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ORIGINAL PAPER

Electrochemical reforming of an acidic aqueous glycerol solution on Pt electrodes

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Abstract The feasibility of the electrochemical conversion of glycerol to alternative, more valuable compounds was evaluated with platinum electrode under galvanostatic conditions. The results indicated a potentially good feasibility of reforming glycerol by electrolysis, particularly under strong acidic conditions (pH 1). Indeed, under controlled conditions at pH 1, various commercially valuable compounds, such as propanediol, glycidol, and 2-propenol, amongst others, were produced. The mechanism for the generation of the key compounds is proposed.

Keywords Value-added glycerol · Reforming · Electrochemical technique · Pt electrode · Propanediol

1 Introduction

Glycerol, also called glycerin or glycerine, is an organic, colorless, odorless, and viscous liquid that is widely used in various industries. For example, glycerol serves as a humectant, solvent, and sweetener in the foods and beverages industry, as a filler in commercially prepared low-fat foods (e.g., cookies) and as a thickening agent in liqueurs. It is also used to manufacture mono- and di-glycerides for use as emulsifiers, as well as polyglycerol esters for use as shortenings and margarine. In addition, it can be used as a raw material in the cosmetic and pharmaceutical industries, as well as in other more minor uses. Since glycerol forms the backbone of triglycerides, it can be produced by saponification of animal fats in the soap production industry, and also as a by-product from the transesterification reaction of triglycerides from vegetable oils or fats with alcohols (typically in the presence of a homogenous base catalyst) to produce biodiesel [1]. Currently, the world's capacity for biodiesel production has increased dramatically, and this is also the case in Thailand where a fourfold increase from less than 2.1×10^6 L day^{-1} in 2008 to an expected 8.4×10^6 L day^{-1} in 2012 is predicted [2]. Note that the production of 10 kg of biodiesel yields approximately 1 kg of crude glycerol [3], and so any further increase in biodiesel production rates would raise the quantity of crude glycerol surplus in the environment and further reduce its market value.

Many processes have been developed to make value-added glycerol-based products. For example, biofermentation was used to convert glycerol to either docosahexaenoic acid by *Schizochytrium limacinum* [4] or to ethanol and co-products by *Escherichia coli* [5]. High-temperature and high-pressure catalytic processes have been used to produce gaseous hydrogen using a diverse array of catalysts, including platinum (Pt) [6, 7], Pt/WO_3/ZrO_3 [8], Ni/ZrO_2 [9], Ni catalysts supported on ceria oxide (CeO_2) and ceria-promoted alumina (Al_xCe, $x = 5$, 10 or 15), Al_2O_3 [10], and Pt-based catalysts supported on a diverse array of metal oxides, such as Al_2O_3, ZrO_2, MgO, and CeO_2 [11]. In addition, glycerol has been converted to (i) acrolein by a zeolite-based catalyst [12] or by HSiW/C [13]; (ii) to acrylic acid with a mixed acid catalyst (FeP, Mo_3VO, and W_3VO) [14]; (iii) to acetol or 1-hydroxypropan-2-one over Na-doped CeO_2, Al_2O_3, ZrO_3, or Ga_2O_3 [15]; (iv) to fuel additives, such as di-tert-butylglycerols

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and tri-tert-butylglycerol, by sulfonic-acid-functionalized mesostructured silicas [16]; and finally, (v) to propanediol by Ru/Al_2O_3 and Ru/ZrO_2 [17], Ru/C [18], $Pt/WO_3/ZrO_2$ [19, 20], Ru/SiO_2 and $Ru–Re/SiO_2$ [21], Ru/TiO_2 [22], $Ir\text{-}ReO_x/SiO_2$ [23], and Pt/ASA [24] catalysts. However, many of these processes have drawbacks, such as the lack of sufficient selectivity and yield, or these processes requiring specialized or high running-cost production systems (e.g., high temperature and pressure) or requiring a long reaction time, which prevent them from being commercially viable. Against this, the in-depth research and development of glycerol conversion to high value products has largely not been conducted because of glycerol's historically high price. To overcome the drawbacks of the conventional catalyst and biological conversion, and to facilitate the commercial conversion of glycerol to valuable compounds, the electrochemical technique was evaluated as an alternative method that might be used to convert glycerol waste from the biodiesel industry to valuable alternative compounds. This is because of its relative simplicity and robustness in structure and operation. However, very little information on the electrochemical technique for glycerol reforming is currently available. A one-pot electrocatalytic oxidation has been reported to be effective in the synthesis of 1,3-dihydroxyacetone in a basic solution in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl [25], where prolonging the reaction time afforded comparable amounts of hydroxypyruvic acid. For gaseous chemicals, a high production rate of H_2 was obtained when using electrochemical reforming of an aqueous glycerol solution in a PEM electrolysis cell compared to that obtained with comparable sized microbial cells [26]. In this article, the electrochemical technique was used to reform glycerol in an acidic aqueous glycerol solution with a Pt electrode. The product distribution and their production mechanisms are proposed.

2 Experimental

2.1 Chemical substances

The aqueous glycerol solution was prepared from a commercial glycerol stock [99.5% (v v^{-1}), Fisher] at a constant concentration of 0.5 M, with the pH set using analytical grade H_2SO_4 (98%, Mallinckrodt).

2.2 Polarization curve

The possibility of electrochemical reforming of an aqueous glycerol solution was first explored using a rotating electrode with a Potentiostat/Galvanostat (Auto Lab, model PG stato) and with a Pt sheet, a Pt rod with a total surface area of 0.79 cm^2, and a Ag/AgCl electrode as the counter-, working- and reference electrodes, respectively. The evaluation was performed at three pH values within the acidic range (pH 1, 3.5, and 6). The scan potential was varied in the range from $+2{,}000$ to $-2{,}000$ mV with a scan rate of 5 mV s^{-1}. Before the start up of the experiment, the aqueous glycerol solution was purged with gaseous N_2 for 20 min to decrease the oxygen concentration in the electrolyte solution. In each trial, the system was agitated by a magnetic stirrer at a constant rate of 400 rpm.

2.3 Electrochemical system

The electrochemical reforming of glycerol was performed at a laboratory bench-scale at ambient temperature (around 30 °C) and pressure. The electrochemical reactor was comprised of a coaxial cylindrical electrochemical cell made from Pyrex glass and having a total capacity of 0.5 L. Two Pt grids in a cylindrical shape, with a total surface area of 66.49 and 124.34 cm^2 were used as the anode and cathode, respectively. The temperature of the electrolytic cell was controlled by a cooling system, and to achieve a good mass transfer in the system, a magnetic bar was used to stir (400 rpm) the electrolyte in the electrolytic cell. A regulated DC power supply (ZS 3205-2X type) was employed to supply the external electricity at a galvanostatic mode (4.5 A).

2.4 Analytical methods

The chemical compounds generated in the electrochemical reactor were analyzed by gas chromatography equipped with flame ionization detector (G3174A, Agilent) and analyzed with the Hewlett–Packard Chemstation software. A metal capillary column coated with polyethylene glycol and immobilized by chemical crosslinking (inside diameter 0.25 mm, 0.25 μm film thickness) was utilized. The flow rate of the carrier gas (He) was 1.5 mL min^{-1} at the capillary column, maintained by means of a splitter.

3 Results and discussion

3.1 Polarization curve

The current density–potential curve of the aqueous glycerol solution at the three different pH values in the acidic range, obtained by a rotating disk electrode, revealed that the oxidation–reduction peaks of glycerol were not observed in the weakly acidic pH 6 solution (Fig. 1), and so this is not discussed further. However, the oxidation–reduction peaks

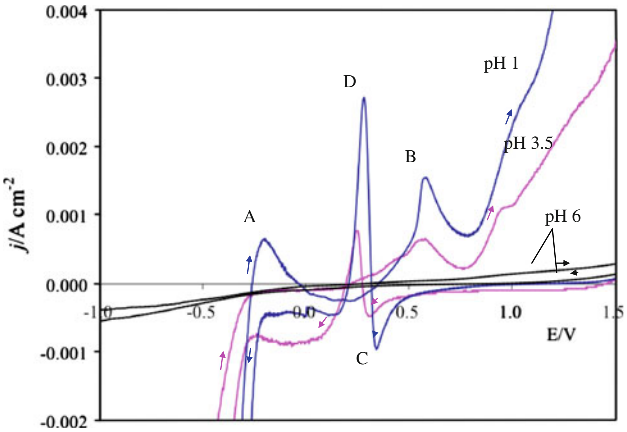


Fig. 1 Polarization curves of glycerol solutions at three different pH values (1, 3.5, and 6), evaluated with a Pt electrode at a stirring rate of 400 rpm and a scan rate of 5 mV s^{-1} with a Ag/AgCl reference electrode

of glycerol were clearly observed in the two strong acid solutions (pH 1 and 3.5) (Fig. 1). For the forward sweep, two oxidation peaks (peaks A and B) were observed in the pH 1 solution, whereas only one oxidation peak was observed (peak B) at pH 3.5. In addition, the observed peak B obtained in the pH 1 solution was higher than that observed in the pH 3.5 solution and was also shifted to a slightly more positive potential. The maximum oxidation potential of these two acidic (pH 1 and 3.5) glycerol solutions, the potential that provides the highest current density, were around 0.59 and 0.57 V, corresponding to current densities of 1.5 and 0.64 mA cm^{-2}, respectively. The difference might be attributed to the different proton concentrations according to the Nernst's Equation. In contrast, during the forward sweep, the peak shapes were practically the same in each of the two different pH glycerol solutions, with a single reduction (peak C) and oxidation (peak D) peak. Rather, the principal differences between the pH 1.0 and 3.5 glycerol solutions were the oxidation–reduction peak potentials and the current densities, where the maximum oxidation peaks were observed at 0.28 and 0.285 V, respectively, corresponding to a current densities of 2.7 and 1.0 mA cm^{-2}, respectively. For the reduction peaks, the maximum potential of the pH 1 glycerol solution was observed at 0.034 V, which is significantly higher than that seen at pH 3.5 (around 0.004 V), while the intensity of the current was some twofold higher in the pH 1 solution than that seen in the pH 3.5 solution. According to the polarization curve, it is clear that the oxidation–reduction of glycerol was principally observed under very strong acid conditions. Therefore, the products derived from glycerol reforming by the electrochemical technique were further explored at a solution pH of 1 and not 3.5.

3.2 Potentially commercially valuable compounds and their production mechanisms

From the GC/MS spectra of the pH 1 glycerol solution in the absence of electrolysis (Fig. 2a), three chemical species were observed, namely 1-hydroxyl-2-propanone (acetol), acrylaldehyde (acrolein), and 2-propene. On the other hand, after electrolysis under otherwise the same conditions, at least 17 other (valuable) compounds were detected, such as 1-hydroxyl-2-propanone, acrylaldehyde, acetaldehyde, 2-propenol, 2,3-dihydroxyl-propanal, 5-hydroxy-1,3-dioxolane, 1,2-propanediol, 1,3-dioxolane-4-methanol-2-ethyl, 1,3-dioxolane-2-methyl, propene, 1,3-propanediol, ethylene glycol, formic acid, propanoic acid, glycidol, and xylitol (Fig. 2b). Some of these compounds have a higher market value compared with crude glycerol (0.04 USD lbs^{-1}) [27] and also have a high market capacity and application in various industries, as listed in Table 1.

Compared to glycerol, all of these formed compounds have many hydrogen and oxygen substitutions with C_2 to C_6 carbon compounds being principally formed. While some of these compounds have known reaction pathways from glycerol, others do not. To optimize or standardize the electrochemical reforming of glycerol, it is important to know, and so to evaluate, the mechanisms of synthesis of these valuable compounds from glycerol. However, it is still difficult to deduce the exact synthesis route of each compound from glycerol by electrolysis in an acid solution. Rather, a hypothetical general scheme (Scheme 1) can be proposed with some paths more or less possible for each studied system. According to this scheme, the reforming of glycerol under strong acidic (pH 1) conditions, both in the presence and in the absence of electricity, can be classified into three main routes: (i) acid protonation and hydration, (ii) direct oxidation with electricity, and (iii) oxidation with hydroxyl radicals ($OH^{\bullet}$) that are generated by the adsorption of water on the electrode surface (M), as demonstrated in Eq. 1 [30].

$$\boldsymbol{M} + H_2O \rightarrow \boldsymbol{M}(OH^{\bullet})_{ads} + H^+ + e^- \qquad (1)$$

All routes lead to the formation of an identical carbon molecule intermediate species. Subsequent changes to other chemical compounds can include to smaller carbon compounds by breaking of the C–C bond or to larger carbon compounds by isomerization.

In the absence of electricity, either the 1°- or 2°-alcohol group of glycerol can be dehydrated and consequently protonated to form two types of intermediates; either 2,3-dihydroxypropene or 1,3-propenediol or 3-hydroxypropanal, the latter two of which rapidly rearranges to 1-hydroxyl-2-propanone and acrylaldehyde, respectively. These two species can also be produced by the electrochemical reforming of glycerol in an acidic aqueous

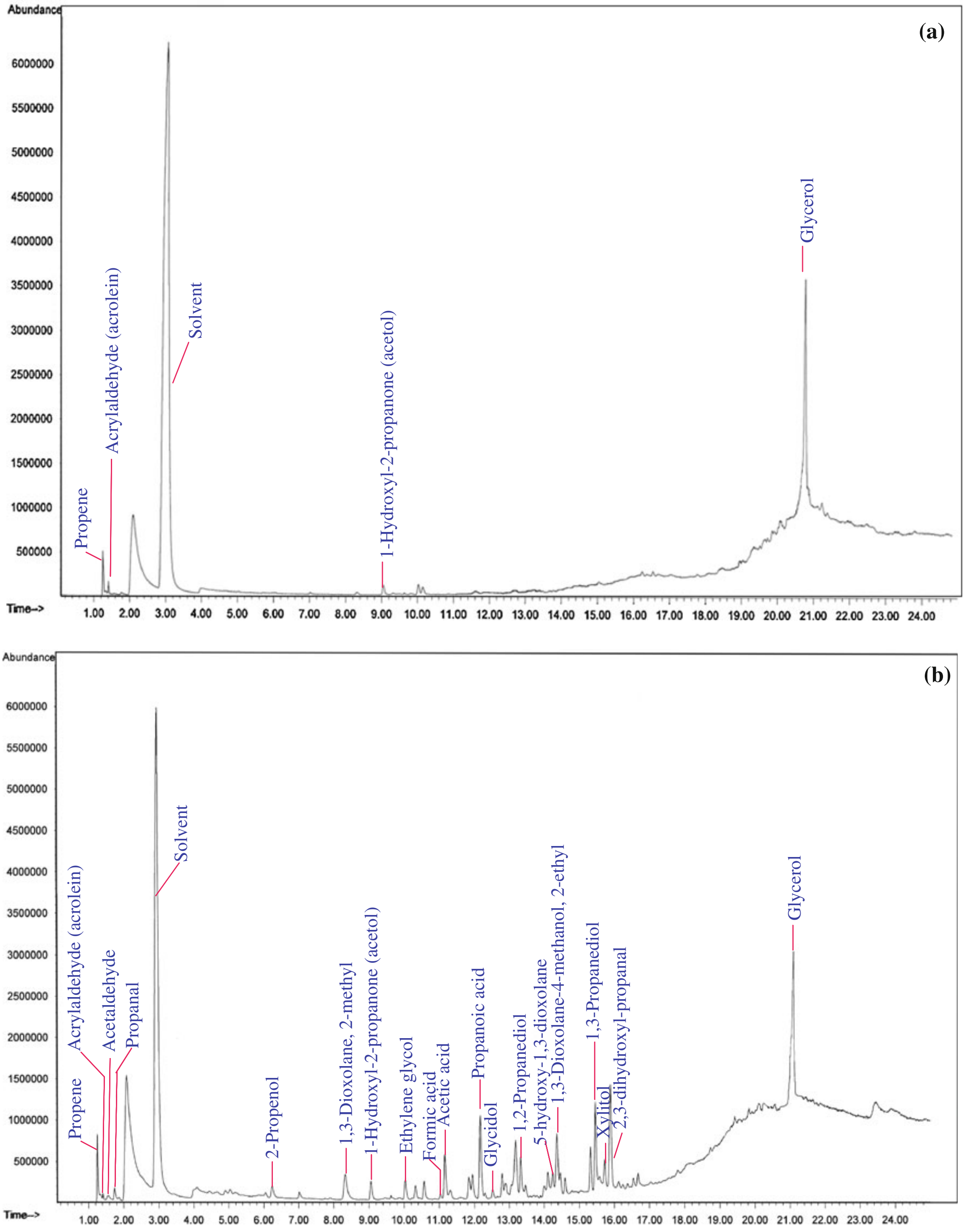


Fig. 2 Representative GC/MS spectra of glycerol solution at pH 1 in **a** the absence of electricity and **b** after electrolysis at a current of 4.5 A for 6 h

solution. Namely, when the electricity was applied, $OH^{\bullet}$ radicals produced from the oxidation reaction of H_2O on the Pt electrode can extract the H atom of the –OH group at the C_1 or C_2 position of the glycerol molecule and consequently, through dehydration, lead to the formation of two enol intermediate species that rapidly rearrange to acrylaldehyde and 1-hydroxyl-2-propanone, respectively. These two species are themselves very reactive. Acrylaldehyde can be dehydrated further to propene or hydrolyzed, protonated, and reduced to 1,3-propanediol, while 1-hydroxyl-2-propanone can be rearranged to the more stable propanoic acid, dehydrated to propanal, or protonated

Table 1 List of compounds generated from glycerol reforming by the electrochemical technique under strong acidic conditions

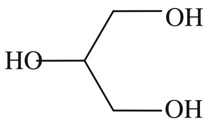
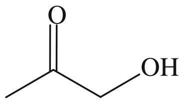
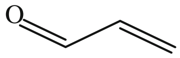
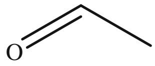
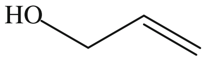
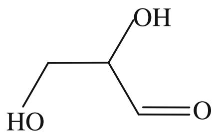
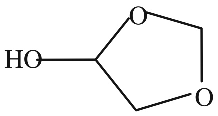
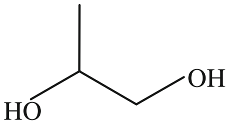
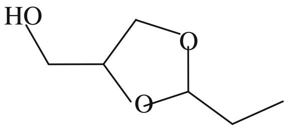
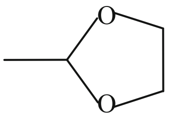
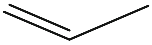
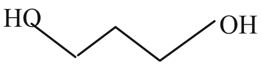
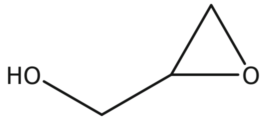
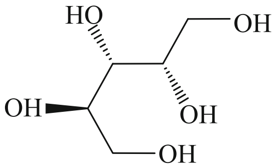
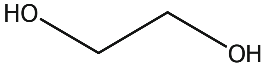
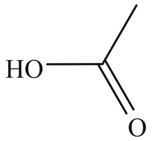
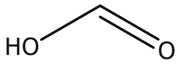
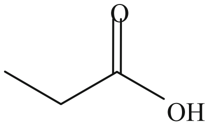
IUPAC name	Other names (Molecular formula)	Chemical structure	USD lbs^{-1} (Purity, %) [28, 29] [CAS no.]
Propane-1,2,3-triol ($C_3H_8O_3$)	1,2,3-Propanetriol or Glycerol		3.95 (>99.5%)^{a} 0.36 (99.5%)^{b} 5.47 (>99.5%)^{c} [56-81-5]
1-Hydroxypropan-2-one ($C_3H_6O_2$)	1-Hydroxyl-2-propanone or Acetol		N/A [111-09-6]
Prop-2-enal (C_3H_4O)	Acrylaldehyde or Acrolein		393.57 (>95%)^{a} [107-02-8)]
Acetaldehyde (C_2H_4O)	Ethanal		222.85 (>99%)^{c} [75-07-0]
Prop-2-en-1-ol or Allyl alcohol (C_3H_5O)	2-Propenol		1.37 (99.5%)^{b} [107-18-6]
Propionaldehyde (C_3H_6O)	Propanal		161.24 (>97%)^{a} [123-38-6]
2,3-Dihydroxyl-propanal ($C_3H_6O_3$)	Glyceraldehyde		1,2061.45 (>95%)^{a} [56-82-6]
1,3-Dioxolan-2-ol ($C_3H_6O_3$)	Hydroxy-1,3-dioxolane		N/A N/A
Propane-1,2-diol ($C_3H_8O_2$)	Propylene glycol or 1,2-Propanediol		4.77 (>99.5%)^{a} 0.52 (99.5%)^{b} 4.97 (>99%)^{c} [57-55-6]
2-Ethyl-1,3-dioxolan-4-yl) methanol ($C_6H_{12}O_3$)	2-Ethyl-1,3-dioxolane-4-methanol		N/A N/A
2-Methyl-1,3-dioxolane ($C_4H_8O_2$)	Acetaldehyde ethylene acetal		N/A [89579-87-3]
Propene (C_3H_6)	Propylene		0.46^{d} [115-07-1]
Propane-1,3-diol ($C_3H_8O_2$)	Trimethylene glycol or 1,3-Propanediol		102.34 (>98%)^{a} [504-63-2]

Table 1 continued

IUPAC name	Other names (Molecular formula)	Chemical structure	USD lbs^{-1} (Purity, %) [28, 29] [CAS no.]
Oxiranylmethanol ($C_3H_6O_2$)	2,3-Epoxy-1-propanol or Glycidol		233.24 (>95%)[a] [556-52-5]
(*2R,3R,4S*)-Pentane-1,2,3,4,5-pentol ($C_5H_{12}O_5$)	1,2,3,4,5-Pentahydroxypentane or Xylitol		15.21 (>98.5%)[a] 18.52 (98.%)[d] [87-99-0]
Ethane-1,2-diol ($C_2H_6O_2$)	Ethylene glycol		0.84 (99.9%)[b] 2.96 (99%)[c] [107-21-1]
Acetic acid ($C_2H_4O_2$)	Ethanoic acid		0.70 (99.8%)[b] 27.49 (>99.7) [64-19-7]
Formic acid or Methanoic acid (CH_2O_2)	Hydrogen carboxylic acid		0.64 (85%)[b] 2.76 (>96%)[c] [64-18-6]
Propanoic acid ($C_3H_6O_2$)	Ethanecarboxylic acid		1.20 (99%)[b] 11.68 (>99.5%)[c] [79-09-4]

[a] Natural grade

[b] Industrial grade

[c] Reagent grade

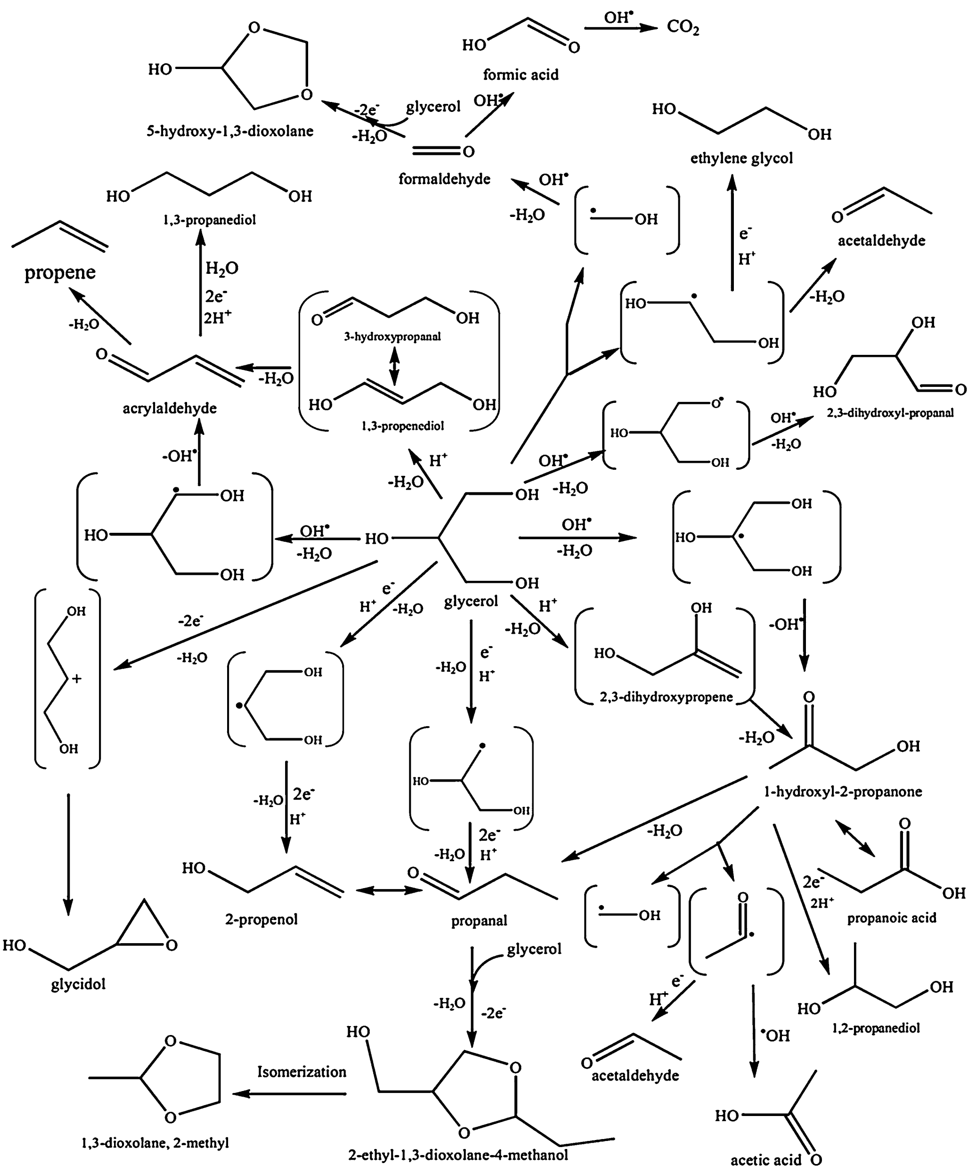
[d] No report grade

[e] Food grade

by the excess protons in the acidic solution to 1,2-propanediol, a commercially valuable chemical. In addition, 1-hydroxyl-2-propanone can cleave the C_1–C_2 bond leading to the formation of formaldehyde and a C_2-free radical, which can further reduce or react with $OH^\bullet$ to form acetaldehyde and acetic acid, respectively.

With respect to the propanal species, besides the dehydration of 1-hydroxyl-2-propanone, it can be produced from the two-step reduction of glycerol. The generated propanal can be considered as an isomer of 2-propenol, which can subsequently react with glycerol to form 1,3-dioxolane-4-methanol-2-ethyl and can further isomerize to form 1,3-dioxolane-2-methyl. In addition to the above, the $OH^\bullet$ radical can directly attack the unpaired electron of the 1°-OH group of glycerol and then, via a dehydration reaction and rearrangement, lead to the formation of 2,3-dihydroxyl-propanal. Regarding the reactions with radicals, the C_1–C_2 bond of glycerol is proposed to be cleaved by the oxidation reaction to form a C_1 alcohol free radical, which is then further dehydrated to formaldehyde, and the C_2 ethylene-free radical that is further dehydrated to acetaldehyde or reduced to ethylene glycol. The generated formaldehyde is unstable and can either react with glycerol to form the stable 5-hydroxy-1,3-dioxolane, or further oxidized by $OH^\bullet$ radicals to formic acid and then to CO or CO_2 gas [31]. An additional valuable compound observed to be formed by the electrochemical reforming of glycerol is glycidol. It is believed that the glycerol molecule is protonated by H^+ at the 2°-OH group, and consequently dehydrated leading to the formation of the glycerol carbonium ion, which is further rearranged to glycidol.

Scheme 1 Proposed reaction pathways for glycerol in acid solution transformation with and without electrolysis



The product yield for each generated compound is not reported here because the optimum conditions for each compound have not yet been determined. Different electrochemical conditions will likely provide different yields of each compound. To achieve a higher yield of each desired compound, the specific electrochemical conditions, such as the electrode type, applied current density, etc., need to be resolved first.

4 Conclusion

The electrochemical technique offers an opportunity for the biodiesel industry to convert glycerol into a wide variety of value-added products, such as propanediol, glycidol, and 2-propenol. These compounds will play an important role in the advancement of the integrated biorefinery concept for fuel and chemical production. However, this technique still needs additional research and development to reliably provide a higher selectivity and yield of these valuable compounds compared with their conventional production by catalysis and biological conversion, and also to make their manufacture and purification by this method both economically and operationally feasible.

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