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Effect of additives on one-pot electrochemical conversion of enriched crude glycerol

Payia Saila* **and Mali Hunsom***,**,†

*Fuels Research Center, Department of Chemical Technology, Faculty of Science,
Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand
**Center of Excellence on Petrochemical and Materials Technology (PETRO-MAT),
Chulalongkorn University, 254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand

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Abstract–One-pot electrochemical conversion of enriched crude glycerol to higher value compounds was performed in a simple electrochemical reactor under a galvanostatic condition at an initial pH of 1 with a platinum electrode. The effect of different concentrations of hydrogen peroxide (H_2O_2), sodium persulfate ($Na_2S_2O_8$) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), as oxidizing agents, on the glycerol conversion and on the product distribution and yields was explored. The presence of different additives affected the concerted reaction mechanism involving the oxidant on the electrode surface, resulting in the generation of different value-added products. In the absence of an oxidizing agent, the principal reaction products was glycidol, whereas in the presence of one of H_2O_2, $Na_2S_2O_8$ and TEMPO the main product was glycidol, ethylene glycol and 1,3-dihydroxyacetone, respectively.

Keywords: Crude Glycerol, Electrochemical Conversion, Additive, Value-added Compound

INTRODUCTION

Glycerol, which is one of the twelve building block chemicals since it is a highly functionalized molecule [1,2], is an attractive starting material for the synthesis of high-value oxygenated chemicals. Recently, a great deal of research effort has been spent to find new applications of glycerol for commercially viable value-added compounds, such as hydrogen (H_2) [3,4], ethanol and butanol [5,6], acrylic acid [7,8], dihydroxyacetone (DHA) [9,10], polyglycerols [11], and propanediol (PD) [12,13], amongst others.

Typically, glycerol can be obtained from non-triglyceride sources via synthesis, such as in the epichlorohydrin process [14]. However, it can also be obtained from the triglycerides from vegetable oils or animal fats via their hydrolysis, saponification and transesterification [15]. Due to the fast depletion of the non-renewable fossil fuel resources, a rapid development and expansion of the biodiesel industry are being established, and this results in the generation of a large volume of crude glycerol. In 2011, more than 66.2% of the total glycerol was obtained from the biodiesel industry, and it is expected to surge over the next five years owing to the increasing penetration of biofuels in mainstream applications [16]. Any further increase in biodiesel production rates will significantly raise the quantity and surplus of crude glycerol in the environment.

Previous attempts to enrich crude glycerol from biodiesel production plant using solvent extraction and adsorption reported that solvent extraction provided a better quality glycerol than the adsorption process [17-19]. The effect of operating parameters on electrochemical conversion of enriched crude glycerol was also studied. It was found that various added-value compounds, such as glycidol, acrolein and propanediol were generated under galvanostatic mode via Pt electrode [20]. In this work, we attempted to achieve a higher glycerol conversion and product yield distribution by the addition of various additives (H_2O_2, $Na_2S_2O_8$, TEMPO) into the electrochemical system. Finally, a mechanism for the generation of the key compounds is proposed.

EXPERIMENTAL

1. Preparation of Enriched Crude Glycerol

Due to the presence of organic and inorganic contaminants such as such as lauric acid, methyl myristate, myristic acid, and methyl palmitoleate, as demonstrated in Fig. 1 of our previous work [20], the crude glycerol obtained from a local biodiesel plant in Thailand was first partially enriched as previously reported [18,19]. In brief, the crude glycerol was acidified with phosphoric acid (85% H_3PO_4, Qrec) to pH 2.5 with shaking at 200 rpm (CTL, model SK electric shaker) for 1 h and then left for 12 h until the solution phase-

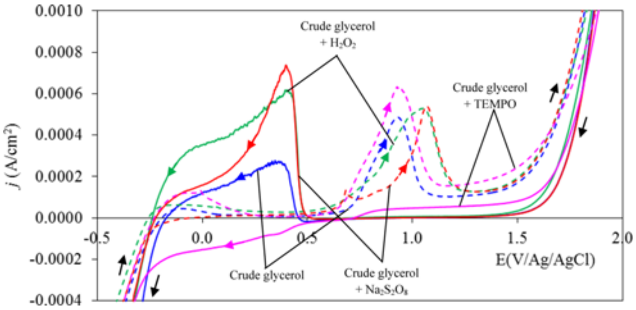

Fig. 1. Cyclic voltammogram of enriched glycerol in the absence and in the presence of additives at an initial pH of 1.0 using a Pt electrode: anodic scan (---) and cathodic scan (—).

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†To whom correspondence should be addressed.
E-mail: mali.h@chula.ac.th

Table 1. Characteristics of the crude glycerol [20]

Parameter	Crude glycerol		
	Untreated	Pre-treated	Enriched
pH	9.5-9.8	7.0-7.2	5.5-6.0
Glycerol content (wt%)	29.8±0.14	51.9±0.15	97.9±0.02
Ash (wt%)	7.90±0.5	23.4±1.1	0.86±0.07
Other contaminants (wt%)	62.3±1.04	24.8±0.16	1.29±0.05
Density at 20 °C (g/cm^3)	1.03±0.024	1.27±0.03	1.28±0.05
Viscosity at 40 °C (cSt)	48.3±0.172	53.8±1.29	69.0±0.74
Color (10^3 Pt-Co units)	484.9±10.5	221.6±7.3	15.4±1.1

separated into the three distinct layers of a top free fatty acid-rich layer, a middle glycerol-rich layer and the bottom inorganic salt-rich layer. The middle glycerol-rich layer was harvested and then neutralized by the addition of 12.5 M sodium hydroxide (98% NaOH, Merck) to pH 7.0, left for a while and then filtered to eliminate the precipitated salt. The pre-treated crude glycerol was obtained after drying at 110 °C for 15 h. Subsequently, to remove the remaining contaminants, it was subjected to solvent extraction with *n*-propanol (99.99% C_3H_7OH, Fisher Scientific) at a 2 : 1 solvent : pre-treated crude glycerol volume ratio. After mixing by shaking at 200 rpm for 4 h, it was then left for 2 h to allow phase separation into the glycerol-alcohol phase on the top and the crystallized salt on the bottom. The top layer was separated from the bottom layer by slow decantation, and after evaporation of the residual solvent at 95 °C for 12 h, the enriched crude glycerol preparation with a purity of around 98% was obtained [20]. The characteristics of untreated, pre-treated and enriched crude glycerol are summarized in Table 1.

2. Electrochemical Conversion of Enriched Crude Glycerol

A one-pot laboratory scale electrochemical conversion of the enriched crude glycerol was performed under galvanostatic mode at ~25 °C and ambient pressure in the undivided electrochemical reactor, made from Pyrex glass with a total capacity of 600 mL. The electrolytic cell temperature was controlled by a cooling system. A regulated DC power supply (ZS 3205-2X type) was employed to supply the external electricity at a constant current density of 0.14 A/cm^2. The concentration of enriched crude glycerol was fixed at 0.3 M and pH 1.0. The three types of oxidant additives, hydrogen peroxide (30% H_2O_2, Qrec), sodium persulfate ($Na_2S_2O_8$; Qrec) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), were added at required concentrations in the electrochemical system.

3. Analytical Procedures

All liquid product samples were analyzed by high performance liquid chromatography (HPLC, Agilent 1100) with a RID-10A refractive index detector. The stationary phase was a Pinnacle II C18 column (240×4.6 mm), and the mobile phase was a 99.9 : 0.1 (volume) ratio of 10 mM sulfuric acid: methanol, passed through the column at 0.5 mL/min. Standard solutions of glycerol and the major expected generated-components of ethylene glycol (EG), glycidol (GCD), acetol (ACT), acrolein (ACL), glycolic acid (GCA), 1,2-PD, 1,3-PD and 1,3-DHA were run to identify the retention times and to determine the relationships between the peak area and compound concentration. The glycerol conversion as well as the yield of the potential value-added compounds obtained from the electrochemical process was calculated according to Eqs. (1) and (2), respectively [20]:

$$\text{Glycerol conversion (\%)} = \frac{\text{amount of glycerol converted (C-based mole)}}{\text{Total amount of glycerol in reactant (C-based mole)}} \times 100 \qquad (1)$$

$$\text{Product yield (\%)} = \frac{\text{amount of glycerol converted to each product (C-based mole)}}{\text{total amount of glycerol in reactant (C-based mole)}} \times 100 \qquad (2)$$

RESULTS AND DISCUSSION

1. Steady-state CVs of Crude Glycerol Solution

Typical steady-state cyclic voltammetry (CV) curves of the enriched glycerol solution at pH 1 in the absence and in the presence of additives during an applied potential of +2.0 to −0.50 V are shown Fig. 1. In the presence of solely enriched crude glycerol, an anodic peak was observed at electrode potential of +0.905 V, related to the oxidation of glycerol. At a potential greater than +1.50 V, a sharp increase in the current density was observed, which was attributed to the oxidation of H_2O to O_2. For the backward scan, one oxidation peak was observed, at an electrode potential around +0.39 V, and this was attributed to the incomplete oxidization of carbonaceous residues on the catalyst surface during the negative sweep [22]. These carbonaceous residues can accumulate tightly on the Pt surface and block the active catalyst sites for the next turnover, resulting in sluggish electrochemical reactions [22].

In the presence of additives including H_2O_2, $Na_2S_2O_8$ and TEMPO, their CV curves still exhibited the oxidation peak of crude glycerol in anodic scan. Slightly high current density was observed compared with that in the absence of additives, suggesting that the presence of H_2O_2, $Na_2S_2O_8$ and TEMPO affected positively on glycerol oxidation. In cathodic scan, the peaks exhibited an incomplete oxidization of carbonaceous residues on the catalyst surface were still pronounced for H_2O_2 and $Na_2S_2O_8$, but not for TEMPO. This is probably due to the nature of the corresponding oxidizing derivatives of TEMPO, nitrosonium cations (TEMPO$^+$) [21], which can accumulate on the surface of working electrode to proceed the reduction reaction, which probably hides the incomplete oxidization peak of carbonaceous residues.

2. Electrochemical Conversion of Crude Glycerol in the Presence of Additives

Prior to the study of the effect of additives on electrochemical conversion of crude glycerol, a blank experiment was first carried out in the presence of only additives (1 mM) and glycerol (0.3 M) and in the absence of electricity as exhibited in Fig. 2. It was found that less than 5.78, 4.39 and 4.17% of glycerol were converted within 8 h in the presence of H_2O_2, $Na_2S_2O_8$ and TEMPO, respectively. This suggests that the presence of only additives cannot enhance the conversion of glycerol effectively.

The variation in the glycerol conversion as a function of electrolysis time in the absence- and in the presence of one of the three additives (H_2O_2, $Na_2S_2O_8$ and TEMPO) at 1 mM is summarized in Fig. 2. As expected, the glycerol conversion increased with increasing electrolysis time. In the absence of additive, the glycerol

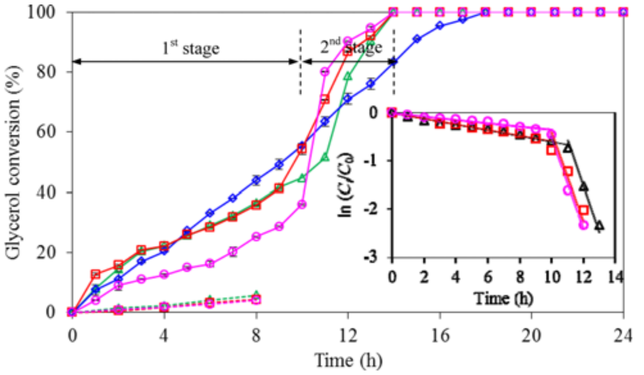


Fig. 2. Glycerol conversion in (---) the absence of electricity or blank experiment and (—) the presence of electricity with a current density of 0.14 mA/cm^2; (◇) without additive and with additives of (△) H_2O_2, (□) $Na_2S_2O_8$ and (○) TEMPO at initial glycerol concentration of 0.3 M, 1 mM oxidant and solution pH of 1.0.

conversion increased smoothly (almost linearly) over time up to 14 h to a complete conversion within 18 h of electrolysis time. However, in the presence of the respective oxidant (additive), a markedly faster conversion rate was seen from 10 h onwards, giving a shorter reaction time of 14 h being required for complete glycerol conversion. Interestingly, two stages of the glycerol conversion were observed in the presence of the oxidant in all three cases (slow to ~8 h and then very rapid to completion), suggesting that the kinetics of the electrochemical conversion of glycerol under a galvanostatic mode is a two-step process in the presence of these oxidative additives.

Using a macro-kinetics model [23], both stages were found to fit very well to a first-order kinetics model, with a determination coefficient (R^2) of greater than 0.9630 (Insert of Fig. 2). From the linear part, the rate constants (k_1) of glycerol conversion in the first stage were 1.54×10^{-5}, 1.41×10^{-5} and 0.95×10^{-5} s^{-1} in the presence of H_2O_2, $Na_2S_2O_8$ and TEMPO, respectively. On the other hand, in the second stage the rates (k_2) were 2.24×10^{-4}, 1.72×10^{-4} and 2.26×10^{-4}, respectively. At this stage, it is difficult to conclude exactly which principal reaction occurred in each stage in the presence of each oxidant. We hypothesize that the anodic surface of Pt may indeed play a role in a concerted reaction mechanism involving the simultaneous hydrogenolysis (dehydration and hydrogenation), cyclization and oxidation [24].

The variation in the yield of the value-added products during a long-term electrolysis time of the enriched crude glycerol in the absence or presence of oxidant is shown in Fig. 3. In the absence of any oxidant, glycidol and acrolein were the main generated products. Glycidol was produced steadily throughout the 24-h period reaching ~46% at 24 h. In contrast, acrolein was not detectably produced until after 8 h and peaked at 21 h (~33%) before sharply declining over the last 3 h to <17% at 24 h, and EG was produced from about 7-8 h and reached a peak plateau at 10-12 h (~16.5%), where at this stage it was the most common product, before declining to around 9.5% by 16 h onwards. Of the other detected products, only low levels (<3%) of 1,2-PD and 1,3-PD were detected from 10 and 15 h, respectively, onwards whilst acetol increased from 14 h (~3%) slowly reaching ~13% at 23 h.

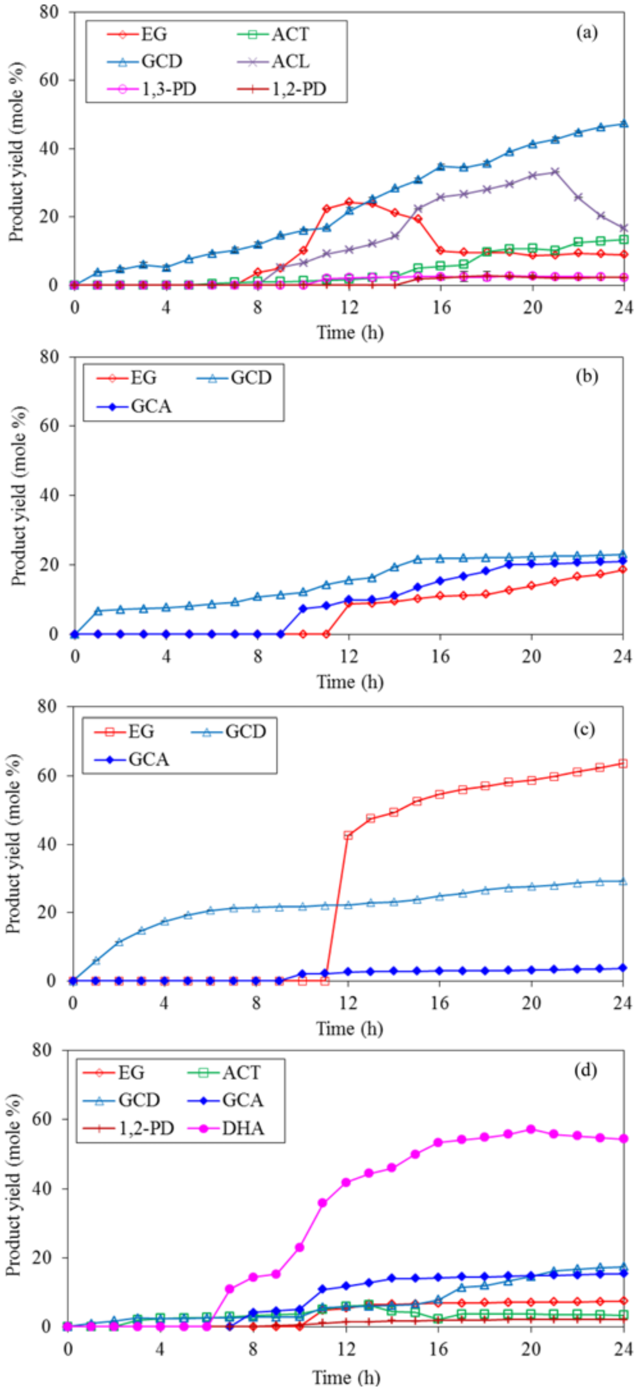


Fig. 3. Product yield in the (a) absence of any oxidant additive and in the presence of (b) H_2O_2, (c) $Na_2S_2O_8$ and (d) TEMPO at an initial glycerol concentration of 0.3 M, 1 mM oxidant and solution pH of 1.0 with a current density of 0.14 mA/cm^2 and a Pt grid electrode.

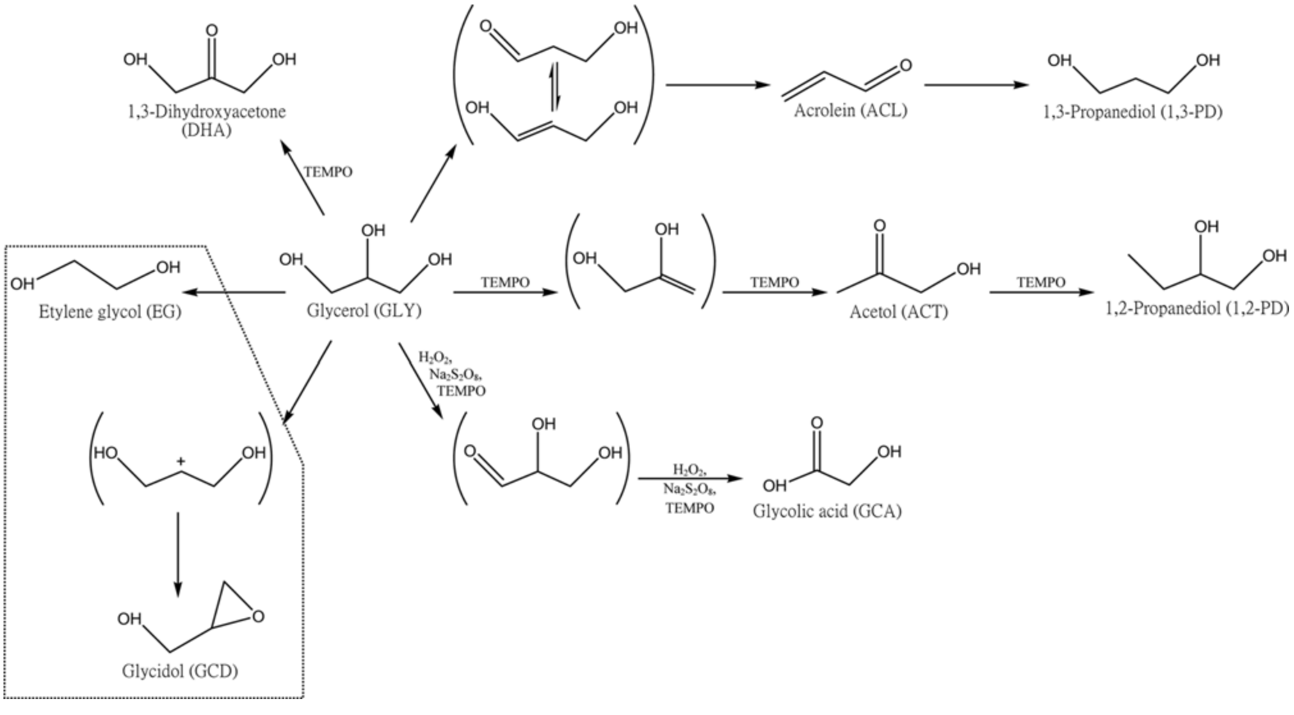
The addition of oxidants caused a different product profile. In all cases, the yield of glycidol was lower than that without any oxidants, being at approximately 20-22%, 25-30% and 10-15% in the presence of H_2O_2, $Na_2S_2O_8$ and TEMPO, respectively. For the addition of H_2O_2 or $Na_2S_2O_8$, no acetol, 1,2-PD or 1,3-PD production was noted, but a marked increase in the production level of EG was found with the addition of $Na_2S_2O_8$, with its production being very rapid from 11-12 h and then steady to >63% at 24 h. The addition of H_2O_2 provided the highest yield of glycolic acid, starting from 9 h and reaching ~21% at 24 h. Otherwise, with the addition of TEMPO, the main product was 1,3-DHA, being formed from 7 h onwards to a maximum at 18-24 h of ~55%. This surprisingly high yield of 1,3-DHA in the presence of TEMPO was 2.29-fold greater than that found with the electrocatalytic oxidation of glycerol under a potentiostatic condition (1.1 V/Ag/AgCl) at pH 9.1 with bicarbonate (0.2 M) in the presence of 7.5 mM TEMPO [24]. Glycolic acid was also generated in the presence of all the additives, particularly with H_2O_2 and TEMPO.

From the previously proposed reaction pathway for the electrochemical conversion of glycerol in an acid solution [25], the EG was likely to have been obtained from the oxidative cleavage of the C_1-C_2 bond of glycerol. The primary product of this cleavage is the C_1 alcohol free radical, which is then further dehydrated to formaldehyde, while the C_2 ethylene-free radical is further dehydrated to acetaldehyde or reduced to EG. That, in the absence of oxidant, the EG yield declined from its maximum value at 12 h onwards suggests that it can be converted to other species, such as formic acid [26,27]. However, in the presence of oxidants, EG was still detected after 12 h of electrolysis time and increased thereafter, particularly in the presence of $Na_2S_2O_8$. This might be due to the high oxidative power of $Na_2S_2O_8$ that facilitates the higher cleavage rate of the C-C bond intermediate species, and so compensates for the rate of its conversion to other species.

With respect to glycidol, its yield increased almost instantaneously as electricity was applied in all cases, indicating that the glycerol can convert directly to this compound. The presence of different oxidants had unimportant marked effect on the conversion of glycerol to glycidol. As mentioned previously [25,28], glycidol is obtained from the rearrangement of the glycerol carbonium ion or the cyclization, derived from the protonation of the primary -OH group of glycerol.

Acetol and acrolein were obtained from the transformation of 2,3-dihydroxypropene and 3-hydroxypropanal/1,3-PD by the dehydration of adsorbed glycerol molecules at the primary- and secondary -OH groups [29,30] that are then further reduced to 1,2-PD and 1,3-PD, respectively [25]. However, only a small quantity of acetol and 1,2-PD was generated in the presence of TEMPO, but not in the presence of H_2O_2 and $Na_2S_2O_8$. Presumably, in the presence of a strong oxidizing agent, the glycerol was directly oxidized at the primary -OH group to glyceraldehyde, and then the C-C cleavage of this intermediate species resulted in the formation of glycolic acid [28]. In addition, in the presence of a weak oxidizing agent, the direct oxidation of glycerol under an acidic condition preferentially occurs at the secondary -OH group [31], resulting in the formation of 1,3-DHA [9]. With some paths more or less possible for each studied system, a simplified diagram showing the possible major reaction pathways of enriched glycerol conversion by electrochemical technique under these galvanostatic conditions with a Pt electrode is shown in Scheme 1.

The variation in the glycerol conversion as a function of electrolysis time in the presence of different concentrations of TEMPO (1, 3 and 5 mM) is shown in Fig. 4. The higher concentrations of TEMPO gave a faster initial glycerol conversion, reaching, for exam-



Scheme 1. Proposed reaction pathways for the electrochemical conversion of the enriched glycerol (0.3 M) over a Pt electrode at an initial pH of 1.0 in the presence of the indicated oxidant. The products in the dashed-box can occur in both the absence and presence of an added oxidant.

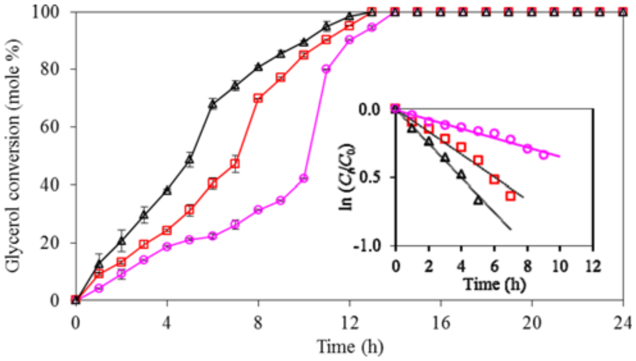


Fig. 4. Glycerol conversion level in the presence of TEMPO at a concentration of (◯) 1 mM, (☐) 3 mM and (△) 5 mM, all at an initial glycerol concentration of 0.3 M and solution pH of 1.0 with a current density of 0.14 mA/cm^2 and a Pt grid electrode.

ple, a 50% glycerol conversion after ~4.9, ~7.1 and ~10.2 h for 1, 3 and 5 mM TEMPO, respectively, but the times required for the complete conversion of glycerol in the presence of 3 and 5 mM TEMPO were equal at 13 h compared to 14 h for 1 mM TEMPO. The two-stage behavior of glycerol conversion was weakly observed in the presence of 3 and 5 mM TEMPO, where the first-order reaction rate constants for glycerol conversion increased with increasing TEMPO concentrations. Namely, the addition of TEMPO at 1, 3 and 5 mM can enhance the conversion of glycerol at the first stage with the rate constant of 0.95×10^{-5}, 2.43×10^{-5} and 3.57×10^{-5} s^{-1}, respectively.

Regarding the effect of the TEMPO concentration on the product yield, the main product obtained from the electrochemical conversion of glycerol was still 1,3-DHA and its yield increased with increasing TEMPO concentrations from 57.2 to 69.2% at 1 to 5 mM TEMPO (Fig. 5). This is attributed to the fact that in the presence of a higher TEMPO concentration, a larger amount of the nitrosonium cation, the active oxidizing species obtained from the oxidation of TEMPO, was produced which could then oxidize more secondary -OH groups of glycerol to correspondingly form more 1,3-DHA. Based on the glycerol conversion and the generated products, it seems to be that the principal reaction that occurred in the first stage in the presence of TEMPO was the hydrogenolysis and/or cyclization to acetol and glycidol, and this was then followed by the main oxidation reaction that started after 5 or 6 h, depending on the TEMPO concentration.

CONCLUSIONS

The electrochemical conversion of enriched crude glycerol to higher value compounds was successfully developed in a simple electrochemical reactor under a galvanostatic condition (0.14 mA/cm^2) for a 0.3 M glycerol solution at an initial pH of 1.0 with a Pt electrode. The presence of the utilized oxidants enhanced the glycerol conversion rate, which was attributed to the concerted reaction mechanism involving the oxidant on the electrode surface. In the absence of oxidant, the glycerol conversion was mainly performed by dehydration and reduction reactions, but principally occurred by the direct oxidation of glycerol at the primary- or secondary -OH group in the presence of the oxidants.

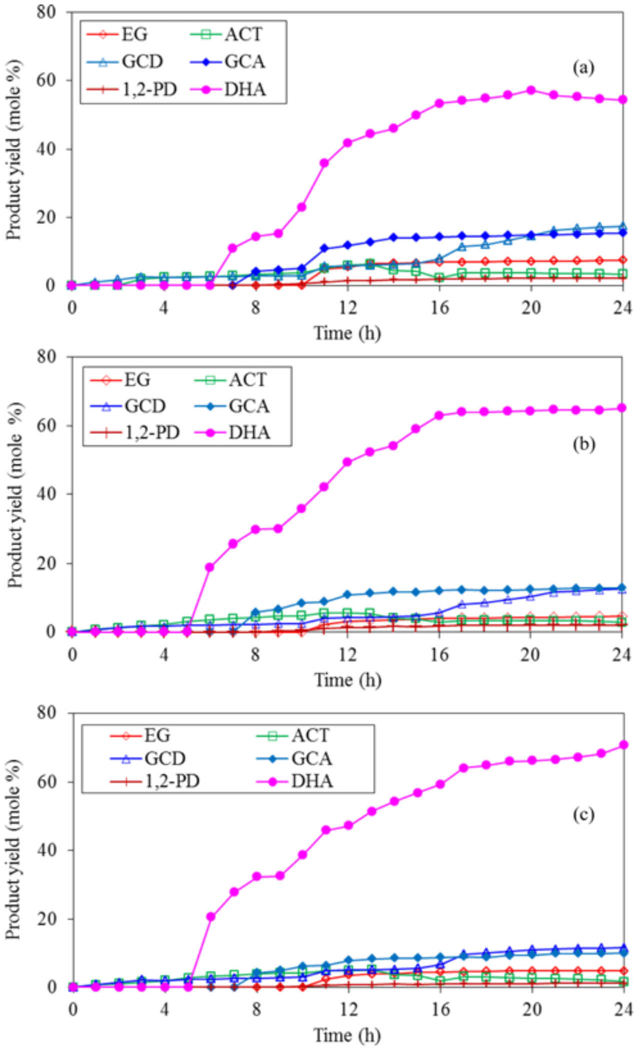


Fig. 5. Product yield in the presence of TEMPO at (a) 1 mM, (b) 3 mM and (c) 5 mM at an initial glycerol concentration of 0.3 M and solution pH of 1.0 with a current density of 0.14 mA/cm^2 and a Pt grid electrode.

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