

New products from partial oxidation of glycerol

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Abstract

A surplus of glycerol production due to several reasons has initiated investigation of several routes of oxidative glycerol upgrading. Among the reaction products are substances such as dihydroxyacetone and several acids from oxidative upgrading of glycerol. Several routes of chemical oxidation and electrochemical oxidation have been published in literature.

The ongoing project has focused on the investigation of electrochemical routes of partial glycerol oxidation. Direct anodic treatment through membrane electrolysis and oxidative treatment with mediators has been subject of investigation.

In the first part of direct anodic treatment the effect of operating conditions on the yield and selectivity of products has been investigated, mainly considering the electrolyte composition, the type of anode material, the current density and the temperature of electrochemical operation. Results of direct anodic treatment show reasonable yields but suffer still from a lack of product selectivity.

In extension to anodic oxidation oxidative treatment with redox mediators has been considered too. The concentration of redox mediators can be varied, offering a wider range of oxidation conditions. Improved product selectivity is expected. On the other hand separation of spent redox mediators from the reaction mixture and regeneration increase the overall technical demand.

1 Introduction

Due to a worldwide surplus of glycerol from fat-splitting processes and in recent years due to the increased production of bio diesel, with glycerol as by-product, new routes of usage have to be found. Partial oxidation of glycerol to several products like dihydroxyacetone (DHA), glyceraldehyde (GLADH), glycolic-, formic-, or acetic acid is a possible route of processing surplus glycerol.

Fundamental works for alkaline oxidation conditions were published by Weber [1] and Tkaczuk [2]. Both authors investigated the effect of several electrode materials like nickel, silver gold and platinum on the electrochemical oxidation of glycerol. Both authors achieved usable conversion of glycerol but with a lack of product selectivity and a huge excess of sodium hydroxide. The electrochemical oxidation of glycerol in acidic electrolytes is barely investigated. Roquet [3] worked on the electrochemical oxidation of glycerol in 0.1 M HClO_4 . Under acidic conditions the main products GLADH and formic acid were formed. Compared with the results of Weber [1] obtained from electrolysis in caustic electrolyte a smaller conversion rate of 37% glycerol after 44.5 h electrolysis time was observed under acidic operation conditions.

These investigations were based on direct conversion of glycerol at the electrode surface without any mediator. Redox mediators can enlarge the reaction zone to the electrolyte bulk phase and commute the heterogeneous redox reaction at the electrode surface to a homogeneous redox reaction in the bulk phase. Figure 1 shows the principle activity of redox mediators in anodic oxidation reactions.

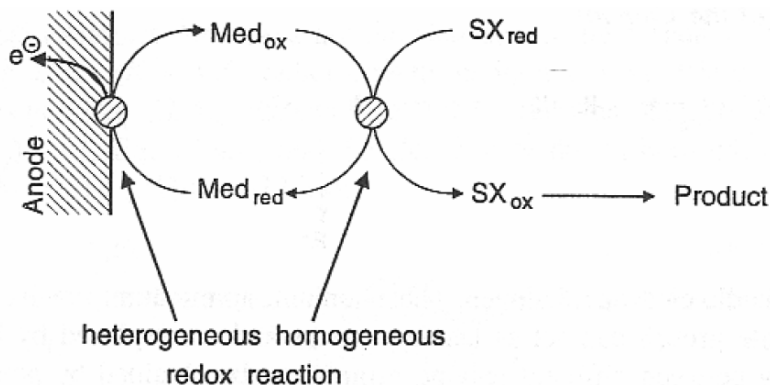


Fig. 1: Effect of redox mediators in anodic oxidation

In the project the effect of the redox mediator Mn (II/III) on oxidation of glycerol was investigated.

2 Experimental setup

2.1 Apparatus and electrolysis

Most experiments described in this work were carried out in a divided membrane electrolysis cell equipped with the cation exchange membrane type Nafion 966[®]. The cathode was made of a platinum net and the anode was made of platinized titanium. Anolyte and catholyte were separately circulated with peristaltic pumps. The temperature of the electrolyte solution was kept constant with a temperature control loop. 1 M H₂SO₄ solution was the basic electrolyte. Glycerol was admixed to the anolyte to provide a mixture of 1 M glycerol.

2.2 Analyses

Analyses was carried out by HPLC with a HPLC column type Acclaim OA[®] of Dionex. A 100 mM NaSO₄ buffer solution adjusted to pH = 2.65 was necessary to detect the reaction products. For glycerol analysis a cation exchange column type Rezex ROA[®] from Phenomenex with a 0.01 N H₂SO₄ solution as mobile phase was needed. In both applications the substances were detected by an UV/Vis- detector with variable wavelength.

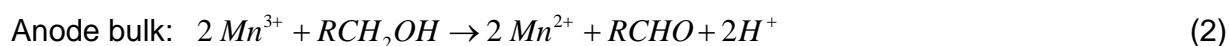
2.3 Experimental procedure

In a first series the effect of the membrane on the electrolysis with and without mediator was investigated. Then the dependence of the distribution of reaction products on the concentration of the redox mediator, based on 0.02 to 0.08 M MnSO₄ and the temperature dependence between 20° and 50°C were subject of investigation. In a further test series the effect of current density between 100 and 200 A/m² on the product distribution was determined.

3 Results and discussion

3.1 Effect of redox mediator on oxidation of glycerol in membrane electrolysis

Experiments were carried out with mediator concentration between 0.02 and 0.08 M MnSO₄ at constant temperature of 50°C and at constant current density of 100 A/m². The overall oxidation reaction with the redox mediator MnSO₄ for oxidation of glycerol to GLADH is shown in Eqn. (1) to (3):



The results of redox mediated oxidation of glycerol and the comparison with direct anodic oxidation are summarized in Figure 2 and 3:

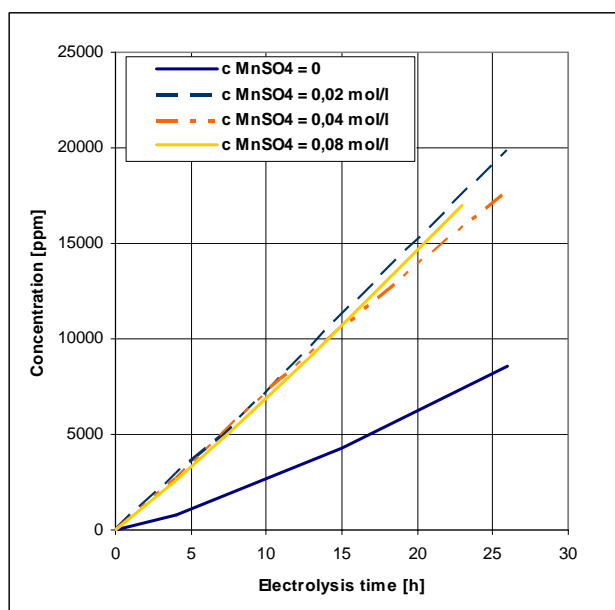


Fig. 2: Effect of the redox mediator Mn^{2+} on formation of formic acid

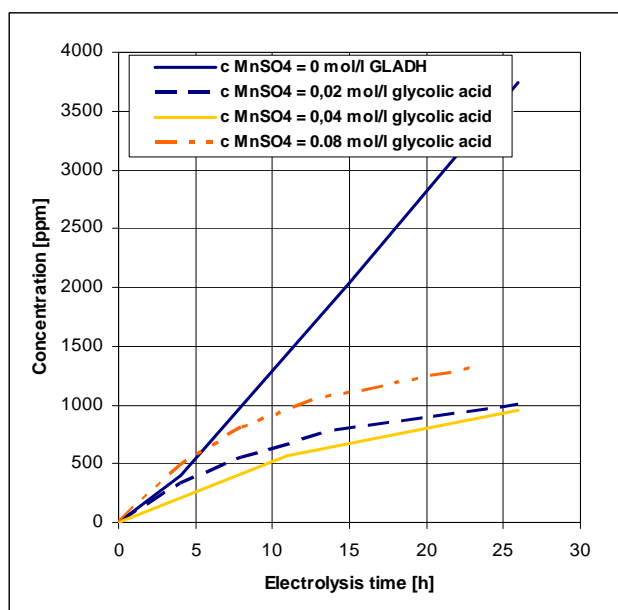


Fig. 3: Effect of the redox mediator Mn^{2+} on formation of GLADH and glycolic acid

GLADH and formic acid were mainly formed during direct electrolysis. DHA, glycolic-, glyceric- and acetic acid were identified in low concentration. MnSO_4 supported cleavage of glycerol. Formic acid was formed in major concentration. Formation of GLADH was almost completely suppressed. Glycolic acid was detected in smaller concentration (1000 ppm). The mediator concentration has a minor effect on the distribution of oxidation products shown in figures 2 and 3. These experiments showed that the yield of the main oxidation products formic acid and glycolic acid was almost independent of the mediator concentration. A comparison with and without mediator shows a doubling of the formic acid production. The addition of MnSO_4 favours cleavage reactions.

3.2 Effect of open cell electrolysis on glycerol oxidation

To estimate the influence of open cell electrolysis on oxidation of glycerol the membrane was removed from the electrolysis cell. Oxidation was carried out with and without redox mediator. In experiments with redox mediator the Mn^{2+} concentration was kept constant at 0.02 M Mn^{2+} . In Figure 4 and Figure 5 the product composition of both modes of operation is compared.

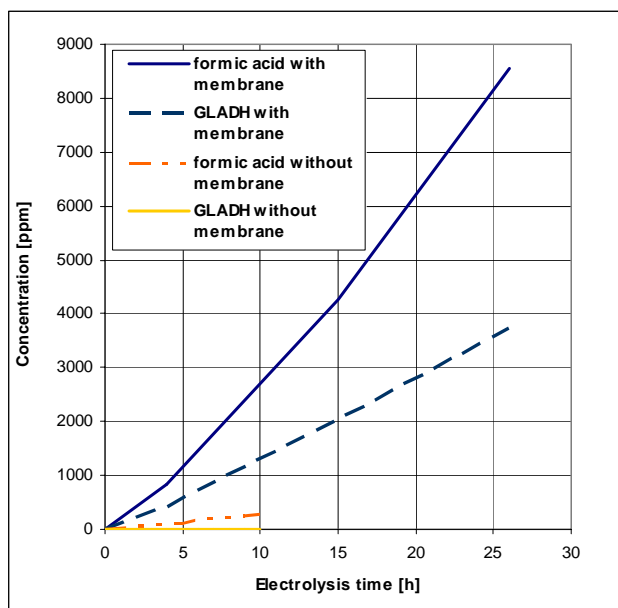


Fig. 4: Product concentrations vs. electrolysis time without redox mediator

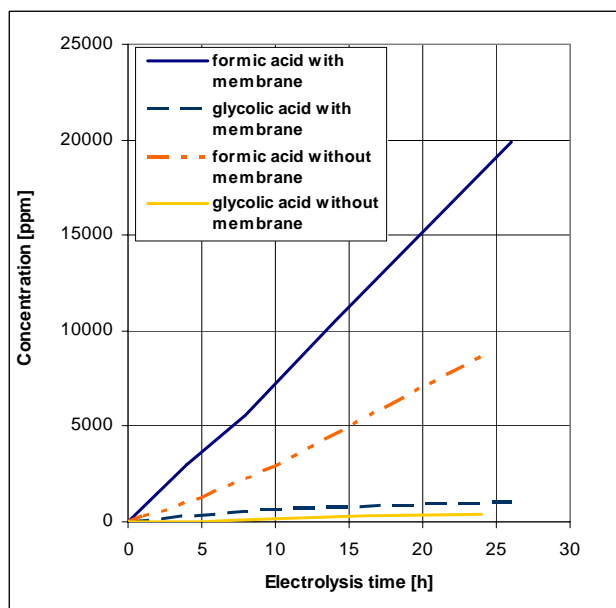


Fig. 5: Product concentrations vs. electrolysis time with 0.02 M redox mediator

Open cell operation results in lower product concentration in principle because of favoured water decomposition. It does not affect the activity of the redox mediator.

3.3 Effect of temperature

Several test series were carried out at constant current density of 100 A/m^2 and constant concentration of $0.02 \text{ mol/l MnSO}_4$. The temperature influence was investigated between 20° and 50°C . The results are shown in figures 6 and 7.

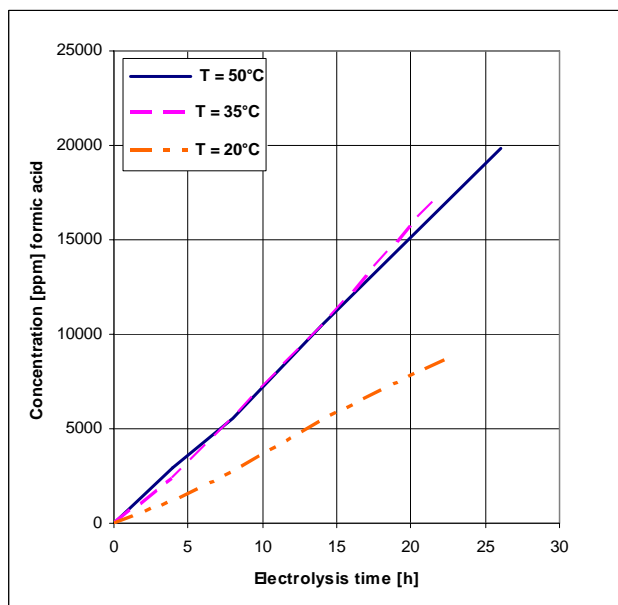


Fig. 6: Formic acid concentration vs. electrolysis time depending on temperature

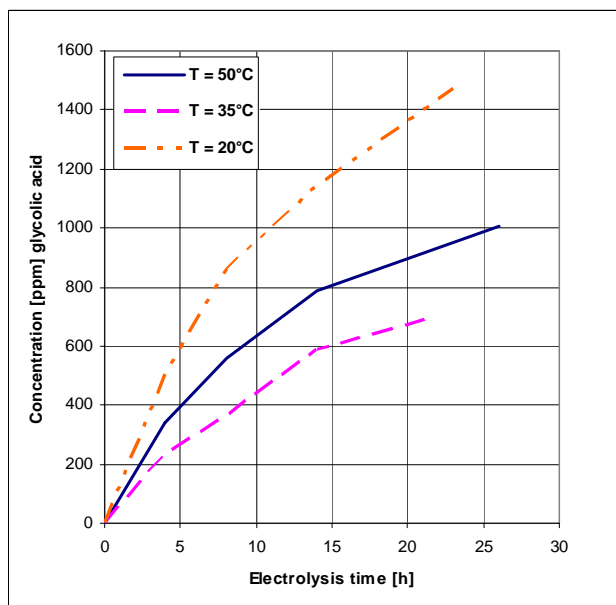


Fig. 7: Glycolic acid concentration vs. electrolysis time depending on temperature

A comparison of the experiments at 35° and 50°C shows only a minor effect of temperature on the formation of formic acid. At low temperature the intermediate product glycolic acid is less oxidized than in experiments at elevated temperature.

3.4 Effects of current density

In a further series of experiments the effect of current density on the product distribution was subject of investigation. Current density was varied between 100 and 200 A/m². Temperature was kept constant at 50°C and the redox mediator concentration was kept constant at 0.02 M MnSO₄. The results are shown in figures 8 and 9.

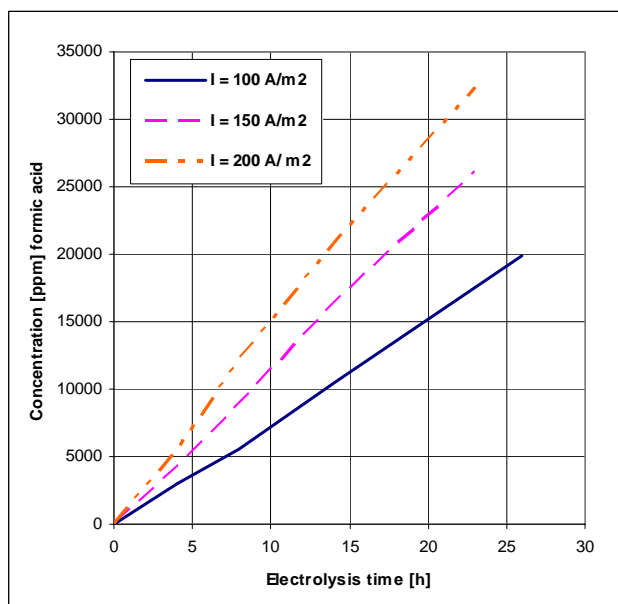


Fig. 8: Formic acid concentration vs. electrolysis time depending on current density

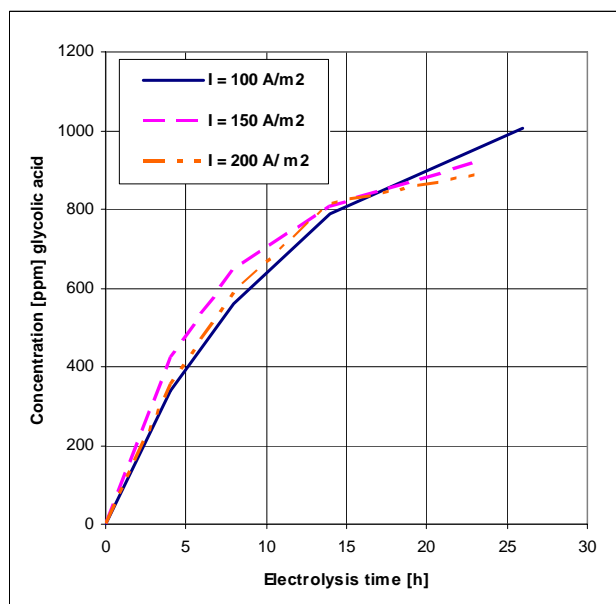


Fig. 9: Glycolic acid concentration vs. electrolysis time depending on current density

The comparison of Figure 8 and Figure 9 indicates that cleavage and downgrading of intermediates to the final product formic acid is preferred at high current density.

Formation and consecutive oxidation of glycolic acid is nearly unaffected by current density within the investigated range.

4 Summary

In this work the electrochemical oxidation of glycerol with MnSO₄ as redox mediator and the dependence of oxidation on temperature, mediator concentration, current density and the type of cell were investigated. The redox mediator MnSO₄ favours formation of formic acid and oxidation of intermediate products. Concentration dependence of specific reactions on the mediator concentration was not being found. The effect of temperature on the redox reaction of the mediator demonstrated a shift from complete oxidation to formation of intermediates. The variation of the current density showed an electron transfer controlled formation of formic acid.

Acknowledgements

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