Value-added processing of crude glycerol into chemicals and polymers

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Abstract

Crude glycerol is a low-value byproduct which is primarily obtained from the biodiesel production process. Its composition is significantly different from that of pure glycerol. Crude glycerol usually contains various impurities, such as water, methanol, soap, fatty acids, and fatty acid methyl esters. Considerable efforts have been devoted to finding applications for converting crude glycerol into high-value products, such as biofuels, chemicals, polymers, and animal feed, to improve the economic viability of the biodiesel industry and overcome environmental challenges associated with crude glycerol disposal. This article reviews recent advances of biological and chemical technologies for value-added processing of crude glycerol into chemicals and polymers, and provides strategies for addressing production challenges.

Keywords: Crude glycerol; Value-added processing; Purification; Biological conversion; Chemical conversion

1. Introduction

Crude glycerol, also referred to as crude glycerin, is commonly generated during the production of biodiesel. Crude glycerol is traditionally refined to pure glycerol, a useful raw material for industries, such as foods and beverages, pharmaceuticals, cosmetics, tobacco, and textiles. In 2014, over 67% of the pure glycerol globally produced is from biodiesel-derived crude glycerol (Radiant Insight Inc., 2015).

Biodiesel production in the United States grew rapidly from 250 million gallons in 2006 to 1.8 billion gallons in 2013 (National Biodiesel Board, 2014). With approximately 1 kg of crude glycerol generated for every 10 kg of biodiesel produced, the large quantities of crude glycerol produced each year have impacted the glycerol market, resulting in low prices of refined glycerol and crude glycerol. Crude glycerol has been a financial and environmental liability of the biodiesel industry. Thus, it is imperative to convert crude glycerol into higher-value products in order to improve the economic sustainability of the biodiesel industry and reduce environmental impacts of crude glycerol waste disposal.

One route for value-added processing of crude glycerol is to produce pure glycerol, *via* refining processes, e.g. the “Universal Recovery Strategy” that has been developed for recovery of valuable compounds from food by-products (Galanakis, 2012). Purified glycerol can be converted into various value-added products, which has been well reviewed previously (Clomburg and Gonzalez, 2013; Tan et al., 2013). However, this route may not be economically feasible for small- or medium-sized biodiesel producers due to the high cost of refining processes. Shipping crude glycerol to a glycerol refinery is only viable when a group of biodiesel plants are located within a limited area. Another route is to directly convert crude glycerol into value-added products, which can be achieved via either biological or chemical pathways. In recent years,

there has been an increase in research on direct utilization of crude glycerol for the production of value-added products, such as butanol, 1,3-propanediol, 2,3-butanediol, citric acid, lipid, poly(hydroxyalkanoates), acrolein, monoglycerides, maleated glycerides, polyglycerol, solketal, polyols, and bio-oils. These chemicals and polymers have extensive applications as biofuels, fuel additives, detergents, polymeric materials, and other uses. There are a number of articles that have reviewed conversion of crude glycerol to value added products (Almeida et al., 2012; Clomburg and Gonzalez, 2013; Dobson et al., 2012; Rahmat et al., 2010; Tan et al., 2013; Yang et al., 2012). However, some value-added products, such as 2,3-butanediol, polyglycerol, and polyols have generally been overlooked in these reviews. Besides, strategies for specific issues in conversion of crude glycerol to value added products have not been well discussed in previous reviews. In addition, most of the reviews focus on only one approach, either biological or chemical conversion (Almeida et al., 2012; Clomburg and Gonzalez, 2013; Dobson et al., 2012; Rahmat et al., 2010).

This paper reviews the chemical composition of crude glycerol from different biodiesel production processes, as well as routes for value-added conversion of crude glycerol, with a focus on direct utilization of crude glycerol to produce chemicals and polymers, including 1,3-propanediol, butanol, 2,3-butanediol, citric acid, lipid, poly(hydroxyalkanoates), acrolein, monoglycerides, maleated glycerides, polyglycerol, polyols, and others. Both biological and chemical pathways are discussed. Strategies for addressing challenges to value-added processing of crude glycerol into chemicals and polymers are also provided.

2. Characteristics of crude glycerol

Biodiesel is produced by the transesterification reaction of triglycerides (including vegetable oils, animal fats, waste cooking oils, and algae oil) with an alcohol, mostly methanol, in the presence of a catalyst. In general, the transesterification reaction can be carried out using either acid or base catalysts. Acid catalysts such as sulfuric acid, hydrochloric acid, and solid acids, are suitable for the transesterification of low-grade oils containing water and free fatty acids, while base catalysts are commonly used for the transesterification of triglyceride feedstocks with low free fatty acids contents (Tan et al., 2013). Base catalysis also has advantages of high reaction rates and low methanol to triglyceride molar ratios. The base catalysts include alkaline metal alkoxides and hydroxides and heterogeneous solid metal-oxide catalysts. Among these, sodium hydroxide and potassium hydroxide are the most widely used alkali catalysts. Besides acids and bases, enzymes have also been developed to catalyze transesterification.

During the biodiesel production process, two phases usually form, with biodiesel located in the upper phase and crude glycerol in the lower phase, due to differences in densities and polarities. Crude glycerol is a mixture consisting of glycerol and some impurities, such as water, methanol, soap, and matter organic non-glycerol (MONG). Depending on the feedstock, the process used for biodiesel production, and the post-treatment methods used, the crude glycerol components vary. When seed oils such as Ida Gold Mustard, Pacific Gold mustard, rapeseed, canola, crambe, and soybean, and waste cooking oils were used as feedstocks, crude glycerol contained 62.5 to 76.6% (w/w) glycerol (Tan et al., 2013). During the base catalyzed processes for biodiesel production, soap is usually formed and included in the crude glycerol. In a biodiesel production process that used canola oil as a feedstock and sodium hydroxide as a catalyst, about 15.3% (w/w) soap was detected in the crude glycerol stream (Pyle et al., 2008). In another process for the production of biodiesel from soybean oil using potassium hydroxide as a catalyst,

crude glycerol with approximately 25.2% (w/w) soap was obtained (Pyle et al., 2008). Compared to heterogeneous alkaline catalysts, homogeneous alkali catalysts resulted in relatively high salt contents (5.0-7.0% based on weight) of crude glycerol (Yang et al., 2012). Additionally, crude glycerol with higher purity of glycerol were obtained by enzymatic catalysis than by acid- and base-catalysis (Tan et al., 2013). In some cases, post-treatment of crude glycerol is conducted to improve the purity of glycerol. For instance, the methanol content of crude glycerol was reduced dramatically to less than 1.0% (w/w) by vacuum distillation (Rehman et al., 2008). Table 1 provides results of several studies and shows glycerol contents ranging from 20.0 to over 85.0% (w/w), methanol contents from less than 1.0 to over 25.0% (w/w), soap contents from 0 to more than 25.0% (w/w), and MONG contents from 0 to more than 35% (w/w). Because of these impurities, crude glycerol varies from liquid to wax at room temperature and shows a substantially different color, ranging from light yellow to dark brown (Ciriminna et al., 2014).

3. Refining of crude glycerol to pure glycerol

Generally, recovery of target compounds can be achieved through five distinct stages, including macroscopic pre-treatment, macro- and micro- molecules separation, extraction, isolation and purification, and product formation (Galanakis, 2012). This “Universal Recovery Strategy” has been well-established in the field of nutraceuticals recovery (Galanakis, 2012). Similar processes can be used for refining crude glycerol to pure glycerol, although some steps may be eliminated depending on the characteristics of wastes. The refining process of crude glycerol to pure glycerol generally consists of three stages (Fig. 1): 1) neutralization to remove soaps and salts; 2) vacuum evaporation to remove methanol and water; and 3) deep refining to further improve glycerol purity. During the neutralization stage, an acid, such as phosphoric acid,

hydrochloric acid, or sulfuric acid, is added to convert soaps into free fatty acids. The residual alkaline catalyst is neutralized to yield salts and water, resulting in a mixture of three phases. The fatty acids and residual fatty acid methyl esters are located in the top phase and can be easily removed by decantation. Glycerol, alcohol (e.g., methanol or ethanol), and water are in the middle phase, and the insoluble salts are in the bottom phase. After filtration, the insoluble salts are removed and the glycerol-rich phase, which has been shown to contain 40-70% (w/w) glycerol, can be obtained (Ardi et al., 2015; Cai et al., 2013). Alcohols are removed and recycled during the second stage. Abundant unreacted methanol is considered to be a major contaminant due to its toxicity in food and pharmaceutical applications. The excess methanol is usually removed using vacuum evaporation or a flash unit because of its low boiling point. Moreover, water can also be evaporated in this process. After the vacuum evaporation step, the glycerol content of crude glycerol could reach around 85% (w/w) (Ardi et al., 2015).

In order to obtain high-purity glycerol, it is necessary to perform further refining. Currently, four deep refining technologies have been developed, including vacuum distillation, ion exchange, membrane separation, and activated carbon adsorption. Table 2 summarizes and compares their advantages, disadvantages, and performance. Among these four deep refining technologies, vacuum distillation is the most common method for industrial purification of crude glycerol and has many advantages, such as feasibility for small- to large-scale continuous operations, low chemical costs, process adaptability, and acceptable glycerol purity (at least 95.5 %, w/w) (Stojković et al., 2014). However, it requires an intensive energy supply which increases the process costs. Compared to the conventional vacuum distillation method, a higher quality of refined glycerol (95-99%, w/w) (Ardi et al., 2015; Kale et al., 2015) is achieved using ion exchange techniques, which can be conducted with lower energy inputs and at ambient

temperature. Impurities such as fatty acids, salts, and free ions can be removed in the ion exchange process. Due to poor regeneration of the ion exchange beds and the generation of large volumes of waste water during the process, the ion exchange technique is more applicable for smaller refineries (Ardi et al., 2015). As an emerging technology in the crude glycerol purification process, membrane separation technology is very attractive because of its simple operation, environment-friendly process, low energy and cost requirements, and decent purification performance with glycerol contents of up to 99.0% (w/w) (Muralidhara and Ko, 2008). Despite having many advantages for crude glycerol purification, this technology faces some challenges, such as the fouling and durability issues of membranes and the lack of suitable membranes for specific operations. The activated carbon adsorption technique is a commonly used purification method to reduce color and adsorb some small molecular compounds. It is mainly carried out at the final step of the crude glycerol refining process. Studies have demonstrated that activated carbon exhibited ideal effects on color removal of crude glycerol and on elimination of some fatty acids, such as lauric acid and myristic acid (Manosak et al., 2011). The purity of refined glycerol can reach 99.7% (w/w) with the final active carbon adsorption (Manosak et al., 2011).

The consideration for adopting suitable purification technologies for crude glycerol is strongly influenced by the contaminants and their content, the quality of refined glycerol required for specific applications, and the operational feasibility for refineries. According to the purity and application standards, refined glycerol in the market can be divided into three grades, i.e., technical grade (> 96% glycerol, w/w), United States Pharmacopeia (USP) (99.5% glycerol, w/w), and Food Chemical Codex (FCC) (99.7% glycerol, w/w) (Ardi et al., 2015). Technical grade refined glycerol is primarily used for the production of chemicals and polymers. It cannot

be used for food and pharmaceutical applications. For USP grade, glycerol can be derived from both animal fats and vegetable oils, but FCC level glycerol is only obtained from vegetable oils (Ardi et al., 2015).

In addition, it should be mentioned that several emerging technologies, such as electro-osmotic dewatering and ultrasound-assisted extraction, have been applied in production of nutraceuticals from agricultural by-products (Galanakis, 2013). These emerging technologies may potentially be used to improve the crude glycerol refining process, although further investigations are needed to examine their performance.

4. Biological conversion of crude glycerol to value-added products

Glycerol can be biologically converted into various value-added products, such as 1,2-propanediol, *n*-butanol, 2,3-butanediol, docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA), citric acid, lipids, and poly(hydroxyalkanoates) (PHA), using different types of microorganisms (e.g., bacteria, fungi and microalgae) via different pathways. The conversions can be conducted under anaerobic, microaerobic, or aerobic conditions depending on the required product. The performance of the biological conversion of crude glycerol to value-added products is summarized in Table 3, and discussed in the following subsections.

4.1. 1,3-propanediol

Conversion of glycerol to 1,3-propanediol via anaerobic fermentation or micro-aerobic fermentation with bacteria such as *Klebsiella oxytoca*, *Klebsiella pneumoniae*, *Clostridium butyricum*, and *Lactobacillus diolivorans* has been widely investigated (Table 3). Different reactor operation modes, including batch, fed-batch, and continuous operation, have been used in

1,3-propanediol production from crude glycerol (Lee et al., 2015). Compared to fed-batch and continuous fermentation, batch fermentation is relatively simple. However, high amounts of glycerol may result in substrate inhibition, which limits the initial concentration of glycerol, and thus the final concentration of 1,3-propanediol (Lee et al., 2015; Szymanowska-powalowska, 2014). Continuous fermentation generally obtained high productivities (up to 3.4 g/L/h) with final concentrations of 1,3-propanediol of 32-48 g/L (Szymanowska-powalowska, 2014). Higher concentrations of 1,3-propanediol (up to 83 g/L) were obtained in fed-batch fermentation with productivities of 0.45-2.3 g/L/h (Hiremath et al., 2011; Lee et al., 2015; Pflügl et al., 2014; Szymanowska-powalowska, 2014; Wilkens et al., 2012). Despite the differences in reactor operations, the reported yields of 1,3-propanediol from glycerol were generally comparable to each other (0.39-0.57 g/g), although a very high 1,3-propanediol yield of 0.7 g/g has been reported (Hiremath et al., 2011; Lee et al., 2015; Szymanowska-powalowska, 2014; Wilkens et al., 2012).

To date, the best results on crude glycerol-based 1,3-propanediol were reported by Wilkens et al. (2012), who used fed-batch fermentation with *Clostridium butyricum* AKR102a in a 1-L reactor, producing 76.2 g/L of 1,3-propanediol from non-sterile crude glycerol with a productivity of 2.3 g/L/h and a yield of 0.514 g/g crude glycerol (Table 3). When the fermentation process was scaled up to 200 L, 61.5 g/L of 1,3-propanediol was obtained with a productivity of 2.1 g/L/h (Wilkens et al., 2012).

4.2. *n*-butanol

Currently, the only viable biological approach for conversion of glycerol to *n*-butanol is the acetone-butanol-ethanol (ABE) fermentation by microorganisms, such as *Clostridium*

pasteurianum, under anaerobic conditions (Clomburg and Gonzalez, 2013) (Table 3). *Clostridium pasteurianum* DSM 525 was also able to produce butanol from crude glycerol, although supplements of other carbon sources may be needed (Ahn et al., 2011). This strain produced 7.2 g/L of butanol in 48 hours by directly utilizing thin stillage that contained about 20 g/L of glycerol with other compounds, such as lactate, acetate, and 2,3-butanediol (Ahn et al., 2011). Besides, butyrate addition was found to improve butanol production from glycerol with *Clostridium pasteurianum* DSM 525 and *Clostridium pasteurianum* CH4 (Gallardo et al., 2014; Kao et al., 2013). Furthermore, a simultaneous dual-substrate cultivation strategy was proposed using sugarcane bagasse (25 g/L) and biodiesel-derived crude glycerol (60 g/L) as dual-substrates (Kao et al., 2013). This strategy achieved a butanol concentration, productivity, and yield of 11.8 g/L, 0.14 g/L/h, and 0.33 mol/mol glycerol (or 0.265 g/g glycerol), respectively (Kao et al., 2013).

4.3. 2,3-butanediol

Klebsiella and *Bacillus* spp. have been studied for producing 2,3-butanediol from crude glycerol (Table 3). When using biodiesel-derived glycerol as the sole carbon source for *Bacillus amyloliquefaciens* B10-127, 43.1 g/L of 2,3-butanediol was obtained with a productivity of 0.45 g/L/h (Yang et al., 2013). When using biodiesel-derived glycerol (80%, w/v) with beet molasses (15%, w/v) as a co-substrate, the 2,3-butanediol production was significantly improved, reaching a concentration, yield, and productivity of 83.3 g/L, 0.42 g/g, and 0.87 g/L/h, respectively (Yang et al., 2013).

Besides strain specificity and aeration, pH was found to be the most important factor for 2,3-butanediol production (Petrov and Petrova, 2010). For example, when the fermentation was

conducted at an initial pH of 8 without controlling pH during the process, 49.2 g/L of 2,3-butanediol was produced with no significant amounts of by-products. When a constant pH of 5 or 7 was maintained, low 2,3-butanediol yield was observed. It was suggested that the strain can self-control the pH by alternatively producing acetate and 2,3-butanediol from glycerol. Thus, the formation of 2,3-butanediol was due to this adaptive mechanism responding to the pH drop during glycerol fermentation. Further improvement in 2,3-butanediol production was achieved by a forced pH fluctuation strategy. Under the optimal conditions, 70 g/L of 2,3-butanediol were produced with a maximum yield of 0.40 mol/mol (or 0.39 g/g) glycerol and a productivity of 0.47 g/L/h (Petrov and Petrova, 2010). It should be noted that up to 16.3 g/L of 1,3-propanediol was still produced, and these results were obtained using pure glycerol, not crude glycerol.

Recently, a metabolically engineered strain, *Klebsiella oxytoca* M1, has been developed by deleting the pduC (encoding glycerol dehydratase large subunit, accession number AIE72369) and ldhA (encoding lactate dehydrogenase, accession number AIE70186) (Cho et al., 2015). The mutant was able to produce 2,3-butanediol without 1,3-propanediol generated as a byproduct. During a fed-batch fermentation process using crude glycerol as the carbon source, the mutant obtained a high final concentration, yield, and productivity of 131.5 g/L, 0.44 g/g crude glycerol, and 0.84 g/L/h, respectively, compared to other strains (Table 3).

4.4. Citric acid

Although citric acid production from sugar has been commercialized, citric acid production from glycerol or biodiesel-derived crude glycerol has not been widely studied. Glycerol-based citric acid production was generally performed with *Yarrowia lipolytica* under nitrogen limitation conditions, obtaining citric acid concentrations up to 62.5 g/L (Papanikolaou et al.,

2008) (Table 3). Higher citric acid concentrations (more than 100 g/L) were obtained with acetate-negative mutants of *Yarrowia lipolytica* using crude glycerol as the substrate (Rymowicz et al., 2010; Rywińska and Rymowicz, 2010) (Table 3).

The cultivation mode is another important factor for citric acid production from glycerol. Although high citric acid concentration was achieved using batch fermentation, the productivity decreased over time (Rymowicz et al., 2010; Rywińska and Rymowicz, 2010). This issue was addressed by a repeated-batch strategy, resulting in high productivities of 0.85-1.05 g/L/h with concentrations of 124-154 g/L and yields of 0.77-0.78 g/g crude glycerol (Rymowicz et al., 2010; Rywińska and Rymowicz, 2010).

4.5. Polyunsaturated fatty acids

Marine microorganisms are known to be able to accumulate docosahexaenoic acid (DHA) via fermentation. Some species, such as *Aurantiochytrium limacinum* MYA-1381 and *Schizochytrium limacinum*, have been studied for the production of DHA using glycerol (Abad and Turon, 2012) (Table 3). Currently reported DHA concentrations, yields, and productivities from crude glycerol are 2.0-5.0 g/L, 0.17-0.55 g/g biomass, and 26-38 mg/L/h, respectively (Abad and Turon, 2012; Ethier et al., 2011; Pyle et al., 2008). Besides, crude glycerol can also be used to produce eicosapentaenoic acid (EPA) via fungal fermentation with *Pythium irregular* (Athalye et al., 2009). When *Pythium irregulare* was cultivated with 30 g/L of crude glycerol and 10 g/L of yeast extract, 90 mg/L of EPA was obtained with a productivity of 14.9 mg/L/day (Athalye et al., 2009) (Table 3).

4.6. Lipids

Various types of microorganisms such as microalgae, yeast, and fungi have been studied for lipid production from crude glycerol (Yang et al., 2012). Fifteen eukaryotic microorganisms were tested for their ability to convert crude glycerol to metabolic products. It was found that yeast accumulated lipids up to 22% (w/w), while fungi accumulated higher amounts of lipids (18.1%-42.6%, w/w) in their mycelia (Chatzifragkou et al., 2011). The fresh water microalga, *Chlorella protothecoides*, was shown to convert crude glycerol to lipids with a lipid yield of 0.31 g/g substrate (O'Grady and Morgan, 2011), or a lipid productivity of 3 g/L/day (Chen and Walker, 2011). The marine microalgae, *Schizochytrium limacinum* SR21, was found to grow faster on crude glycerol and accumulate high amounts of lipids (Liang et al., 2010b). For batch cultivation using crude glycerol derived from yellow grease, cell growth was significantly inhibited at crude glycerol concentrations as low as 35 g/L due to substrate inhibition and the presence of methanol. When using treated crude glycerol (10-fold by dilution and filtration with 0.2 μ m filter), the optimal substrate concentration was increased to 35 g/L and a high lipid content of 73.3% (w/w) was obtained (Liang et al., 2010b).

Generally, fed-batch operations obtained higher lipid production than batch operations, since the substrate inhibition can be effectively alleviated (Chen and Walker, 2011; Liang, et al., 2010a). Lipid production can be further improved by using a two-stage fed-batch operation. This strategy was demonstrated in a study of 12-day cultivation of *Cryptococcus curvatus* with crude glycerol derived from yellow grease. The two-stage fed-batch strategy achieved higher cell density (32.9 g/L) and lipid content (52%, w/w) than that obtained by the one-stage fed-batch operation (cell density of 31.2 g/L and lipid content of 44.2%, w/w) (Liang et al., 2010a) (Table 3).

4.7. Poly(hydroxyalkanoates) (PHA)

Pseudomonas oleovorans NRRL B-14682 and *Pseudomonas corrugata* 388 were found to produce polyhydroxybutyrate (PHB) (a type of PHA) and *mcl*-PHA, respectively, when cultivated in 1-5% (w/v) biodiesel-derived crude glycerol (Ibrahim and Steinbüchel, 2009). Later studies on glycerol-based PHA production mainly focused on PHB (Cavalheiro et al., 2009; Dobroth et al., 2011; Ibrahim and Steinbüchel, 2009). A process was designed for large-scale production of PHB with *Cupriavidus necator* DSM 545 (Cavalheiro et al., 2009). Cultivation conditions such as aeration rate and gas stream composition were found to be important for high cell densities and growth rates. Under optimal conditions, a final PHB productivity of 1.1 g/L/h and a PHB content of 50% (w/w) were obtained using crude glycerol. The molar mass of PHB was 790,000-960,000 g/mol (Cavalheiro et al., 2009) (Table 3).

A common issue in utilization of crude glycerol for PHB production is the inhibitory effect of high salinity on cell growth (Cavalheiro et al., 2009). In a study that used *Zobellella denitrificans* MW1, comparable productivity (1.09 g/L/h), and higher concentrations (up to 54.3 g/L) and content (66.9%, w/w) of PHB were obtained by fed-batch cultivation with optimized feeding of crude glycerol and ammonia (Ibrahim and Steinbüchel, 2009) (Table 3). More importantly, this performance was achieved in the presence of 20 g/L of sodium chloride, which makes it more attractive for large-scale production of PHB from crude glycerol (Ibrahim and Steinbüchel, 2009). Another issue is that sterile conditions were required for most of the studies of PHB production that used pure cultures. However, a concept of using mixed microbial consortia for PHA synthesis has been demonstrated using crude glycerol (Dobroth et al., 2011), and may be effective for PHB production. Compared to pure cultures, a mixed microbial consortia provides

an opportunity to further reduce energy inputs for maintaining axenic conditions (Dobroth et al., 2011).

4.8. Other products

The production of glycerol carbonate by dimethyl carbonate reaction with crude glycerol catalyzed via a heterogeneous lipase biocatalyst has been recently investigated (Tudorache et al., 2014). The reaction was sensitive to crude glycerol impurities, such as methanol and water. The methanol content showed a higher inhibition impact on glycerol carbonate yield than water content. After the removal of methanol and water, around 95.0 wt% relative yield (or 1.22 g glycerol carbonate/ g glycerol) was achieved from soybean oil-based crude glycerol compared to pure glycerol. The preliminary pretreatment of crude glycerol is necessary for the lipase-catalyzed production of glycerol carbonate, especially for crude glycerol with high contents of methanol and water.

A few bacteria such as *Enterobacter aerogenes*, *Citrobacter freundii*, *Klebsiella oxytoca*, and *Escherichia coli* were found to be able to convert crude glycerol to ethanol with concentrations of 10-25 g/L, yields of 0.20-0.47 g/g, and productivities of 0.20-0.83 g/L/h (Table 3). Some of them, such as *Klebsiella oxytoca*, also co-produced formic acid and lactic acid (up to 16.8 g/L) (Clomburg and Gonzalez, 2013).

5. Chemical conversion of crude glycerol to value-added products

Crude glycerol can also be chemically converted into many value-added products, such as acrolein, monoglycerides, polyglycerol, polyols, polyurethanes, solketal, lactic acid, and bio-oil, using catalysts. The impurities in crude glycerol can impact the value-added conversion process

and may participate in reactions as a reactant or catalyst for the production of chemicals and polymers, depending on the reaction mechanism.

5.1. Acrolein

The production of acrolein can be conducted in catalytically thermochemical processes via the dehydration reaction of crude glycerol. Most of the processes produced acrolein along with allyl alcohol, propylene, propionic acid, acetone, and other products. In a catalytic conversion of crude glycerol performed in a fixed-bed flow reactor at 350 °C under atmospheric pressure over $\text{ZrO}_2\text{-FeO}_x$ catalyst, only 4.6% (mol/mol) carbon (C) of acrolein was achieved, while 25.4 % (mol/mol) C of ketones and 24.1% (mol/mol) C of propylene were obtained (Konaka et al., 2013). In a gas-phase dehydration process, an aqueous solution of crude glycerol (20%, w/w) containing NaCl or Na_2SO_4 was fed directly to a fluidized bed, vaporized, and then reacted to form acrolein over a tungsten doped zirconia catalyst ($(\text{WO}_3)_{0.056}(\text{ZrO}_2)_{0.944}$ with DIKK trade name Z-1044) (Sereshki et al., 2010). As the temperature increased from 300 to 350 °C and the time increased from 4 to 42 h, the acrolein yield increased from 4 to 21% (w/w). When glycerol evaporated in the fluidized bed reactor, salts in the crude glycerol formed either a discontinuous layer on the surface of the catalyst particles or crystals independent of the catalyst (Sereshki et al., 2010). The salts could be easily detached from the catalyst with mechanical agitation to avoid accumulation in the reactor. This process demonstrated the potential of using crude glycerol containing salts for the production of acrolein. Recently, supercritical and subcritical water has been used as a reaction media for glycerol dehydration (Cheng et al., 2013). Using sulfuric acid as the catalyst, the highest acrolein yields of 56.0 % and 81.1% (mol/mol) were achieved from crude glycerol for supercritical (380 °C and 27.6 MPa) and subcritical water processes (335 °C

and 20.0 MPa), respectively. The subcritical water process is more favorable for the formation of acrolein than the supercritical water process due to its fewer side reactions and lower operating temperature. Additionally, under the subcritical water process, the acrolein yield (81.1%, mol/mol) from crude glycerol was comparable to that (84.9%, mol/mol) from refined glycerol, indicating that the interference from the low contents of methanol ($\leq 3.8\%$, w/w) and soap ($\leq 3.3\%$, w/w) in the crude glycerol were minimal (Cheng et al., 2013).

5.2. Monoglycerides and their derivatives

A few studies have investigated the production of monoglycerides by the glycerolysis of triglycerides with crude glycerol. Monopalmitin with a yield of about 60.8% (w/w) and a purity of about 62.6%, was prepared by the glycerolysis of palm stearin with crude glycerol under an optimum condition (Chetpattananondh and Tongurai, 2008). Both the yield and purity were comparable to those (yield: 65.4%, w/w; purity: 67.7%) of monopalmitin derived from pure glycerol and palm stearin (Chetpattananondh and Tongurai, 2008). The addition of a catalyst was unnecessary due to the residual alkaline in crude glycerol. Following a two-step process involving the removal of residual glycerol and crystallization, the purity of monopalmitin was increased significantly and reached up to 99.0% (Chetpattananondh and Tongurai, 2008). Recently, monoglycerides from soybean oil and crude glycerol were prepared along with diglycerides (Echeverri et al., 2011). The concentration of the produced monoglycerides varied with the type and content of the residual alkaline catalyst in the crude glycerol. Lower concentrations of monoglycerides were obtained with the samples of crude glycerol containing sodium methoxide than of those containing sodium hydroxide. A highest concentration of monoglycerides (about 42.0%, w/w) was obtained from crude glycerol with a low content of

remaining alkaline catalyst (2.7% (w/w) NaOH) (Echeverri et al., 2011). Additionally, the glycerolysis of crude fatty acid methyl esters with crude glycerol for monoglyceride production has also been investigated. The maximum monoglyceride yields were in the range of around 43.0-45.0% (w/w) for methyl esters from different oils such as soybean oil and castor oil (Echeverri et al., 2013a, 2013b).

Very recently, crude glycerol-based monoglycerides have been modified by maleinization to produce maleated soybean oil glycerides and maleated castor oil glycerides (Echeverri et al., 2015, 2013b, 2013c). These derivatives are important renewable precursors that can react with styrene via polymerization for the production of plastics (Echeverri et al., 2015).

5.3. Polyglycerol and polyols

Crude glycerol has been proven to be a promising feedstock for the production of polyglycerol and polyols. Polyglycerol contains high hydroxyl functionality. It is commonly synthesized by the polymerization of glycerol using an alkaline catalyst. Due to the presence of a residual alkaline catalyst and soap, crude glycerol can be directly used for the production of polyglycerol without the addition of a catalyst. Five samples of biodiesel-based crude glycerol with various soap contents and pH values were investigated to produce polyglycerol (Din et al., 2013). With an increase of soap content, the polyglycerol yield increased. The highest polyglycerol yield of about 94.9% (w/w) was obtained from crude glycerol containing 12.5% (w/w) soap.

In studies by Hu et al. (2015), Li et al. (2014), and Luo et al. (2013), a one-pot thermochemical process was used to successfully convert crude glycerol to polyols which had suitable properties for the production of polyurethane products such as foams and coatings. The use of a catalyst, such as sulfuric acid, was dependent on the composition of crude glycerol. For

crude glycerol with high soap content, sulfuric acid was added to convert soap into fatty acids for further esterification with glycerol. For crude glycerol with low soap content, no catalyst needed to be added as the residual soap in the crude glycerol catalyzed transesterification between glycerol and fatty acid methyl esters. The impurities, such as soap, free fatty acids, and fatty acid methyl esters participated in reactions and played important roles for the formation of polyols. Crude glycerol-based polyols were a mixture primarily consisting of monoglycerides, glycerol, and diglycerides. Under different reaction conditions, crude glycerol-based polyols had hydroxyl numbers ranging from around 350 to 500 mg KOH/g and acid numbers ranging from below detection limit to approximately 5 mg KOH/g (Hu et al., 2015; Li et al., 2014; Luo et al., 2013), showing a great potential for the production of polyurethane foams and coatings. Studies have demonstrated that the performance of polyurethane foams from crude glycerol-based polyols was comparable to that of some petroleum-based analogs (Li et al., 2014; Luo et al., 2013). The crude glycerol-based waterborne polyurethane coatings showed excellent adhesion to steel surfaces, good pencil hardness, but relatively low flexibility (Hu et al., 2015). The integration of petroleum-based polyether polyols with crude glycerol-based polyols was able to improve the flexibility of crude glycerol-based waterborne polyurethane coatings (Hu et al., 2015).

In addition, crude glycerol has been used to liquefy lignocellulosic biomass, such as soybean straw, corn stover, and bamboo residues for the production of polyols and polyurethane foams (Gao et al., 2010; Hu and Li, 2014; Hu et al., 2012b). The biomass conversion yields varied from 15.0 to 97.9% (w/w) with different liquefaction conditions (Hu and Li, 2014; Hu et al., 2012b). The polyols produced from the liquefaction of soybean straw and corn stover in crude glycerol and the resulting polyurethane foams exhibited properties comparable to those obtained from conventional petrochemical solvent-based liquefaction processes (Hu and Li, 2014; Hu et al.,

2012b). More importantly, certain impurities in crude glycerol, such as soap, fatty acids, and fatty acid methyl esters, improved the properties of biomass liquefaction-derived polyols and polyurethane foams due to their synergistic interactions with glycerol and/or biomass components (Hu et al., 2012b). These results suggested that the direct use of crude glycerol to liquefy lignocellulosic biomass for polyol production could potentially improve the economics and sustainability of liquefaction processes. Crude glycerol has also been used in the glycolysis of polyethylene terephthalate (PET) waste with diethylene glycol to produce polyols for high-performance polyurethane foams applications (Luo and Li, 2014).

5.4. Other products

Besides the above chemicals and polymers, other products such as solketal ((2,2-dimethyl-1,3-dioxolan-4-yl) methanol), lactic acid, and bio-oil have also been produced from crude glycerol. Currently, two types of catalysts have been developed and tested for the acetalization of crude glycerol to produce solketal, including sulfonic acid-functionalized mesostructured silicas (Vicente et al., 2010) and niobium oxyhydroxide catalysts (Souza et al., 2014). Salts in crude glycerol were found to have significantly negative impacts on the acetalization reaction catalyzed by niobium oxyhydroxide catalysts. Only 13.0% (w/w) of glycerol conversion was obtained in the presence of niobium oxyhydroxide catalysts. After the removal of sodium chloride in crude glycerol, the glycerol conversion was increased to 58.0% (w/w) (Souza et al., 2014). When sulfonic acid-functionalized heterogeneous catalysts were used, 81.0% (w/w) of glycerol conversion was obtained (Vicente et al., 2010). However, high sodium contents in crude glycerol can deactivate the sulfonic acid sites. The acidification of the catalyst is needed for its regeneration to achieve high glycerol conversion.

A study reported the production of lactic acid from crude glycerol using CaO as a solid base catalyst (Chen et al., 2014). The highest yield of lactic acid achieved was 52.3% (w/w) under optimum conditions with crude glycerol containing less than 10% (w/w) water. This yield was even higher than that (40.8%, w/w) obtained from refined glycerol under the same reaction conditions. The alkali residue in crude glycerol most likely helped improve the lactic acid yield. However, when the water content in crude glycerol was 10% (w/w) or higher, the lactic acid yield significantly decreased, as water reacted with CaO forming Ca(OH)_2 , which has lower alkalinity than that of CaO (Chen et al., 2014).

Bio-oil has also been produced by co-pyrolysis or co-liquefaction of crude glycerol with biomass such as swine manure and corn straw (Delgado et al., 2013; Xiu et al., 2011, 2010; Ye et al., 2012). With an increase of crude glycerol loading from 0 to 75% (w/w), the bio-oil yield was increased from approximately 40 to 70% (w/w) and from about 25 to 68% (w/w) under the co-pyrolysis of crude glycerol with corn straw (Delgado et al., 2013) and the co-liquefaction of crude glycerol with swine manure (Xiu et al., 2010), respectively. The increased yield of bio-oil was mainly ascribed to non-glycerol organic matter such as fatty acids in crude glycerol. Table 4 summarizes the yield of chemicals and polymers mentioned above with production processes and using crude glycerol as feedstock.

6. Strategies to address challenges

Despite the significant potential of the direct conversion of crude glycerol into value-added products, most of the technologies discussed above still face many challenges for industrial applications, such as low product yield and productivity and impacts of impurities in crude

glycerol on the performance of some products. Strategies need to be developed to overcome these hurdles.

6.1. Genetic engineering of strains for improved yield

Various by-products are normally generated during fermentation processes with natural strains, resulting in decreased yield of target products, which can be addressed by genetic engineering of strains. For example, in order to improve the 1,3-propanediol yield, studies have been conducted to identify major byproducts and to inactivate or eliminate enzymes responsible for the production of byproducts. Using this strategy, 1,3-propanediol yields of up to 0.7 mol/mol pure glycerol have been achieved using engineered *Klebsiella pneumoniae* (Lee et al., 2015). The best performance in production of 1,3-propanediol from crude glycerol was obtained using the strain *C. butyricum*, which was a wild type isolated from soil samples at Braunschweig, Germany (Wilkens et al., 2012). Further studies could be conducted on genetic engineering of *C. butyricum* for better performance of 1,3-propanediol production from crude glycerol.

6.2. Process design for high product concentration

For those products, such as n-butanol, that inhibit cell growth or conversion processes, it is desirable to maintain a low concentration of the product in reactors. A strategy that combines butyrate addition and *in situ* butanol removal via membrane distillation has been proposed to improve butanol fermentation with *Clostridium pasteurianum* CH4 (Lin et al., 2015). The inhibition from high butanol concentration was avoided by *in situ* removal of butanol using vacuum membrane distillation (VMD). The butanol yield was increased from 0.24 to 0.39 mol/mol glycerol, with a butanol production rate of 0.29 g/L/h and a high butanol concentration

of 29.8 g/L in the permeate of VMD (Lin et al., 2015). A gas stripping pervaporation process is also promising for improving butanol titer by *in situ* butanol recovery, and has obtained ABE containing 75.5 g/L butanol with a butanol productivity of 0.34 g/L/h using glucose as a carbon source (Xue et al., 2016). Although *in situ* butanol recovery strategies have been successfully used to reduce butanol inhibition during butanol fermentation from pure glycerol or glucose, its effectiveness in improving butanol production from crude glycerol still needs further evaluation.

Dissolved oxygen levels are a major factor that influences the DHA production. Low levels of dissolved oxygen resulted in lower biomass concentration, but higher DHA content. Therefore, a two-stage cultivation strategy has been proposed to supply sufficient oxygen for cell growth in the early stage of fermentation, followed by limited oxygen supply in the late stage for improved DHA yield (Rosa et al., 2010). However, this strategy has only been demonstrated for DHA production from pure glycerol. As a result, DHA production from crude glycerol could be further improved by using the two-stage cultivation strategy.

6.3. Strategies for addressing the impurity issues

Depending on the conversion mechanism of crude glycerol, the impurities have either positive or negative impacts on the production processes of value-added products. For some alkaline catalyzed processes, the residual alkaline and soap in crude glycerol can be used as catalysts to improve the conversion of glycerol without the addition of other catalysts. In contrast, for some biological processes, impurities in crude glycerol, such as soap, methanol, and salts, can inhibit cell and fungal growth and result in low productivity. For some chemical and biological catalytic processes, the impurities can reduce the activity of both chemical catalysts and enzyme biocatalysts, causing low product yield. Three strategies have been developed to address the

impurities issues, including the design of robust chemical and enzyme catalysts, simple pre-treatment prior to the processing, and the development of new technologies that effectively utilize the impurities in crude glycerol. The latter strategy is very attractive for the cost-effective production of some highly valuable products. Through this strategy, monoglycerides and their derivatives and polyols have been recently developed from crude glycerol (Chetpattananondh and Tongurai, 2008; Echeverri et al., 2015, 2013a, 2013b, 2013c, 2011; Hu et al., 2015; Li et al., 2014; Luo and Li, 2014; Luo et al., 2013).

6.4. Strategies for multi-objective optimization

Multiple and conflicting objectives appear frequently in catalytic processes, which challenges the process optimization. Several techniques, such as weighted-sum method, goal attainment method, normal-boundary intersection method, multi-objective indirect optimization method, and multi-objective evolutionary algorithm, have been studied for multi-objective optimization. Recently, the weighted-sum and normal-boundary intersection methods were used to simultaneously optimize any two of four objectives (production rate of 1,3-propanediol, conversion rate of glycerol to 1,3-propanediol, conversion rate of glycerol, and concentration of by-product ethanol) for continuous bio-dissimilation process of glycerol to 1,3-propanediol (Xu et al., 2016). It was found that the normal-boundary intersection methods can successfully solve all proposed multi-objective problems (Xu et al., 2016). The above mentioned methods should be promising for multi-objective optimization in conversion of crude glycerol to value-added products.

7. Conclusions

Crude glycerol not only can be refined to high-purity glycerol, which is a versatile raw material for various applications, but also can be directly converted into value-added chemicals and polymers via biological and chemical pathways. Industrial applications of direct utilization of crude glycerol could be hindered due to low product yield and productivity and the impact of impurities. However, these issues may be addressed by strategies, such as genetic engineering of strains, process optimization, design of robust chemical and enzyme catalysts, simple pre-treatment prior to processing, and the development of new technologies that effectively utilize the impurities of crude glycerol.

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792 **Figure Captions**

793 **Fig. 1** A general refining process of crude glycerol

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798 Table 1 Chemical compositions of crude glycerol from various sources

Sources of crude glycerol		Glycerol	Methanol	Soap	MONG ^a	Reference
Feedstock	Catalyst (w/w)	(w/w)	(w/w)	(w/w)	(w/w)	
Soybean oil	KOH ^c	62.0 %	12.8 %	25.2 %	n/a	Pyle et al., 2008
Chicken fat/Soybean oil (50/50, w/w)	KOH ^c	62.3 %	14.4 %	23.2%	n/a	Pyle et al., 2008
Canola oil	NaOH ^c	56.5 %	28.3 %	15.3 %	n/a	Pyle et al., 2008
Sunflower oil	0.5 % NaOH	75.0 % ^d	1.0 %	9.3 %	n/a	Rehman et al., 2008
Sunflower oil	0.5 % NaOH	90.0 % ^d	<1.0 %	n.d. ^e	n/a	Rehman et al., 2008
Seed oils ^f	3.8-4.2 % NaOCH ₃	62.5-76.6%	n/a	n/a	n/a	Tan et al., 2013
Soybean oil	n/a	63.0 %	6.2 %	n.d.	n.d.	Hu et al., 2012a
Soybean oil	n/a	22.9 %	10.9 %	26.2 %	23.5 %	Hu et al., 2012a
Soybean oil	n/a	33.3 %	12.6 %	26.1 %	22.3 %	Hu et al., 2012a
Waste vegetable oil	n/a	27.8 %	8.6 %	20.5 %	38.8 %	Hu et al., 2012a
Jatropha oil	n/a	18.0-22.0 %	14.5 %	29.0 %	11.0-21.0 %	Hiremath et al., 2011
Palm oil	n/a	80.5 %	0.5 %	n/a	<2.0 %	Liu et al., 2013

799 Note: ^a MONG: matter organic non-glycerol; ^b n/a: not available; ^c The detailed catalyst loading is not available; ^d
800 Crude glycerol was pre-treated by phosphoric acid; ^e n.d.: not detected; ^f Seed oils include Ida Gold Mustard, Pacific
801 Gold Mustard, rapeseed, canola, crambe, and soybean, and waste cooking oils.
802

807 Table 2 Comparison of four deep refining technologies

Technology	Advantages	Disadvantages	Purity of refined glycerol (w/w)
Vacuum distillation	Simple and wide adaptability; Applicable for small to large-scale continuous operation; High quality glycerol	Intensive energy requirement; Temperature sensitive to feed steam variations	94-96.6%
Ion exchange	Low energy input; Suitable for small- and medium-sized plants	Generation of pollutant waste water; Strict requirement for salt content in crude glycerol; High cost for resin reuse	95-99% (Technical grade)
Membrane separation	Low energy requirement; Easy to control and set up unit; Environment compatibility; Various membrane materials	Fouling and durability issues of membranes; Lack of suitable membranes for specific operations	~99.0% (Technical grade)
Activated carbon adsorption	Easy to operate; Efficient color reduction	Inefficient for the removal of other impurities, such as oleic acid and stearic acid	~99.7% (USP & FCC-grade)

808 *Note:* Food Chemical Codes (FCC); United States Pharmacopeia (USP); Technical grade has not been exactly
809 defined, mostly > 96.0%.

Table 3 Biological conversion of crude glycerol into value-added products

Product	Strain/Biocatalyst	Concentration (g/L)	Yield (g/g)	Productivity (g/L/h)	References
1,3-propanediol	<i>Klebsiella oxytoca</i> ; <i>Klebsiella pneumoniae</i> ; <i>Clostridium butyricum</i> ; <i>Lactobacillus diolivorans</i>	21 - 83	0.39 - 0.70	0.45 - 3.4	Hiremath et al., 2011; Wilkens et al., 2012; Pflügl et al., 2014; Szymanowska-powalowska, 2014; Lee et al., 2015
n-butanol ^a	<i>Clostridium pasteurianum</i>	6 - 12	0.19 - 0.44	0.03 - 0.15	Ahn et al., 2011; Kao et al., 2013; Gallardo et al., 2014
2,3-butanediol	<i>Klebsiella oxytoca</i> ; <i>Klebsiella pneumoniae</i> ; <i>Bacillus amyloliquefaciens</i>	43 - 132	0.39 - 0.44	0.45 - 0.84	Petrov and Petrova, 2010; Yang et al., 2013; Cho et al., 2015
Citric acid	<i>Yarrowia lipolytica</i> ; <i>Clostridium butyricum</i>	63 - 154	0.56 - 0.78	0.10 - 1.05	Papanikolaou et al., 2008; Rywińska and Rymowicz, 2010
DHA	<i>Schizochytrium limacinum</i>	2 - 5	-	0.026 - 0.038	Pyle et al., 2008; Ethier et al., 2011; Abad and Turon, 2012
EPA	<i>Pythium irregular</i>	0.090	-	6.21×10^{-4}	Athalye et al., 2009
Lipid	<i>Cryptococcus curvatus</i> ; <i>Chlorella protothecoides</i>	-	0.31	0.06 - 0.13	Liang et al., 2010a; Chen and Walker, 2011; O'Grady and Morgan, 2011
PHB ^b	<i>Zobellella denitrificans</i> ; <i>Cupriavidus necator</i>	-	-	1.09 - 1.10	Cavalheiro et al., 2009; Ibrahim and Steinbüchel, 2009
Glycerol carbonate	Lipase-magnetic particle	-	1.22	-	Tudorache et al., 2014
Ethanol	<i>Enterobacter aerogenes</i> ; <i>Citrobacter freundii</i> ; <i>Klebsiella oxytoca</i> ; <i>Escherichia coli</i>	10 - 25	0.20 - 0.47	0.20 - 0.83	Clomburg and Gonzalez, 2013

Note: ^aDual-substrates containing 25 g/L sugarcane bagasse and 60 g/L biodiesel-derived crude glycerol were used in Kao et al. (2013); ^b Molar mass was 790,000-960,000 g/mol in Cavalheiro et al. (2009). DHA: docosaheptaenoic acid; EPA: eicosapentaenoic acid; PHB: polyhydroxybutyrate.

Table 4 Chemical conversion of crude glycerol into chemicals and polymers

Product	Pathway	Feedstock	Glycerol content in CG (w/w)	Catalyst	Product yield (w/w)	Reference
Acrolein	Dehydration, a fixed-bed flow reactor	CG ^a	37.0 %	ZrO ₂ -FeO _x	0.05-3.12 %	Konaka et al., 2013
	Dehydration, a fluidized bed	CG	n/a	A tungsten doped zirconia catalyst	4-21 %	Sereshki et al., 2010
	Super-critical water process	CG	91.7 %	Sulfuric acid	15.7-31.3 %	Cheng et al., 2013
	Sub-critical water process	CG	91.7%	Sulfuric acid	37.2-45.3 %	Cheng et al., 2013
Monoglycerides	Glycerolysis	Palm stearin, CG, (Glycerol/palm stearin: 2.5/1, mol/mol)	70.0 %	- ^b	60.8 %	Chetpattananondh and Tongurai, 2008
	Glycerolysis	Soybean oil/castor oil, CG, (Glycerol/oil: 2.5/1, mol/mol)	88.1-90.1 %	-	18.0-50.4 %	Echeverri et al., 2011, 2013b
	Glycerolysis	Crude methyl esters, CG, (Crude methyl ester/CG: 1.5/1, mol/mol)	88.1 %	-	35.0-45.0 %	Echeverri et al., 2013a, 2013b
Maleated glycerides	Maleinization	CG-based glycerides and maleic anhydride with a weight ratio from 4/3 to 3/2	88.1 %	-	80.2-94.8 % ^c	Echeverri et al., 2013b, 2013c, 2015
Polyglycerol	Polymerization	CG	75.1-93.4 %	-	5.0-94.9 %	Din et al., 2013
Polyols	One-pot thermochemical process	CG	22.9 %	Sulfuric acid	67.9 %	Luo et al., 2013

Solketal	Liquefaction	Soybean straw/Corn stover/Bamboo residues, CG (biomass loading: 20-40 wt%)	39.0-75.0 %	Sulfuric acid/Sulfuric acid-NaOH	15.0-97.9 % ^d	Gao et al., 2010; Hu et al., 2012b; Hu and Li, 2014
	Glycolysis	PET, DEG, CG (PET/DEG:1:2, nol/mol; CG loading: 30-100 wt%)	22.9 %	Titanium isopropoxide	60.5-69.8 %	Luo and Li, 2014
	Acetalization	Acetone and CG with a molar ratio of 6/1	85.8 %	Sulfonic acid-modified heterogeneous catalyst	81.0 % ^e	Vicente et al., 2010
	Acetalization	Acetone and CG with a molar ratio of 2/1	77.0 %	niobium oxyhydroxide catalysts	13.0-58.0 % ^e	Souza et al., 2014
Lactic acid	Thermochemical process	CG	20.4-88.5 %	CaO	3.7-34.9 %	Chen et al., 2014
Bio-oil	Co-pyrolysis	Corn straw and CG with corn straw loading from 0 to 100 wt%	56.2 %	-	~40-70 %	Delgado et al., 2013
	Co-liquefaction with swine manure	Swine manure and CG with swine manure loading from 0 to 100 wt%	<55.1 %	-	25-68 %	Xiu et al., 2010

Note: ^a CG: crude glycerol; ^b no catalyst was used; ^c the conversion of hydroxyl groups; ^d the conversion of biomass; ^e the glycerol conversion.

Fig. 1