Assessment of crude glycerol utilization for sustainable development of biorefineries

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9.1 Introduction

At present, ~90% of the world's energy prerequisite is met through the use of non-renewable fossil fuels, such as coal, oil shale petroleum, natural gas, and bitumens (Rodrigues et al., 2017; Poschl et al., 2010; Srirangan et al., 2012). Among these resources, particularly oil and natural gas are the most imperative feedstocks for the production of fine and commodity chemicals (Liu et al., 2010). Nevertheless, the unhampered use of fossil fuels is considered unsustainable due to the determinate supply and an unequal distribution of natural reserves, coupled with climate change resulting from increasing greenhouse gas emissions (Tan et al., 2013).

All the previously mentioned factors have provoked researchers to have a great interest in finding the substitute biofuels. A substitute fuel should be produced in an eco-friendly manner inadequate amount to solve the energy crisis and to replace the existing resource economically (Owusu and Sarkodie, 2016; Indu et al., 2018). Biodiesel was well received among other biofuels and utilized in almost everywhere in the world for its eco-friendly nature, renewability and biodegradability, and non-toxic characteristics when compared with conservative diesel (Shi et al., 2013).

Biodiesel has the characteristics of petroleum diesel and hence its blend can be used in the transportation sector. Greater use of biodiesel can reduce greenhouse gas emission and other pollutants (Tang et al., 2013; Nguyen et al., 2010). Numerous procedures, such as pyrolysis, supercritical fluid, and transesterification process, have been established for biodiesel production. Transesterification process is carried out with different kinds of feedstocks (vegetable oil, animal fat, algae, and waste cooking oil). When compared with other methods, transesterification process is the most common method used for biodiesel production. Crude is generated as a byproduct during the transesterification process of biodiesel production (Chozhavendhan et al., 2018a; Bet-Moushoul et al., 2016).

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In general, 10% of the crude glycerol is produced as a major byproduct during the production of biodiesel (Chozhavendhan et al., 2016a; Pfromm et al., 2010). The rise of biodiesel production leading to increased production of crude glycerol with copious impurities has resulted in fallen prices for refined and crude glycerol (Quispe et al., 2013). A fundamental question soon arises: what can be done with the crude glycerol? or how could exploit the crude glycerol or convert the low-value crude glycerol into value-added chemicals (Ardi et al., 2015)?

A biorefinery is a network of facilities, which integrates biomass conversion processes and equipment to produce biofuels, energy, and chemicals from biomass or from waste to wealth. The concept of biorefineries is applied to biofuel industries in order to convert or utilize the crude glycerol for the production of 12 major platform chemicals and that could be the major output of integrated biorefinery concept. This, in turn, helps to improve economic feasibility and sustainable development of bio-based industries (Chen et al., 2013; Cherubini, 2010; Cherubini and Ulgiati 2010).

9.1.1 Characteristics of crude glycerol

Biodiesel is generally produced by the transesterification reaction of triglycerides (oils/fats) with alcohols in the presence of a catalyst. During this production process, biodiesel is settled in the upper phase and the rest glycerol settles in the lower phase due to the difference in densities and polarities (Tan et al., 2013). Glycerol obtained from the biodiesel production process is known as crude glycerol and usually presents as highly viscous, alkaline pH, and dark brown in color (Chozhavendhan et al., 2016b). Crude glycerol comprises a mixture of compound usually consist of water, ash, soap, methanol, etc. (Chozhavendhan et al., 2018b). The purity of glycerol may vary from 20% to 80% depending upon the raw material, catalytic process, and purification process.

Glycerol is available commercially in three different forms, namely, (1) crude glycerol, (2) purified or refined glycerol, and (3) commercially synthesized glycerol (Vivek et al., 2017). Glycerol is a versatile compound because of its unique physical and chemical properties. It is highly viscous, hygroscopic liquid with high boiling point and more compatible with many compounds (Zhou et al., 2008). In general, glycerol is capable of reacting with alcohol since chemically it is known as trihydric alcohol. The three hydrophilic hydroxyl groups in glycerol are responsible for its solubility in water and its hygroscopic nature. Therefore crude glycerol can be directly fed as a substrate or feedstock for the production of high-value chemicals, which increases the market value of glycerol and also helps the establishment new employment offers for the new production plants for the conversion of glycerol (Hu et al., 2012). It also finds its application in green refinery process as it is used as a renewable source for biodegradable products (Ayoub and Abdullah, 2012).

9.2 The market scenario of glycerol

Glycerol is produced in two ways: natural glycerin (as a byproduct of soap production or fatty acid methyl esters, such as biodiesel) and synthetic glycerol

(Quispe et al., 2013). In 1846 Soberero invented nitroglycerin, a prominent explosive raw material, which is manufactured from glycerol. Later, glycerol manufactures were established in many nations in Europe, Japan, Russia, and the United States. The boom of biodiesel industries results in increased production of glycerol. Until 2003 the global ultimatum of glycerol was encountered by petrochemical and soap industries. Between 2008 and 2012, global production of glycerol was increased by 9.3% per year which slashed down the price of glycerol. It is estimated that the growth of glycerol demand will be 3.5% per year in 2022. As we know, glycerol is a multipurpose renewable raw material with two large emergence consumer markets. The first one is an already existing market which demands high purity and specifications for the use in food and pharmaceutical industries. The second is the utilization of crude glycerol in the conversion of high-value products and chemical intermediates. Thus market of crude glycerol is characterized by the higher volume of products with lower quality of the substrate. Asia-Pacific is acknowledged as the principal consumer of glycerol with approximately 36% of the world's glycerol production (Kong et al., 2016).

9.3 Refining of crude glycerol

During biodiesel production along with catalyst, an excess amount of methanol is used to convert more fat and oil into biodiesel (Sdrula, 2010). As a result the glycerol phase has the tendencies to contain copious impurities, such as soap, methanol, water, and salts, during the separation of biodiesel (Xu et al., 2012). Hence, crude glycerol cannot be acquiescently used in food or pharmaceutical industries, and also without proper treatment, it cannot be directly disposed to the environment (Escapa et al., 2009; Gervasio et al., 2009). Alternatively, the crude glycerol from biodiesel manufacturing plant can be used as a cheap substrate for production of different valuable products. However, impurities present in crude glycerol restrict its use in food and other industries. Therefore purification of crude glycerol is required, in order to meet the requirements of prevailing and emergent uses (Yang et al., 2012). A sequence or combination of treatment, such as distillation, acidification, phase separation, adsorption with activated carbon, membrane filtration, and ion exchange adsorption, could achieve the maximum purity glycerol of about 97.5%. Various stages of glycerol purification and its application were displayed in Fig. 9.1.

9.3.1 Need for simple purification process

The simple purification process comprises a few processes based on the need and quality of crude glycerol. Usually, the high yield of biodiesel is achieved in biodiesel production process in utilizing excess amount methanol transesterification process. The unreacted excess methanol starts settled at crude glycerol phase as a major impurity and which may inhibit the growth of the microorganism. The

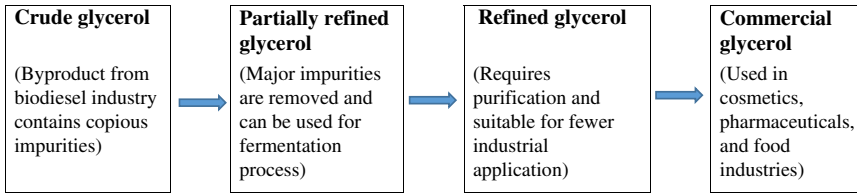


Figure 9.1 Improvement of glycerol concentration and its utilization.

methanol can have deleterious effects on the environment and public health. The boiling point of methanol is 65°C and hence it can be removed by controlled simple distillation process in large-scale process (Sarma et al., 2012). Denver et al. (2008) have suggested that crude glycerol can be autoclaved at 121°C at 15 min to remove a significant amount of methanol before using as a feedstock for bioconversion. Thus for the economic assessment, the retrieved methanol can be reused again in the transesterification process (Chozhavendhan et al., 2017; Bohon et al., 2001).

In the next step, removal of nonglycerol substance (soap) is carried out by precipitation process on adjusting the pH from alkaline to acidic condition (Shannon et al., 2011). Due to the use of base catalyst in the transesterification process of biodiesel production, pH of the crude glycerol is highly alkaline in condition. The alkaline pH may have a deleterious effect on microbial growth. pH of the glycerol sample is altered in order to convert the soluble soap into insoluble fatty acid and to avoid the foam formation during the fermentation process by using mineral acids, such as phosphoric, hydrochloric, sulfuric, and nitric (Chozhavendhan et al., 2015). Phosphoric acid showed a substantial result in separation time and the glycerol liberation amount and the presence of salt in the glycerol-rich phase were also low when compared with other acids. However, a high acidic condition will corrode the material and results in low glycerol liberation, on a contradictory way the weak acids may cause the difficulties in the separation of final products. The glycerol-rich phase separation from the waste stream glycerol is well in the range of pH 4−6 (Chozhavendhan et al., 2016b).

9.3.2 Sophisticated purification process

The final step of purification and refining step can be achieved to the desired degree of purity with the combination of the following methods, such as vacuum distillation, ion exchange, membrane separation process. In ion exchange adsorption process, ion materials are employed in purification of crude glycerol for the removal of impurities, odor, and other inorganic salts through exchanging of ions (Ardi et al., 2015; Rathore et al., 2019). This technique does not require vaporization of crude glycerol and requires a small quantity of water for the removal of salt. The final product is exceptionally high in quality with 95%−99%, which confirms the high-grade distilled glycerol. The chromatograph of HPLC shows a single peak of glycerol with a smooth baseline matching a standard profile. Vacuum distillation is one of the most common methods employed for the industrial purification

process of crude glycerol and purity level of glycerol reaches 95.5% with low chemical cost and process adaptability (Stojkovic et al., 2014; Gerpen, 2005). The change in concentration or electrical potential and hydrostatic pressure are the driving force for the purification of crude glycerol through the membrane separation process and attain the decent purification performance up to 99%. A diverse group of membranes are employed for the purification process and the main drawback with the process is fouling and durability of a membrane (Hasheminejad et al., 2011).

9.3.3 Comparison of properties of crude and partially refined and refined glycerol

Crude glycerol produced from different feedstocks has a different composition and hence purification process is mandatory. Depending upon the usage and effects of impurity, the purification process is carried out in profit measured by controlling the purification cost. In most cases the presence of some contaminants is bearable for the technical utilization of glycerol in the fermentation process. whereas high purity of glycerol is required in the food and pharmaceutical sectors (Tan et al., 2013). Hence physicochemical properties of crude, partially refined, and pure commercial glycerol were compared and discussed in Table 9.1.

9.4 Applications

The excess amount of glycerol generated from the biodiesel industries has created a glut in the market of glycerol. Glycerol is highly functionalized molecule when compared with other hydrocarbons produced through the petrochemical process. Thus glycerol can be considered as renewable building block for the biorefinery by

Table 9.1 Comparison of crude glycerol, partially refined and pure commercial glycerol (Chozhavendhan et al., 2017).

Properties	Crude glycerol	Partially refined glycerol	Commercial pure glycerol
Color	Dark brown	Straw yellow	Colorless
pH	9.6	5	6.7
Density (kg/m^3)	1.29	1.23 ± 0.2	1.25
Flash point (°C)	180	185	177
Fire point (°C)	211	214	204
Carbon residue (%)	18	12	11.25
Ash content (%)	11.26	0.14	Not applicable
Concentration (%)	10.43	42–44	95–99
Solubility with water	Miscible	Miscible	Miscible

producing value-added chemical either biological or chemical route. The application of glycerol and its application in various industries were displayed in Fig. 9.2.

9.4.1 Biological route

Industrial fermentation needs raw materials that fulfill the requirement of the organism for the growth, development, and resultant yield. The higher level of sugar reduction allows the variety of prokaryotic and eukaryotic for known for utilizing crude glycerol as sole or supplementary carbon and energy source for the production of high-value chemicals, such as glyceric acid, lactic acid, ethanol, hydrogen, and lipids pigments (Chatzifragou and Papanikolaou, 2012).

9.4.1.1 Glyceric acid

Glyceric acid, an unfamiliar biotechnological word also known as 2,3-dihydroxy propionic acid, is a functional organic acid, multifunctional monomer, and surfactant (). *Gluconobacter oxydans* is a Gram-negative rod or oval-shaped nonmotile bacterium. An Acetobacter family of *G. oxydans* is capable of converting biologically crude glycerol into glyceric acid. At the temperature of 37°C and pH of 6 the organism is capable of producing GA and maximum precipitation is achieved with 50% calcium chloride (Chozhavendhan et al., 2014).

Gluconobacter sp. was observed to produce a high yield in the range of 71%–90% in both D- and L-forms of glyceric acid when compared with *Acetobacter* sp. In 174 g/L pretreated glycerol with activated charcoal, *Gluconobacter* sp. NBRC3259 could produce 49.5 and 28.2 g/L of glyceric acid (Carreira et al., 2011).

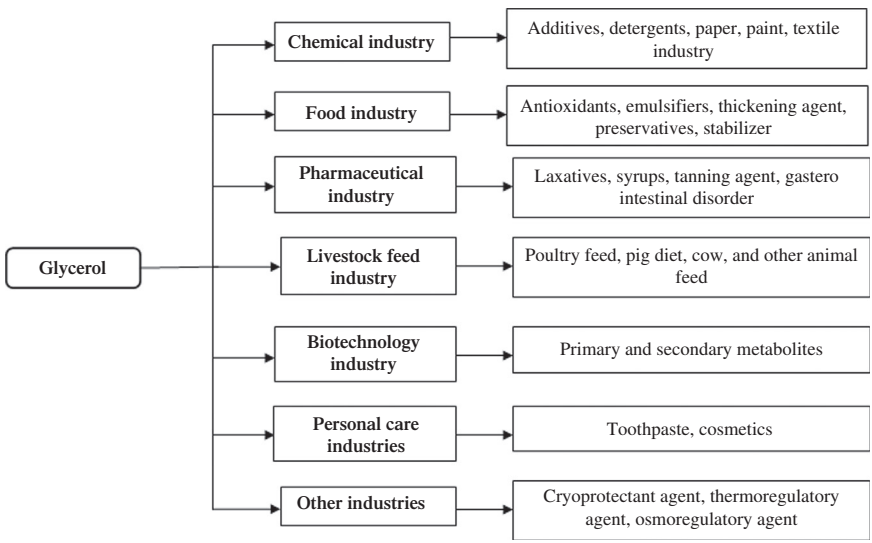


Figure 9.2 Application of glycerol in various industrial process.

The accumulation of docosahexaenoic acid (DHA) in glyceric acid production can be controlled by encoding sld A gene of glycerol dehydrogenase (Habe et al., 2010). In the study by , in a fed-batch fermentation process, *Gluconobacter frateurii* NBRC103465 and *Acetobacter tropicalis* NBRC16470 are capable of producing more than 100 g/L of glyceric acid. *G. frateurii* NBRC103465 produced 136.5 g/L of glyceric acid with a 72% D-GA along with a coproduct of DHA of 0.58 and 0.12 mol/mol glycerol, respectively, under optimized glycerol and aeration conditions. Ninety percent yield of glyceric acid was produced from glycerol by using an immobilized enzyme laccase produced from *Trametes versicolor* under the optimized condition at 25°C for 24 h using 30 mM 2,2,6,6-tetramethyl piperidine *N*-oxyl as a mediator (Hong et al., 2015).

9.4.1.2 Lactic acid

Lactic acid is one among the industrially important organic acid produced by lactic acid bacteria. Lactic acid generally exists in D (+), L (−) or in racemic mixture (+/−) form. The conventional chemical synthesis is known to produce a racemic mixture, whereas biological fermentation was witnessed to yield all the isomeric forms either individually or in a mixture. As lactic acid became an important building block in the chemical industry, its microbial production has advanced significantly (Almeida et al., 2012). Many naturally occurring wild type microorganisms, such as *Escherichia coli*, *Klebsiella*, *Clostridia*, *Bacillus*, and the filamentous fungi *Rhizopus oryzae*, are capable of producing lactic acid from glycerol (Harvey and Meylemans, 2011; Cheng et al., 2006; Bai et al., 2003).

The *E. coli* AC-521 strain has an ability to grow quickly and produces lactic acid on utilizing glycerol as substrate under aerobic condition. The maximum yield and productivity of lactic acid achieved by this strain are 0.9 mol/mol and 0.49 g/g/h, respectively (Hong et al., 2009). Chen et al. (2015) investigated that lactic acid can be produced from glycerol using sodium hydroxide (NaOH) a homogeneous catalyst in fed-batch process. In this process, 93 mol% of glycerol is converted to yield of 82% of lactic acid under optimized reaction temperature at 300°C at reaction time of 220 min with a feed inlet of 1.1 M glycerol. Ftouni et al. (2015) used an inert catalyst Pt/ZrO_2 for conversion of glycerol into lactic acid. When compared with other types of platinum catalyst, Pt/ZrO_2 provides high conversion and stable lactic acid in all condition. The catalyst can able to convert both pure and crude glycerol into 80% lactic acid at 180°C, under helium pressure maintained at 30 bar pressure after the reaction time of 8 h. Since the catalyst Pt/ZrO_2 is expensive, this process is not economically viable for industrial-scale production process of lactic acid.

9.4.1.3 Lipids

From the evidence of various studies, lipid is produced from crude glycerol from numerous types of microorganisms, such as yeast, fungi, and microalgae (Yang et al., 2012). The freshwater microalga, *Chlorella protothecoides*, was capable of

converting glycerol to lipids with a lipid yield of 0.31 g/g substrate (Grady and Morgan, 2011), or a lipid productivity of 3 g/L/day. Chen and Walker (2011) observed that the biomass and lipid concentration was merely doubled in a fed-batch operation when compared with batch operations on utilizing crude glycerol as a carbon source by *C. protothecoides*. Liang et al. (2010a) showcased that the highest cellular lipid content of 73.3% was produced from *Schizochytrium limacinum* SR21 a marine microalga on 35 g/L of crude glycerol derived from cooking oil. Fed-batch system appears to be more advantageous over batch systems in terms of substrate inhibition and increased accumulation of intracellular triacylglycerols (TAGs) (Luo et al., 2016).

9.4.1.4 Hydrogen

The most serious environmental issue for the world is global warming and which causes many deleterious issues. The alternate clean energy source is hydrogen which can be produced by the broad spectrum of substrate and microorganisms. The consumption of hydrogen reduces CO_2, NO_x, particulate, and other emissions that accompany the use of fossil fuels.

The energy content of crude glycerol (25.30 MJ/kg) is high when compared with the pure glycerol (19.0 MJ/kg) due to the presence of methanol and other traces of biodiesel components. The high-energy content of crude glycerol designates as a potential substrate for hydrogen production glycerol can be converted into hydrogen by a number of methods, such as biological, steam reforming, partial oxidation, and auto-thermal reforming. Ito et al. (2005) demonstrated the combined production of hydrogen and ethanol from glycerol by using *Enterobacter aerogenes* HU-101. As the purity of glycerol increases the production of hydrogen increases and has reported a maximum hydrogen yield rate of 80 mmol/L/h. Wu et al. (2011) reveal that *Klebsiella* sp. HE1 can be employed for the production of hydrogen using glycerol as a feedstock (Ken Jer et al., 2011).

9.4.1.5 Other generalities by biological route

1,3-PDO, a diol monomer, was well known for numerous applications in cosmetics, solvents, adhesives, detergents, and resins. Various wild-type strains, such as *Klebsiella pneumoniae*, *Clostridium butyricum*, *Clostridium diolis*, *Citrobacter freundii*, *Lactobacillus diolivorans*, *Lactobacillus brevis*, *Lactobacillus reuteri*, and genetically modified strains of *K. pneumoniae, E. coli*, and *Clostridium pasteurianum* were well reported anaerobic fermentation of glycerol for 1,3-propanediol production (Zhong et al., 2014; Vivek et al., 2016; Vaidyanathan et al., 2011; Jensen et al., 2012). In anaerobic fermentation with glycerol as the sole energy source, *K. pneumoniae* strains were reported to produce 1,3-PDO titers between 60 and 90 g/L (Zhao et al., 2009), and *C. butyricum* strains were observed to produce more than 60 g/L (Wilkens et al., 2012). 1,3-Propanediol production from crude glycerol using *K. pneumoniae* ATCC 15380 was optimized, and yield, purity, and recovery were 56 g/L, 99.7%, and 34%, respectively (Hiremath et al., 2011).

Citric acid is widely used organic acid in the field of food industry as a flavoring agent and in pharmaceutical industry as a polishing agent (Handojo et al., 2019). *Yarrowia lipolytica* is the most commonly studied organism for the production of citric acid from glycerol. The maximum yield of 62.5 g/L of citric acid was produced by *Y. lipolytica* under nitrogen limitation condition (Papanikolaou et al., 2008). Higher citric acid concentrations (more than 100 g/L) were attained with acetate-negative mutants strain of *Y. lipolytica* using crude glycerol as the substrate (Rymowicz et al., 2010; Rywinska and Rymowicz, 2010). Many other products, such as succinic acid, dihydroxyactone, and pigments, can also be produced from the glycerol. The value-added products produced through microbial fermentation of glycerol are displayed in Table 9.2.

9.4.2 Chemical route

9.4.2.1 Acrolein

Acrolein is the simplest unsaturated aldehyde also known as 2-propenal or acrylic aldehyde (Fan et al., 2010). It can be produced from glycerol via aqueous dehydration process with the presence of the catalyst (Alhanash et al., 2010). Acrolein finds its application as a raw material of acrylic acid, medicines, fiber treatment, methionine, fragrance, and dyes, as a slimicide in the production of paper and as a microbicide in oil wells (Kong et al., 2016). A percentage of 85 acrylic acid is produced through conventional acrolein oxidation in the world and mostly used in hygienic pads and diapers by exhibit super adsorbent properties.

Watanabe et al. (2007) produced acrolein from glycerol in hot compressed water using a batch and flow apparatus. The addition of acid catalyst helps to maintain the rate constant of acrolein formation which is always higher than that of decomposition. Percentages of 74 acrolein yield and 81 its selectivity were obtained with the catalyst in the supercritical condition. Cheng et al. (2013) comparatively reconnoitered impurities effect on the direct conversion of pure and crude glycerol to acrolein using sulfuric acid under subcritical water condition. Less than 80 mol% of acrolein yield was obtained in both crude and pure glycerol at the temperature ranging 335°C−380°C in the presence of 45−50 mM H_2SO_4. Bub et al. (2006) reported that dehydration of glycerol is carried out at 300°C with Zr as a catalyst. A percentage of 72 gas phase dehydration of glycerol conversion of acrolein is achieved.

9.4.2.2 Epichlorohydrin

Epichlorohydrin is an organochlorine compound and an epoxide and was first described in 1848 by Marcellin Berthelot. The compound was isolated on reactions between glycerol and gaseous hydrogen chloride. It is a colorless liquid with pungent order, moderately soluble in water and miscible with the most polar organic solvent. It acts as a building block for the manufacture of epoxy resins and also precursors for monomer and polymer of other resins.

Table 9.2 Product produced from glycerol through microbial fermentation process.

Product	Microorganism	Substrate	Mode of operations	Concentration (g/L)	Yield (g/g)	Reference
Glyceric acid	*Gluconobacter frateurii* NBRC103465	Glycerol	Fed-batch	136.5	0.76	Habe et al. (2009b)
	Acetobacter tropicalis NBRC16470	Glycerol	Fed-batch	101.8	0.46	Habe et al. (2009b)
1,3-Propanediol	*Klebsiella pneumoniae* DSM 2026	Glycerol	Fed-batch	59.5	0.52	Chen et al. (2003)
	Escherichia coli K12	Glycerol	Fed-batch	104.4	90.2	Tang et al. (2009)
	Clostridium butyricum AKR102a	Crude glycerol	Fed-batch	76.2	–	Wilkens et al. (2012)
Lactic acid	*E. coli* AC-521	Glycerol	Fed-batch	85.8	0.9	Hong et al. (2009)
Citric acid	*Yarrowia lipolytica*	Glycerol	Repeated batch	124.2	0.77	Rymowicz et al. (2010)
	Y. lipolytica K-1	Glycerol		75.7	0.38	Rymowicz et al. (2006)
Hydrogen	*Rhodopseudomonas palustris strain*	Glycerol	Photo fermentative conversion process	–	0.66	Sabourin-Provost (2009)
Lipid	*Schizochytrium limacinum* SR21	Glycerol	Batch	73.3	–	Liang et al. (2010b)

Almena and Martín (2015) stated that epichlorohydrin formation consists of four stages: purification of crude glycerol, its reaction to mono and dichlorohydrins and their separation, epichlorohydrin production, and final product purification. On using the process integrated MATLAB 10% higher yield (80.5% vs 73% related to the mass of pure glycerol fed to the plant) was achieved in the proposed current industrial process. Lari et al. (2018) stated in his study that solid and recyclable base can be used as an alternative source to alkali hydroxide catalyst for the epichlorohydrin production from dehydrochlorination of glycerol. The optimization of space velocity and controlling the temperature below 423K enable the yield as high as 60%. In the established technologies the production of epichlorohydrin by using a heterogeneous catalyst such as heteropolyacid at 110°C and 5 bar pressure in 5 h reaction time could convert 49.7% of dihydrochloride (Lee et al., 2008). Comparably, Song et al. (2010) achieved 50.9% of epichlorohydrin from dihydrochloride in the presence of a heteropolyacid catalyst in a solid phase gas reactor at 250°C.

9.4.2.3 Triacetin

Triacetin is also known as 1,2,3-triacetoypropane or glycerin triacetate. It is the ester of glycerol that forms with acetic acid. Triacetin can be produced through the acid-catalyzed reaction of acetic acid or acetic anhydride with glycerol. Triacetin finds its application in pharmaceutical, cosmetic, and fuel additives as an anti-knocking agent to minimize the engine knocking. It is used in biofuel to increase in cetane number and to decrease the nitrogen oxide emission (Melero et al., 2007).

Zhu et al. (2013) proposed silver-exchanged phosphotungstic acid (AgPW) catalysts for glycerol acetylation with acetic acid. Partially, silver-exchanged phosphotungstic acid (Ag1PW) showed high activity and good performance in the reaction. The conversion of glycerol is 96.8% at 120°C within 15 min of reaction time. The reason is that Ag1PW shows remarkable stability, unique kegging structure, high acidity, and excellent water-tolerance property. The selectivity of acetylated products is 5.2% for triacetin, 46.4% for diacetin, and 48.4% for monoacetin. Mufrodi et al. (2012) stated that the crude glycerol and acetic acid in the presence of the sulfuric acid catalyst at the temperature of 111°C on the reaction time 90 min yields selectivity of triacetin 77.84%. In the exothermic reaction the production of triacetin increases with increase in reaction temperature since acetic acid starts to evaporate when the temperature is decreased. Sun et al. (2016) investigated that the use of magnetic solid acid catalyst for efficient conversion of glycerol to triacetin with acetic anhydride. Stannic chloride pentahydrate Fe−Sn−Ti (SO_4^{2-}) catalyst aids 100% conversion of glycerol and 99% selectivity of triacetin under an optimized temperature of 80°C and reaction time 30 min.

9.4.3 Alternate uses

The crude glycerol, as a major byproduct during biodiesel production, consists of a copious amount of impurities which inhibits its direct usage in industries. However,

this crude glycerol may be used as supplement energy source for the cattle feed (Chung et al., 2007). At low concentration, crude glycerol can be used as a potential ingredient source for the production of broiler feed and pig feed (Cerrate et al., 2006; Roger et al., 1992; Della Casa et al., 2009). In broiler diets, increasing the intake level of crude glycerol increased feed conversion ratio but did not affect growth performance and nutrient digestibility (McLea et al., 2011).

Due to the high energy content, crude glycerol can be used as a substitute for boiler fuel or cogeneration of electricity/thermal energy. In this case, glycerol can be directly used in large quantities without any refining process. The presence of water and methanol in crude glycerol restricts its usage as cofiring in thermal energy.

Apart from this, glycerol can also find its application as a plasticizer and lubricant in production and as a sizing, lubricating, and softening yarn and fabrics in textile industries. It is also used as a major ingredient in toothpaste and finds its application in preserving the moisture content of tobacco (Donkin Shawn, 2008). Glycerol helps to increase the viscosity of the liquid drug and provides humidity to pills with its wide application in medicine and pharmaceutical industries. Glycerin is an excellent solvent of iodine, bromine, phenol, tannins, alkaloids, and mercury chloride (Ampaitepin and Tetsuo, 2010).

9.5 Conclusion

Glycerol is a versatile, nontoxic, and biodegradable compound that can be converted into numerous chemicals or bio-based products. The demand and supply of crude glycerol are directly correlated with its usage and new outlets. One of the major hurdles in the utilization of crude glycerol is that most of the microorganisms exhibit the substrate mediated inhibition because of the copious amount of impurities present in it. Glycerol-purification technology offers promising opportunities for the production of high-platform chemicals from crude glycerol either by biological or chemical route. These technologies and production of new products from glycerol help to increase the economic status of the bio-based company for the long run. If the biodiesel industries proceed the purification and bioconversion in the biorefineries concept, it enjoys numerous benefits, such as zero liquid discharge, self-disposal, and purging of the risk contamination, trailed by legal sanctions. This technology will have a great substantial impact on the economic and environmental sectors. Thus the utilization of low-cost crude glycerol provides the broad spectrum of option for the production of high-value platform chemicals and also serves as a renewable building block for biorefineries.

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