	Monoacetin, Diacetin, Triacetin	[82]
8.	Glycerol:Acetic acid (1:1)	H-beta Zeolite (HBZ)	100 °C, 1 bar pressure	Monoacetin	[76]
9.	Glycerol:Acetic acid (3:1)	Bio-derived carbon catalyst (2 wt.%)	110 °C, 3 hour	Monoacetin, Diacetin, Triacetin	[49]

2.3. Thermochemical conversion

Though thermal degradation or combustion of glycerol is a solution to consume a large amount of by-product of biodiesel industry named glycerol, but it leads to the emission of harmful toxic gases into the atmosphere which is harmful for the environment. Also, thermal degradation is not viable economically. Therefore, thermo chemical conversion of glycerol via pyrolysis, steam reforming, gasification, partial oxidation is more appropriate methods for converting glycerol into useful energy forms. Mainly three forms of products are produced by the process of pyrolysis or gasification of crude glycerol includes synthesis gas (CO + H₂), liquid products and char. Carbon monoxide, hydrogen, carbon dioxide, methane, and syngas are major products produced by thermochemical conversion [23].

2.3.1. Hydrogen

Hydrogen can be produced by partial oxidation, auto-thermal reforming, steam reforming, supercritical water reforming, aqueous-phase reforming, pyrolysis and catalytic steam reforming of glycerol. The utmost common approach for producing hydrogen is

reforming [86]. It is mainly used in fuel cells in the automotive industry for internal combustion engines. Different reaction conditions that affect the production of hydrogen via different catalytic processes along with various catalysts, optimal reaction conditions and molar ratio of reactants have been reviewed and tabulated in Table 8.

Factors affecting the rates of hydrogen production from crude glycerol have been worked out with respect to molar ratio, time and temperature as presented in Fig. 10(a), (b) and (c), respectively [87–93]. From the Fig. 10, (a) maximum 99 % of yield is obtained with molar ratio of 9 of the reactants to glycerol as increased molar ratio favoured reverse water gas shift reaction leading to H₂ formation [87]; (b) 100 % conversion is achieved at the temperature around 600 °C as hydrogen production via steam reforming occurs significantly only at higher temperatures. Also, catalytic activity could be enhanced at higher temperatures [87,94]. In Fig. 10(c), 99 % of yield is achieved after 8 h of reaction completion.

Higher the temperatures, greater will be the yield of hydrogen. The best temperature was reported as 625 °C and water to a glycerol ratio of 9:1 because under these conditions, methane production was lessened and carbon production was apprehensive [20].

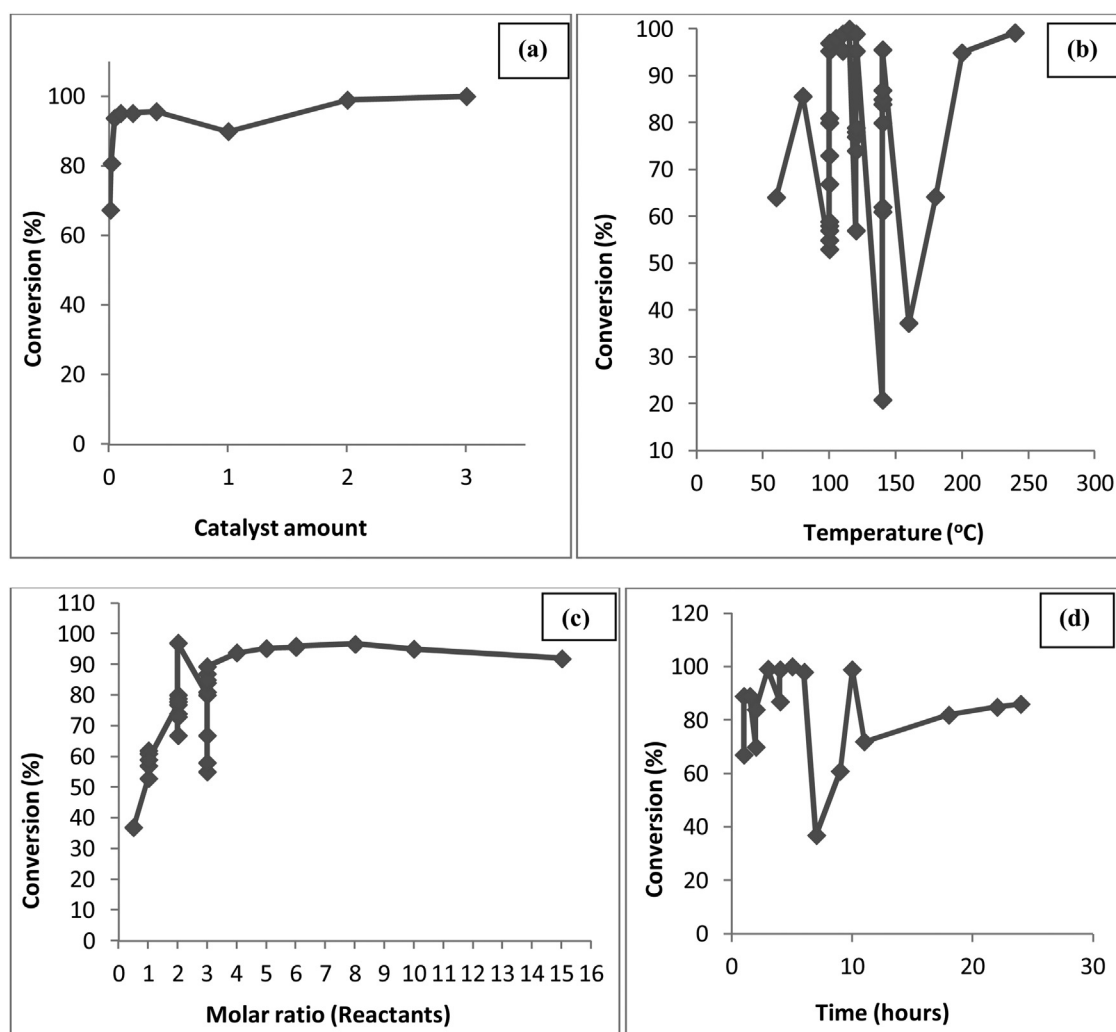


Fig. 9. Effect of (a) Catalyst amount, (b) Temperature, (c) Molar ratio and (d) Time.

Table 8

Different reaction conditions that affect the production of hydrogen.

S. No.	Reactants (Molar ratio)	Catalyst	Optimal reaction condition(s)	Product (s)	Reference
1.	Glycerol:Water (1:9)	Ni/SiO ₂	600 °C	Hydrogen	[87]
2.	10 vol.% glycerol solution	Ni/ZrO ₂	500 °C	Hydrogen	[88]
3.	Water:glycerol (12:1)	NiAl ₂ O ₄	600 °C	Hydrogen	[89]
4.	Concentrated glycerol solutions (50 wt. %)	Carbon-supported Pt-based bimetallic catalyst	300 °C	Hydrogen	[90]
5.	Water:glycerol (1:1)	-	227 °C	Hydrogen and synthesis gas	[91]
6.	Water:glycerol (12:1)	Ni/CeO ₂	600 °C	Hydrogen	[92]
7.	Steam:glycerol (9:1)	Co-Ni/HTIs catalyst	550 °C	Hydrogen	[93]

2.4. Catalytic conversion

The transformation of glycerol mainly by using catalysts either basic or acidic, homogeneously or heterogeneously is known as catalytic conversion [95]. Mostly, heterogeneous catalysts with high selectivity and conversion are preferred for the commercial conversion of glycerol due to their low cost operation and easy separation from the reaction mixture. Various catalytic conversion

processes are: Selective oxidation of glycerol produces dihydroxyacetone (DHA), glyceric acid (GA), tartronic acid (TA), mesoxalic acid (MA) a potent hypoglycemic agent, (hydroxy pyruvic acid, glycolic acid, glyoxylic acid, oxalic acid, glyceraldehyde); dehydration produces acrolein, acrylonitrile; oxidative polymerization gives polyketomalonnate (PKM); hydrogenolysis of glycerol produces propylene glycol, 1,2-propanediol which is used as a plasticizer and stabilizing agent; while glycerolysis produces

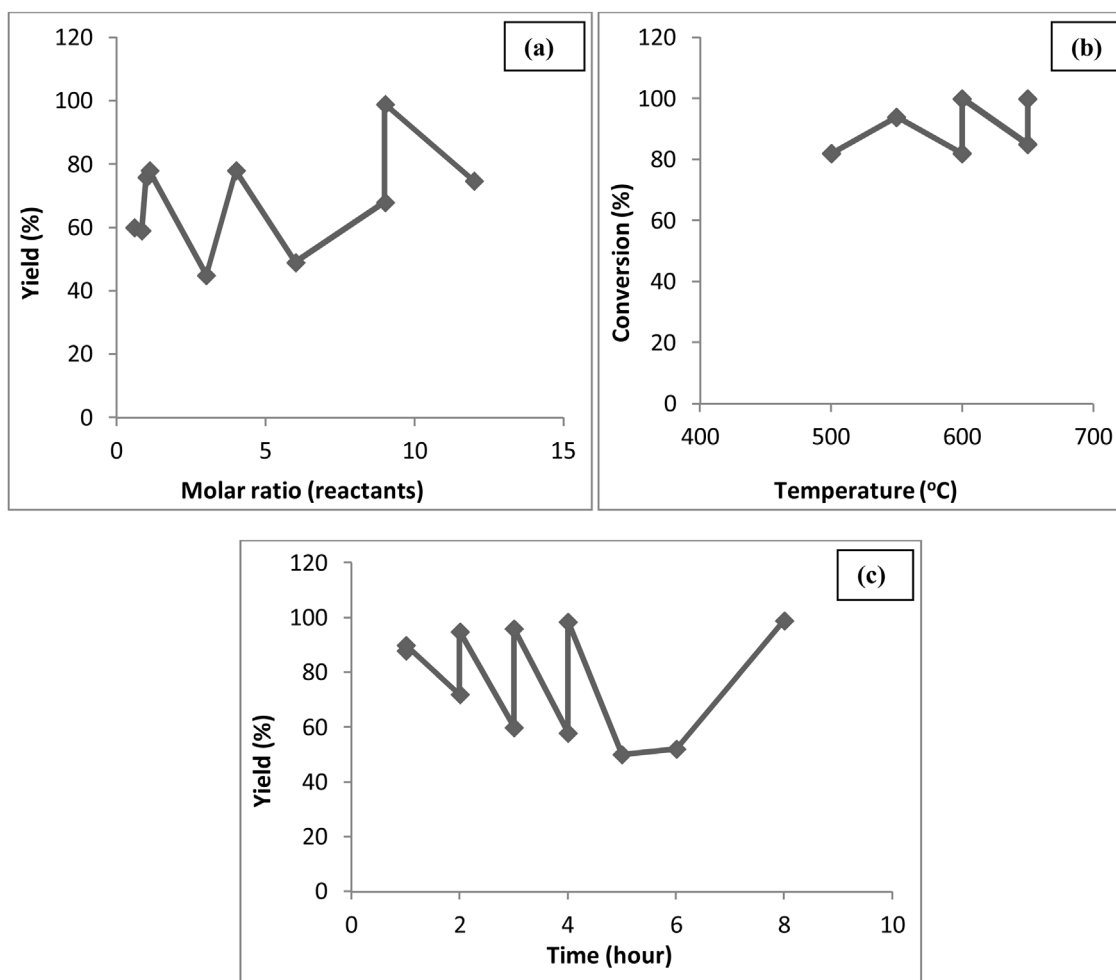


Fig. 10. Effect of (a) Molar ratio, (b) Temperature and (c) Time on production of hydrogen.

monoglycerides [7]. However, the reaction conditions for different conversions are different that resulted in products with varying composition. Catalytic reaction pathways for conversion of glycerol to its derivatives are as shown in Fig. 11.

2.4.1. Propylene glycol

Propylene glycol is also known as 1,2-propanediol. Hydrogenolysis of crude glycerol gives 1,2-PDO. It can also be produced by hydrolysis of propylene oxide and de-hydroxylation of glycerol. Propylene glycol is the substitute of ethylene glycol as ethylene glycol is toxic in nature. Propylene glycol is a good antifreeze and de-icing agent. Polyester resins, functional fluids, pharmaceuticals, foods, detergents, enamels and animal feeds are some of the applications of PG [14]. Oleo-chemical company, Oleon, collaborated with BASF commercially produces 1,2-PDO. The parameters that affect the propylene glycol production viz., the molar ratio of reactants, catalyst type and amount, optimal reaction conditions and the selectivity of the yield have been reviewed and presented in Table 9.

Technical assessment of the yield of the propylene glycol with varying catalyst, time and temperature has been presented in Fig. 12(a), (b) and (c) [107–117]. From the Fig. 12, conversion of glycerol increases with the increase in catalyst amount and it reaches maximum to 78.5 % with 20 wt. % of catalyst, higher concentration of which retarded the reaction [108] 100 % conversion was reportedly achieved at 230 °C, but after further increased in temperature decreased the conversion due to the

conversion of the reactants into lower alcohols instead of PG within 3 h reaction time [108,117].

2.4.2. Acrolein

Various catalysts, heterogeneous in nature, like zeolites and solid acid catalysts have been widely used for producing acrolein by glycerol dehydration. Dehydration is most important catalytic processes among all [118]. In heterogeneous acidic catalyzed reaction, the glycerol was evaporated, leaving behind the impurities in the liquid state and thus enhance the acrolein production. It is the most common intermediate required for the production of acrylic acid. Polymers used in pads and diapers with good absorbent properties are also produced from acrylic acid. The industrial scale production of acrolein has been yet not available. Different reaction conditions that affect the production of acrolein from glycerol is tabulated with respect to the molar concentration of reactants, catalyst types and amount, optimal reaction conditions and selectivity of the product yield as shown in Table 10.

Variation of product yield with respect to time and temperature has been presented in Fig. 13 [119–123]. From Fig. 13, (a) maximum 99 % of conversion is obtained at 325 °C [119] and (b) maximum of 98 % conversion is achieved at 1 h of reaction. However, after one hour with an increase in time, the conversion rate decreases to 9 %. 374 °C was reported as the critical temperature for the production of acrolein and at higher temperatures; there is a decrease in the product selectivity [124]. A complete conversion of glycerol with good selectivity (82 %) to acrolein was detected at 315 °C [125].

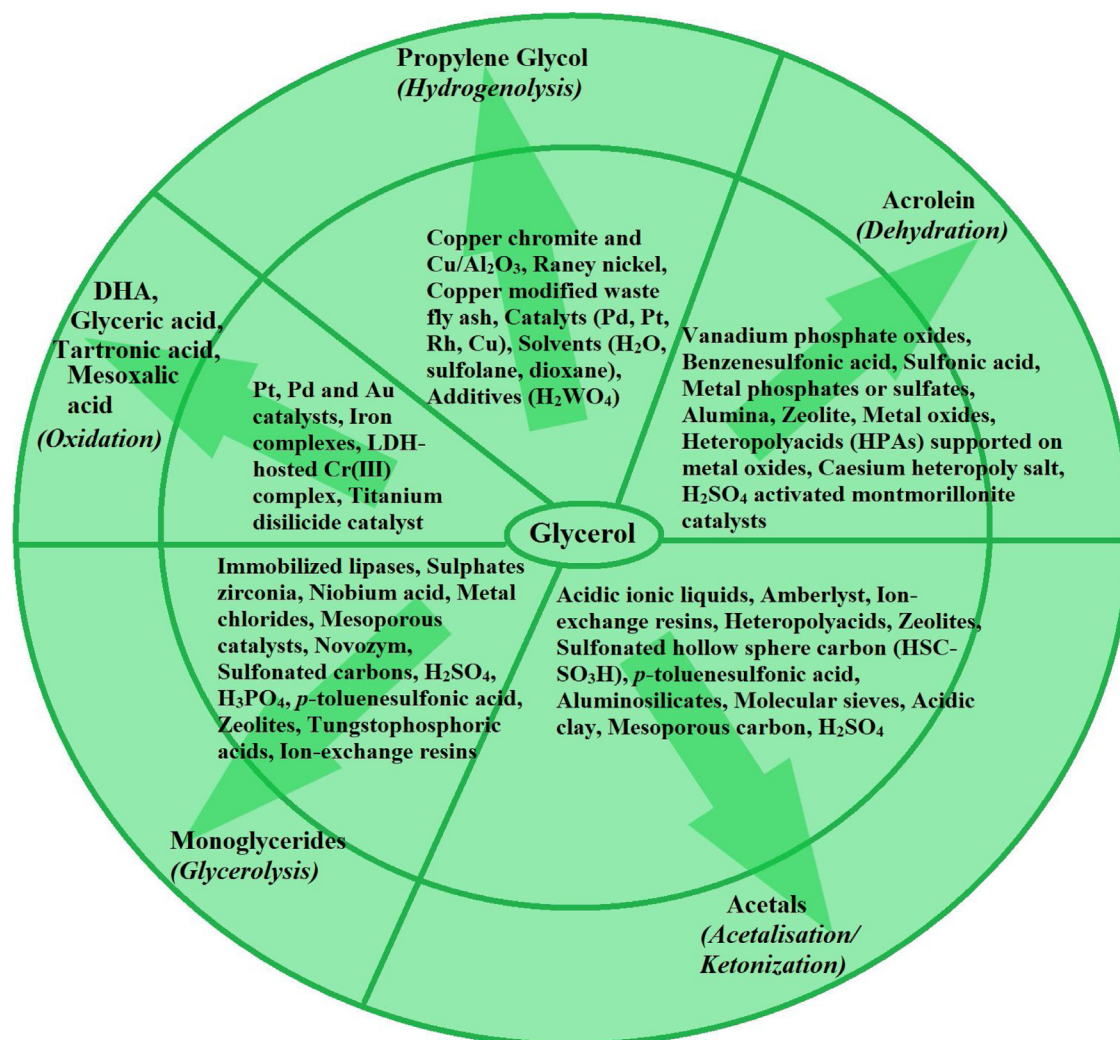


Fig. 11. Catalytic reaction pathways to convert glycerol into its derivatives [96–106].

Table 9

Different reaction conditions affecting production of propylene glycol.

S. No.	Reactants (Molar ratio)	Catalyst (amount)	Optimal reaction condition(s)	Product (s)	Reference
1.	Glycerol:Solvent (1:4)	Cu on acid treated fly ash (1 g)	220 °C, 5 hour, 52 bar	1,2-propanediol	[107]
2.	80 % glycerol solution	copper-chromite	200 °C, 24 hour, 200 psi	propylene glycol	[108]
3.	40 wt.% of aqueous glycerol solution	Cu/SiO ₂ IE (1 g)	200 °C, 15 bar, 7 hour	1,2-propanediol	[109]
4.	Glycerol in water	CuO-ZnO (5 mol%)	180 °C, 80 bar, 48 hour	1,3-propanediol, 1,2-propanediol	[110]
5.	Aqueous glycerol	Cu/Zn/Al – 5 wt. %	200 psig, 200 °C, 24 hour	Propylene Glycol	[111]
6.	H ₂ :Glycerol (2:1)	Mo and W catalysts (3 mL)	60 bar, 24 hours, 325 °C	1,2-propanediol	[112]
7.	1 wt.% glycerol solution	carbon-supported Ru and Pt catalysts	200 °C, 40 bar H ₂ , 5 hour	Propylene Glycol	[113]
8.	10 vol% glycerol solution	Cu-Ni catalysts (1.25 g)	250 °C, 40 bar, 6 hour	Propylene Glycol	[114]
9.	50 wt.% glycerol concentration	H-beta supported Ni-Zr catalyst (0.5 g)	600 psi, 10 hour, 200 °C	Propylene Glycol	[115]
10.	10 wt% aqueous solution of glycerol	B ₂ O ₃	250 °C, 6 MPa	1,2-Propanediol	[116]
11.	H ₂ /Glycerol (10:1)	Promoted Cu/Al ₂ O ₃ Catalyst (2 g) Copper over alumina and copper chromite (4 g)	230 °C, 14 bar, 4 hour	1,2-PDO	[117]

2.4.3. Dihydroxyacetone (DHA), glyceric acid (GA), tartronic acid (TA) and mesoxalic acid (MA)

These products can be derived from the oxidation of glycerol using catalyst. Glycerol oxidation is a complex reaction as compared to other catalytic conversion processes. Dihydroxyacetone (DHA) is

used broadly in the cosmetic industry as in sunless tanning products and industries of alcohol, wine, beverages, and dietary supplement. In oxidation, secondary hydroxyl groups are involved in the reaction process. GA is a compound that has no commercial application but is an intermediate for the synthesis of TA and MA. It is produced by the

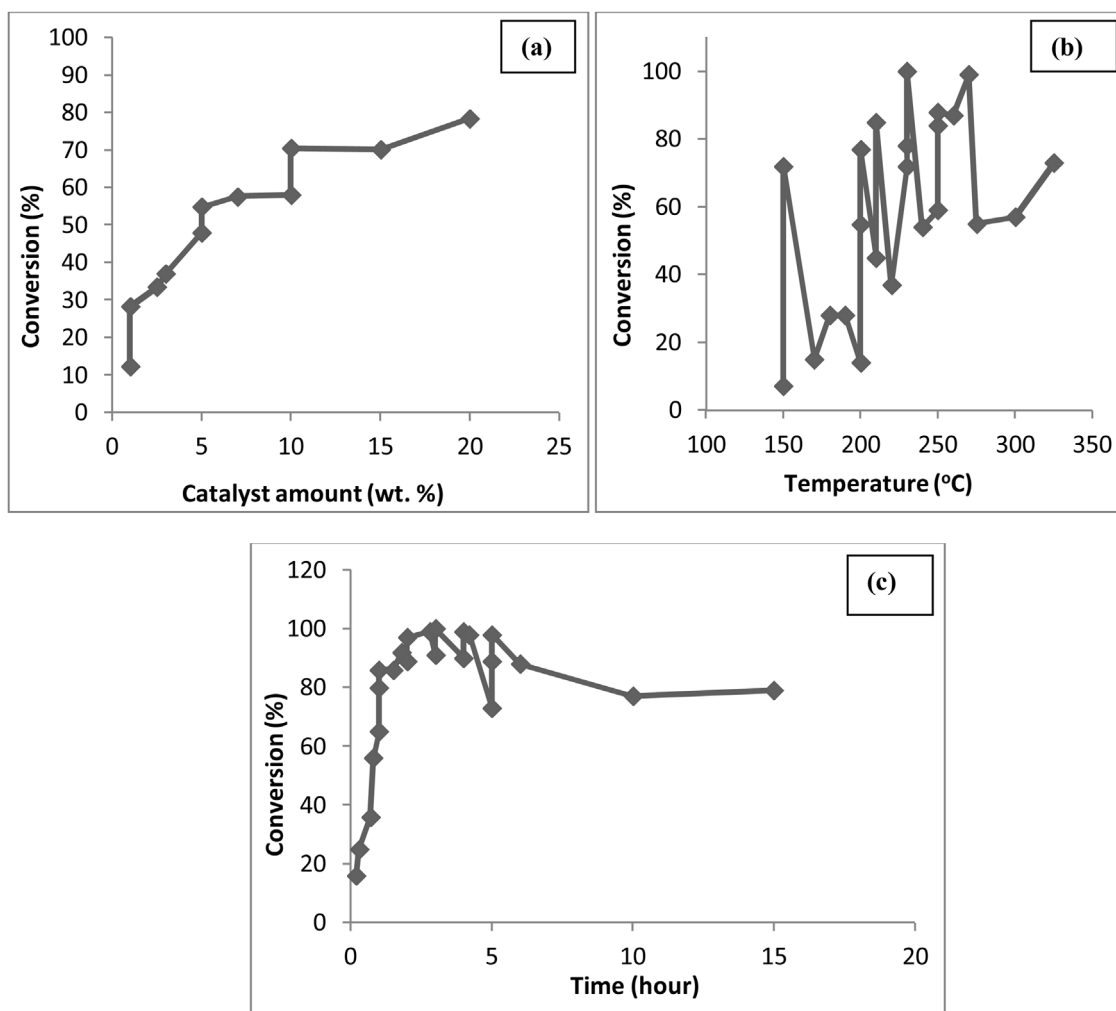


Fig. 12. Effect of (a) Catalyst amount, (b) Temperature and (c) Time on the hydrogenolysis of glycerol for the production of propylene glycol.

Table 10

Different reaction conditions affecting production of acrolein.

S. No.	Reactants (Molar ratio)	Catalyst (amount)	Optimal reaction conditions	Product (s)	Reference
1.	10 wt.% glycerol in water	Zirconium doped mesoporous silica catalysts (0.3 gm)	325 °C, 5 hour	Acrolein, acetaldehyde and acetol	[119]
2.	H ₂ :H ₂ O:glycerol (0.087:0.894:0.019)	Pd/LaY Zeolite (0.3 gm)	573 K	Acrolein and acetol	[120]
3.	Glycerol:Water (1:9)	Solid Acid-Base Catalyst	315 °C	Acrolein	[121]
4.	1% glycerol in water	zinc sulfate	360 °C, 60 second residence time	Acrolein	[122]
5.	20 % (w/w) glycerol solution	MUICaT-5 (1 g)	225 °C, 4 hour	Acrolein	[123]

oxidation of the primary hydroxyl group. TA is mainly used in the pharmaceutical area for the treatment of osteoporosis and obesity. It is produced from the oxidation of TA. The selectivity of the product formation with oxygenates has been tabulated in Table 11.

Effect of catalyst amount, the molar ratio of the reactants, temperature and time upon the oxidation of glycerol has been reviewed for optimal product yield and has been presented in Fig. 14(a), (b), (c) and (d), respectively [101–103,126–128]. From the Fig. 14, (a) maximum 86 % of conversion is achieved using 0.4 g of catalyst as higher amount of catalyst favoured oxidation at primary alcohols rather than oxidation to GLA or Glyceraldehyde [129] (b) maximum of 58.4 % conversion is obtained with 4 M ratio of the reactant to glycerol, (c) Maximum 85.5 % conversion is there at 60 °C but as temperature was increased,

the corresponding conversion was decreased, as further oxidation leads to the formation of GLA rather than DHA or Glyceraldehyde [102,129] and (d) 100 % conversion is achieved at 7 h of reaction.

2.4.4. Monoglycerides

Glycerides are lipid esters of the glycerol molecule and fatty acids. Monoglycerides can be synthesized by chemical processes such as glycerolysis, enzymatic synthesis, alcoholysis and esterification [130]. The main function of the glycerides is as a defoamer. Two types of glycerides are normally formed viz. (1) Neutral glycerides, (2) Phosphoglycerates [104]. Different reaction conditions that affect the production of glycerides have been presented in Table 12.

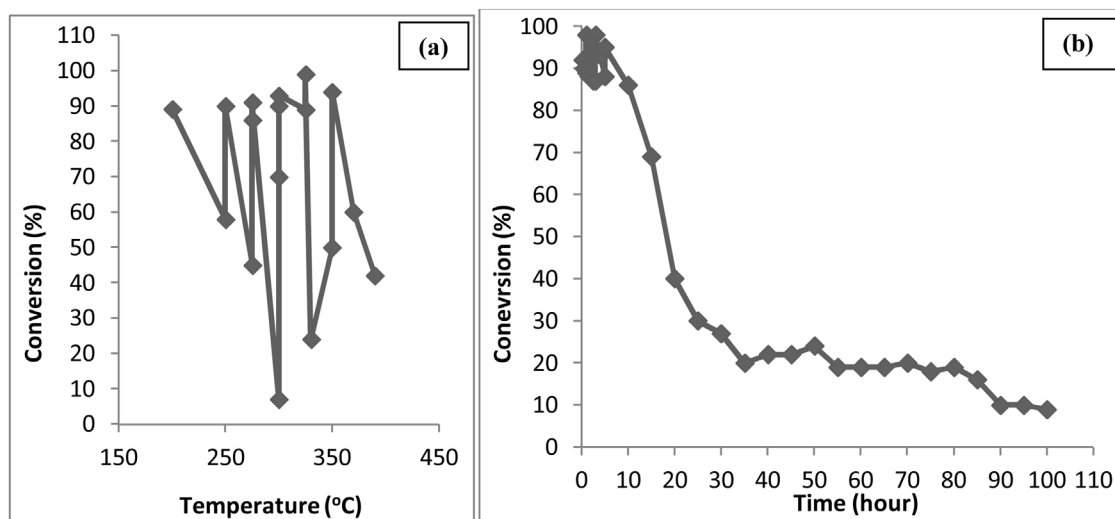


Fig. 13. Effect of (a) Temperature and (b) Time on the dehydration of glycerol.

Table 11

Different reaction conditions affecting the production of oxidation products.

S. No.	Reactants (Molar ratio)	Catalyst (amount)	Optimal reaction condition(s)	Product(s)	Reference
1.	H ₂ O ₂ :Glycerol (2.8:1)	Fe(BPA) ₂ (OTf) ₂	25 °C, 90 minutes	DHA	[101]
2.	Glycerol:Water	LDH-hosted Cr(III) complex (0.2 g)	60 °C, 6 hour	DHA	[102]
3.	NaOH:Glycerol (4:1)	Pt/Al ₂ O ₃ catalyst (0.5 gm)	60 °C, 3 hour	Products	[103]
4.	NaOH/Glycerol (2:1)	Gold catalysts supported on carbon materials (Au/G-SGT) (0.5 g)	60 °C, 1 hour	Glyceric acid, Oxalic acid	[126]
5.	Glycerol/Air	Platinum-Bismuth (5 wt. %)	50 °C, pH -2-4, 4 hour	DHA	[127]
6.	Glycerol:NaOH (1:2)	Gold catalyst supported on carbon (Au/C)	60 °C, 3 hour	Glyceric acid	[128]

Effect of catalyst amount, molar ratio, temperature and time upon the reaction rates glyceride formation have been presented in Fig. 15(a), (b), (c) and (d), respectively [79,104,105,131,132]. From Fig. 15, (a) conversion of glycerol increases as the amount of catalyst increases and reaches a maximum to 96 % with 7.5 wt. % catalyst [105], (b) 99 % of conversion is achieved with equimolar ratio, i.e. 1:1 of reactant to glycerol [105] (c) as the temperature increases the conversion of glycerol increases and reaches to 99 % with 260 °C as lower temperature gave lower yields of MG [105,118] and (d) 99 % of conversion is achieved at 4 h of reaction.

2.4.5. Acetals

The wide use of cyclic acetals is as flavours, disinfectants, surfactants, fuel additives for diesel fuels and reactants to produce enantiomerically pure compounds. These are also used for producing steroids, pharmaceuticals, and fragrances as reported [133]. Acetals are synthesized by acetalization/ketonization. Direct condensation reaction with aldehydes/ketones is called acetalization/ketonization while reaction with aldehyde by exchanging alcohol from another acetal is called trans-acetalization [106]. Different reaction conditions that affect the optimum production of acetals have been reviewed and Tabulated in Table 13.

The effect of time and molar ratio for the production of acetals have been reviewed and shown in Fig. 16 [106,133–138] respectively. From the Fig. 16, (a) the maximum yield of 97 % is obtained with a molar ratio of 1:2 i.e. using an excess of aldehyde and (b) the maximum yield of acetals is 79 % at 14 h. The acetalisation process can be best achieved at the possible mildest conditions even at low or room temperatures without solvent [139].

2.5. Environmental and economic aspects of different routes

Pure glycerol has its own applications in different industries for example pharmaceuticals, food, cosmetics, etc. But, directly using the impure glycerol in industries is bounded due to the presence of impurities. Moreover, these can not be disposed directly in the environment due to their hazardous nature. Therefore, different routes are proposed by researchers for converting glycerol into value-added derivatives. But, each process has its own merits and demerits from both environmental as well as economics point of view.

Hydrogen production by microbial fermentation is a good alternative because production of hydrogen by combustion generates only water as a byproduct which is highly reducing CO₂, NO_x, particulate and other emissions, usually accompanied with the fossil fuel usage [26]. Various micro-organisms that occur naturally and metabolically developed, are capable of utilizing crude glycerol. Thus, economically, microbial conversion is more efficient and safer. Though, DHA production from microbes provides cost effective and environment friendly solution as compared to the chemical conversion, still it cannot be applied on a wide platform. Chemically, multiple reactions took place in a living cell when catalyzed by enzymes and have found to work ex-vivo even when isolated under both natural as well as non-natural environmental conditions. Glycerol oxidation by isolating enzymes can, however, overcome these limitations. The limitations of isolated enzymes like high production cost, expensive redox co-factors, stability, solubility, reusability, workability etc. limits the broad use of them. Thus, solutions to overcome these limitations is protein immobilization [20]. Immobilization of biocatalysts facilitates the easy separation of the product from the reaction

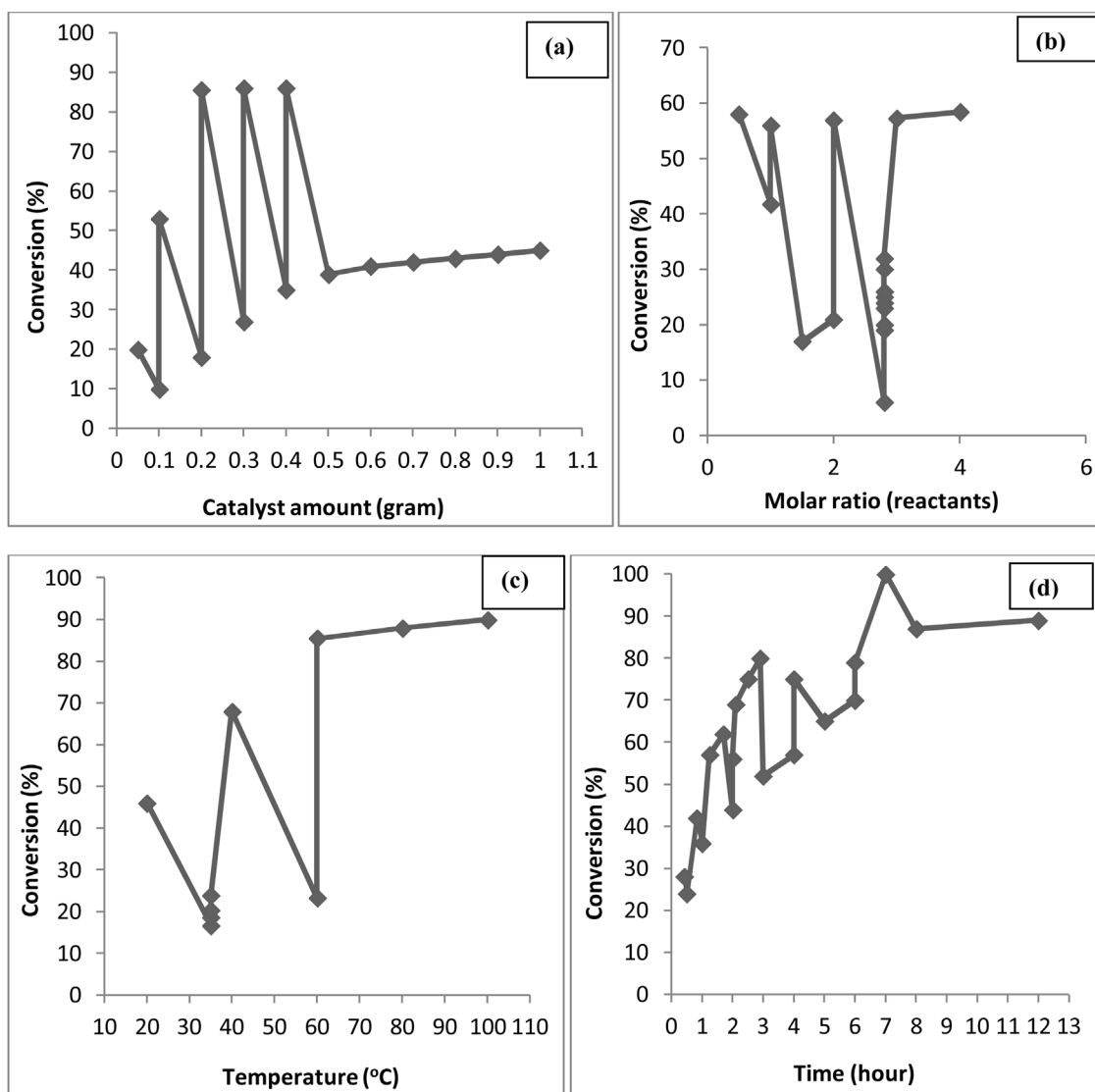


Fig. 14. Effect of (a) Catalyst amount, (b) Molar ratio, (c) Temperature and (d) Time on Oxidation of glycerol.

Table 12

Different reaction conditions affecting the production of glycerides.

S.No.	Reactants (molar ratio)	Catalyst (amount)	Optimal reaction condition(s)	Product(s)	Reference
1.	Glycerol:FA [myristic acid(tetra-decanoic), stearic acid, Oleic acid, Lauric acid] (1:2)	DMC (Fe-Zn double-metal cyanide) (7 wt. %)	180 °C, 8 hours	Glycerides (MG, DG, TG)	[79]
2.	Glycerol:Fatty acids (1:1)	ZnCl ₂ (0.3%)	195 °C, 500 rpm	Glycerides (mono-, di- and tri-)	[104]
3.	Glycerol:Stearin (2.5:1)	-	200 °C, 20 minutes,	Monoglycerides	[131]
4.	Glycerol:Refined oil (1:1)	NaOH (0.13 g for 50 g)	210 °C, 90 minutes	Monoglycerides	[132]
5.	Glycerol:Lauric acid (1:1)	Sulphonted carbon catalysts (0.5 g)	125 °C, 7–24 hour	Monoglycerides	[105]

mixture helps in the reduction of the process cost [140]. Less expensive, carried out at ambient temperature and pressure and simple reactors are some of the merits of the biological route [20]. Economically, the main drawback for hydrogen production is that at low temperature CH₄ formation is favored. Most commonly, hydrogen is produced by steam reforming (SR) in which water vapor reacts with glycerol in the presence of catalyst giving hydrogen, CO₂ and CO. Partial oxidation reforming (POR) is carried out exothermally under atmospheric pressure and its efficiency directly depends on the amount of oxygen entering the reaction

mixture. Auto-thermal reforming (ATR) is similar to POR but in ATR hydrogen produced is more. The compactness and efficiency of this system help in the development of autonomous units for small scale decentralized production. Gasification, liquid phase reforming (LPR) and pyrolysis, provides a huge potential as circular economy, but have many limitations [20]. Long fermentation times, oxygen requirement, high energy consumption for sterilization, high concentration of broth product and substrate concentration, inhibitory effects on the cell growth, their pathogenicity etc. limit their broad application. Isolated enzymes

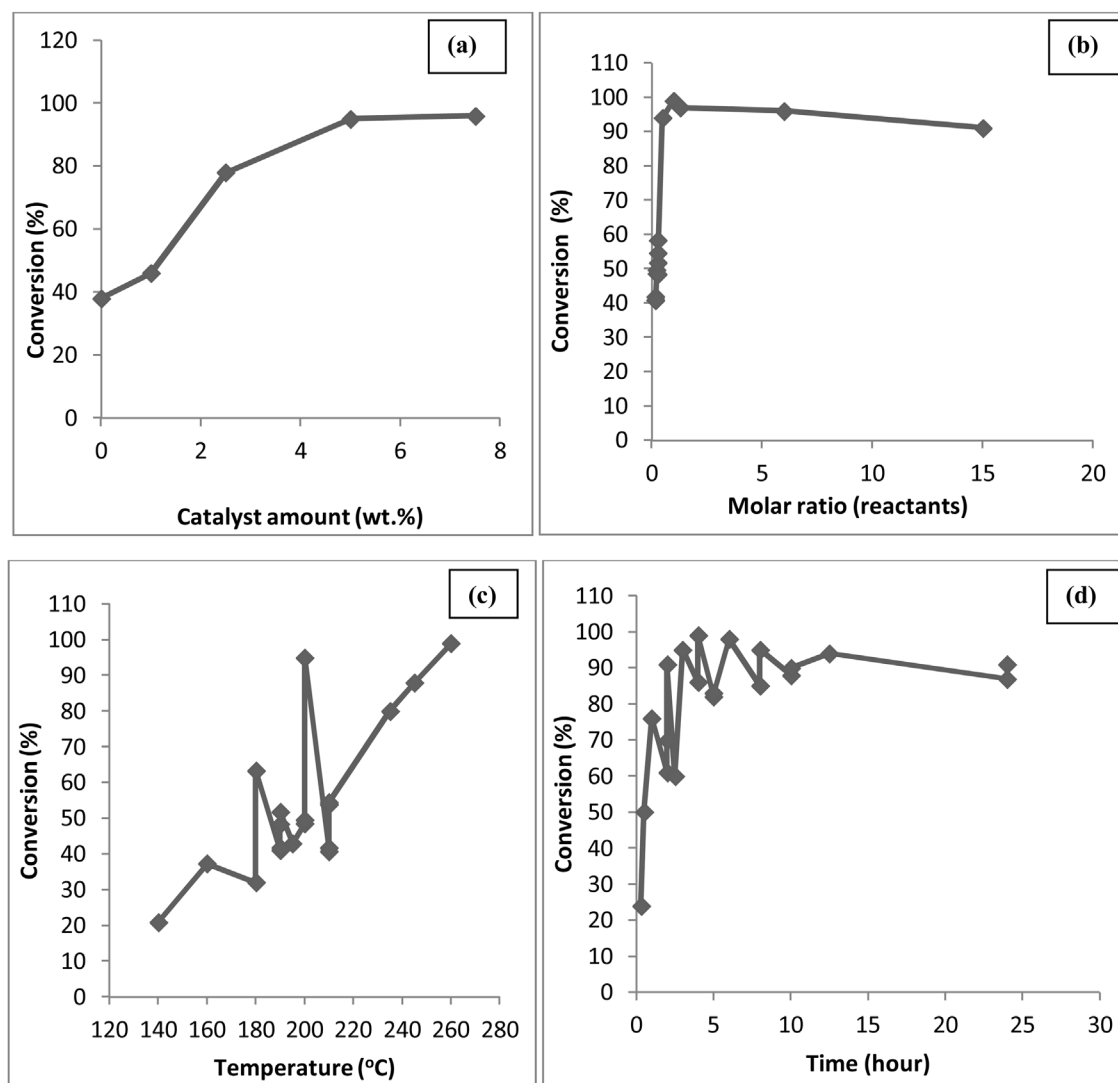


Fig. 15. Effect of (a) Catalyst amount, (b) Molar ratio, (c) Temperature and (d) Time on production of glycerides from glycerol.

Table 13

Different reaction conditions affecting the production of acetals.

S. No.	Molar ratio (reactants)	Catalyst (amount)	Optimal reaction condition(s)	Product(s)	Reference
1.	Glycerol: Benzaldehyde – 1.5:1	[BPy]HSO ₄ (0.88 g, 20 mol% based on PhCHO)	70 °C, 2 hour	Cyclic acetals	[133]
2.	Glycerol:DEE:Ethanol – 1:1:12	Amberlyst 15 - 1.0 kg/m ³	< 45 °C, 24 hour	6-membered acetal	[106]
3.	Glycerol: Benzaldehyde – 1:2	cationic acidic resin (270 mg)	120 °C, 2 hour	Cyclic acetals	[107]
4.	Glycerol:acetaldehyde	Amberlyst-15	30 °C, atmospheric pressure	Glycerol ethyl acetal (GEA)	[134]
5.	Glycerol:acetaldehyde – 3:1	Amberlyst 47 (2 wt. %)	40 °C	5-hydroxy-2-methyl-1,3 dioxane and 4-hydroxymethyl-2-methyl-1,3 dioxolane	[135]
6.	Glycerol: Benzaldehyde	Amberlyst-36 (0.5 g)		Cyclic acetals	[136]
7.	Glycerol: Aldehyde – 1:1.05	Amberlyst-15 (0.36 g)	85 °C, 48 h.	Cyclic acetals	[137]

can overcome these drawbacks which offers techno-economic and environmental advantages [20].

The potential environmental impacts of a process can be estimated by environmental factor assessments like Environmental Impact Assessment (EIA), Strategic Environmental Impact (SEA) and LCA (Life Cycle Assessment) [141]. The environmental issues caused by the low biodegradability of MTBE (pollution of aquifers

and toxicity) led its replacement by ETBE [16]. Three major aspects in which modification is needed for enhancing the economic feasibility are the usage of raw materials in the process, the production method and the byproducts [12]. With reactors, drawbacks are generally associated while scaling-up. So, continuous flow reactors for production of solketal using heterogeneous catalyst is an effective solution. It provides higher heat and mass

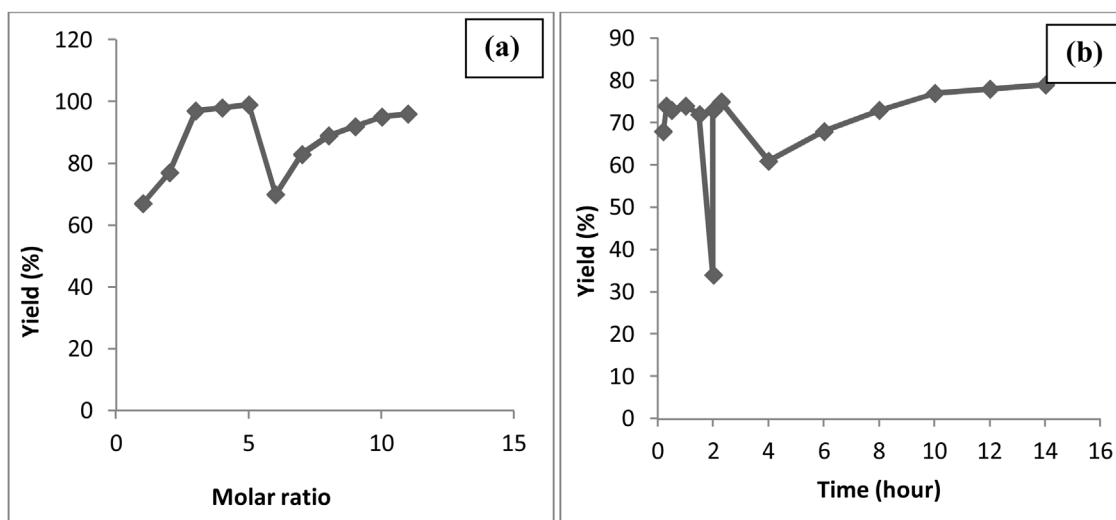


Fig. 16. Effect of (a) Molar ratio and (b) Time on production of acetals.

transfer efficiency, easy scaling-up giving with both environmental and economic advantages [12,142] (Table 14).

3. The commercialization of different products and economic viability

The current utility of the glycerol in the different chemical industry has been worked out and presented in Table 15.

1,3-propanediol (PDO) can either be produced by bio-conversion or chemical conversion of crude glycerol. PDO produced via bioprocess consumes 40 % less energy than petroleum-based PDO [143]. Commercially, PDO is produced from acrolein or ethylene oxide. PDO is commercially used to produce polyester named polytrimethylene terephthalate (PTT) [143]. The major application of PTT is as carpet fibers, apparel fibers, in film and packaging industry, in the ETP area. The unique properties of PTT make it a better product than other polymers. The current market estimation of 1,3-propanediol is at ca. 400 kt y⁻¹. In the near future, it is expected to raise by 10 % per year [144].

Lactic acid (LA) or 2-hydroxypropionic acid is the most commercially used hydroxycarboxylic acids [145]. It can be either produced biologically or chemically from crude glycerol. The prominent manufacturers of LA and PLA are Purac (Netherlands), Cargill, Henan Jindan Lactic acid Technology Co. Ltd. (China) uses dextrose derived from corn starch, Nature Works LLC (USA), Pyramid Bioplastics Guben GmbH (Germany) and Archer Daniels Midland Company (USA) [145,146]. The commercial use of lactic acid is in producing biodegradable thermostable polylactic acid (PLA), which is the major component of bioplastic polymers [146]. In 2012, this polymer was industrially produced in an amount of 180 Kton which will reach to 1Mton by 2020 [147]. In 2015, the estimated market size of lactic acid was 0.33 Mt and is predicted to

Table 15

Consumption of glycerol for different products and industries.

Sector	Consumption (%)
Food	8
Polyether	14
Personal Care	15
Pharmaceuticals	11
Alkyd Resins	8
Detergents	2
Explosives	2
Paper	1
Tobacco	4
Triacetin	10
Resale	15
Others	10-12

expand by ca. 10 % annually until 2025 [144]. Worldwide, acrylic acid is produced from propylene at the 6 Mt y⁻¹ scale and this figure is expected to increase to 8 Mt y⁻¹ by 2020. In 2015, the market volume of Glycerol Carbonate was ca. 200 kt y⁻¹ and is forecasted to reach ca. 3 Mt y⁻¹ in 2020 [144]. Sensiva SC50 (3-[(2-ethylhexyl)oxy]-1,2-propanediol), a glycerol ether, is produced in Industry from epichlorohydrin (ECH) by M/s Schulke and Mayr [8] which is used in the preparation of other functioned ethers. The KAO Co. reportedly involved in the production of glycerol isostearyl ether which is also commercially known as Penetol GE-IS [8].

Propylene glycol (PPG) is produced by M/s Shell and Lyondell, using acid or base catalysed ring opening reaction of propylene oxide and approximately 80,000 tonnes/annum is being produced [148,149]. Shell and Degussa patented the conversion process of PPG produced from petrochemicals [149,150]. The DuPont along with companies like Genencor and Tate & Lyle commercially

Table 14

Unit Production Cost and GHG emission for various conversion processes of crude glycerol.

S. No.	Process (Product name)	Unit production cost	GHG emission
1.	Bioconversion - hydrogen	3.49 \$/kg	Reduce emission by 7.66 kg CO ₂ eq.
2.	Chemical conversion - Epichlorohydrin	1,282 €/t	
3.	Chemical conversion - Esters	1.7 €/kg	-
4.	Catalytic conversion - Acrolein	1.13 EUR/kg	-
5.	Catalytic conversion - DHA	17.02 RMB/kg	-
6.	Catalytic conversion - Ketals/Acetals	12.29US\$/kg	-
7.	Catalytic conversion - Propylene glycol	1.326 \$/kg	CO ₂ emissions - 1.21 million tons of CO ₂ eq. Reduce the CO ₂ emissions by 2.79%

produces 1,3-propanediol via biological conversion of glycerol or glucose [149]. The production of Epichlorohydrin (ECH) via halogenation was commercialized by Solvay in France [150]. Epichlorohydrin obtained from glycerol-based dichloro-propanol is already being produced at the commercial level by M/s Solvay, Dow and Shandong Chemical Companies (Belgium), the United States and China [151]. ECH is a significant intermediate for the synthesis of epoxy resins. Biosuccinim has been producing from renewable carbon sources by Reverdia in Italy since 2012 [152], a joint venture between Corbion Purac and BASF built in 2013, a plant in Spain since 2013 and Myriant and Bioamber, operating in Canada and North America, respectively [152] with the capacity of 10 Kton/year. It turns out that an economic plant size is 26,000 t/yr [153].

Presently, the market of glycerol is likely to change unexpectedly and the price of glycerol market is directly dependent on the supply of biodiesel. An increase in biodiesel production can cause a fall in the price of glycerol. As expected, quantity of biodiesel is hiked by 5 billion liters, reaching a total of ca. 40 billion litres by 2020 [154]. It was projected in 2006 that by 2020, glycerol production would be 6 times more than the demand. The global production of biodiesel will rise by 70 %. Due to such a huge increment in biodiesel production, the commercial price of glycerol falls almost to half from 2004 to 2011 [139]. Glycerol supply is reliant on the performance of the biodiesel market. The surplus of glycerol present in the market raises the question on the sustainable use of the biodiesel [155]. Though one can use pure glycerol for the production of many chemicals with industrial applications, the purification of crude glycerol is costly and economically not viable. Hence, the discovery of new applications and the expansion of the glycerol market will help in growing up the biorefinery at large. The use of recent inventions in the traditional utilization of glycerol will help in the expansion of the glycerol market. Also, new geographical markets should appear as because the developing countries experience improvement in their standard of living with direct or indirect involvement in biorefinery set up, based on vegetable oil. The economic viability of the processes is assessed in terms of net profit, return on investment (ROI), net present value (NPV) and break-even price [155]. For the evaluation of a project, the economic model used is the discounted cash-flow rate of return (DCFROR) which considers the time value money. This model enables to calculate the net present value (NPV) and the minimum selling price by setting a target discount rate [152]. The production cost of a product includes the manufacturing costs and the management costs, which further comprises of raw materials cost, direct and indirect labor, utilities, supplies, maintenance, laboratory, equipment depreciation, insurance and taxes [154]. The total invested capital includes tied-up capital and working capital [154]. The tied-up capital constitutes the direct capital, building expenses, research, and start up and other expenses items. Direct capital is calculated as the sum between the fixed capital and the honoraries [154]. The economic analysis includes the estimation of capital expenditure (CAPEX), annual capital cost (CACC), annual operating cost (CAOC), and revenue (R) [141]. A profitable venture is indicated by positive NPV, a zero NPV indicates the venture breaks even, and loss of a venture is indicated by negative NPV [141] as depicted in (1), (2) and (3).

- (1) $PV = FV / \{(1 + r)^n\}$ where, PV = Present value, FV = Future value, r = interest rate and n is the number of years of investment.
- (2) $NPV = \sum_{n=0}^{n=TPL} Cf / \{(1 + r)^n\}$ where, NPV = Net Present Value, Cf = Cash Flow, n = year, r = discount rate, TPL = plant life
- (3) Cash Flow = Revenue – (Annual operating cost + Annual capital cost)

3.1. Factors affecting the cost and production of different products

The production cost of biodiesel increases by \$0.021/L for every \$0.22/kg cause reduction in glycerol selling price [26]. Mixed cultures have been applied under non sterile conditions to minimize the production cost of 1,3-propanediol [20]. The coproduction of succinic acid with the total production cost (TPC) is round about 4.37 M\$/y [156]. TPC obtained in the production of succinic acid is approximately 3.86 M\$/y, being within a range of variation of less than 12 % from the TPC reported in Vlysidis et al. [152]. The production cost of epichlorohydrin is estimated to be 36 M€/yr [153]. The cost of a unit of ECH production is 1,282 €/t according to the capacity of 26, 540 t/yr of the plant. The selling price of ECH is 1,976.22 €/t in 2014 [153]. The tied-up capital adds up to 55.6 M€. The lower price of glycerol as compared to sugars is a key to lower the material costs [144].

3.2. Barriers in the commercialization of different products

The high price of pure glycerol limits the economic viability of the glycerol transformation [20]. PHA's represent naturally occurring bio-polymers produced via fermentation from several bacterial strains using the mineral medium named glycerol. *Halomonas* sp. SA8, a soil bacteria from Finnish soils and sediments have been reported for the intracellular accumulation of PHA (56 %). The produced PHA, identified as a PHB homopolymer, shows a great hindrance in the commercialised production of PHA's [26]. The possible use of these organisms commercially could be limited due to many reasons such as pathogenicity, strict anaerobic conditions and impurities present in the substrate that may affect conversion rates [20]. The production of 1,3-propanediol by chemical synthesis involves the use of expensive catalysts, high pressure conditions and production of toxic intermediates that are not environmentally friendly which prevents the commercialisation of the process [20]. Similarly, the slow consumption rates of glycerol and unfavorable productivities cause the process unsuitable for industrialization, though fermentation of glycerol provides better yield of ethanol.

In most of the studies, the use of batch reactor for the production of 1,2-propanediol through hydrogenolysis, is a barrier for the commercialisation of the production process [116]. Though, there is wide usage of this process at large scale, but has some undesirable features mainly low yield [153]. Also, in chlorination and hypochlorination steps, it is expensive to dispose of the chlorinated organic, produced by the conventional production along with the waste water [153]. The toxic oxidants used in the oxidation process makes difficult to control the reaction pathway. Thus, bio-conversion is superior approach, but lower conversion and tedious extraction process limits its commercialisation [157]. Therefore, electrochemical oxidation is a green approach that overcomes all the limitations associated with oxidation of glycerol [157]. The main environment drawback of the Lactic acid production is the co-production of gypsum, whose disposal is a harmful [147]. The existence of bulky compounds leads to the deposition of carbon and coke, which is a barrier for the reforming of crude glycerol. This unreasonable coking leads to catalyst inactivation and lowers the yield of hydrogen [11]. Some systems need high running cost production along with high pressure, temperature, long reaction time, hinder the possible commercialisation [158]. Thus, to make the processes environmental and competitive, researchers should focus on the evolution of the catalysts with enhanced ability [144].

4. Conclusion and recommendations

The worldwide vast production of glycerol due to the biodiesel production stimulates the researchers to develop new commercially viable technologies. It helps in the valorisation of glycerol so that the glycerol glut does not alter the sustainability of the biodiesel industry, i.e. contribute positively to the environmental economy of the biodiesel industry. Thus, make this industry a profitable one and can lead to the biorefinery. There can be a change in the market scenario of biofuels due to the development of new technologies involving glycerine-to-methanol and glycerine-to-ethanol production pathway. Use of multi-step pathways and hybrid catalysts along with continuous flow reactor should be investigated on laboratory scale that can further be adapted on an industrial level. For addressing the issue of glycerol, various researchers have reported different processes for the conversion of glycerol into valuable chemicals such as PDO, acetate, butyrate, n-butanol, ethanol, lactic acid, hydrogen, propionic acid, trihalose, glyceric acid, citric acid, succinic acid, DHA, EPA, PHA, biogas, polyglycerols, solketal, MTBE, TTBG, ETBE, DAG, TAG, DCP, ECH, glycerol carbonate, glycerol esters, hydrogen, TA, MA, propylene glycol, monoglycerides, acrolein etc. All these chemicals have definite commercial value that can contribute to the biodiesel economy.

The recent advancement in the technology and commercial utilization of crude glycerol for value-added product formulation clearly establish the fact that crude glycerol can play a vital role in the realization of bio-refining industry based on oilseeds.

Declaration of Competing Interest

None.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.btre.2020.e00487>.

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