Electrooxidation of glycerol as a synthetic tool to more valuable chemicals

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Introduction

Glycerol is the main by-product of biodiesel industry, around 10 % w/w. Despite glycerol has a large direct industrial application, the production of biodiesel, consequently glycerol, has increased so much in the last 20 years, that the segments which consume it traditionally, can not absorb it anymore, the supply is higher than demand and the price has gone down, being the glycerol overproduction one of biggest problems of the biodiesel industry.

Being a highly functionalized molecule and able to several transformations, abundant, low cost and obtained from biomass, the glycerol is a perfect chemical platform to development of biorefineries. Glycerol can be converted into other chemicals through many process, for example, oxidation, leading to several compounds, all of them more valuable than glycerol [1] (figure 1).

Objectives

Study the anodic oxidation of glycerol aiming the electrosynthesis of more valuable chemicals through changings in the process variables, such as: electrode, solvent, potential, supporting electrolyte, substrate concentration, and others.

Results

Electrolysis takes place in an undivided cell, no cathodic product was observed, and without atmospheric control. Gold and Platinum electrodes are able to electrooxidation of glycerol using water as solvent, being gold more active and less stable than Pt. The electron transfer depends on pH, which suggests that metallic oxides play important role in this reaction (figure 2).

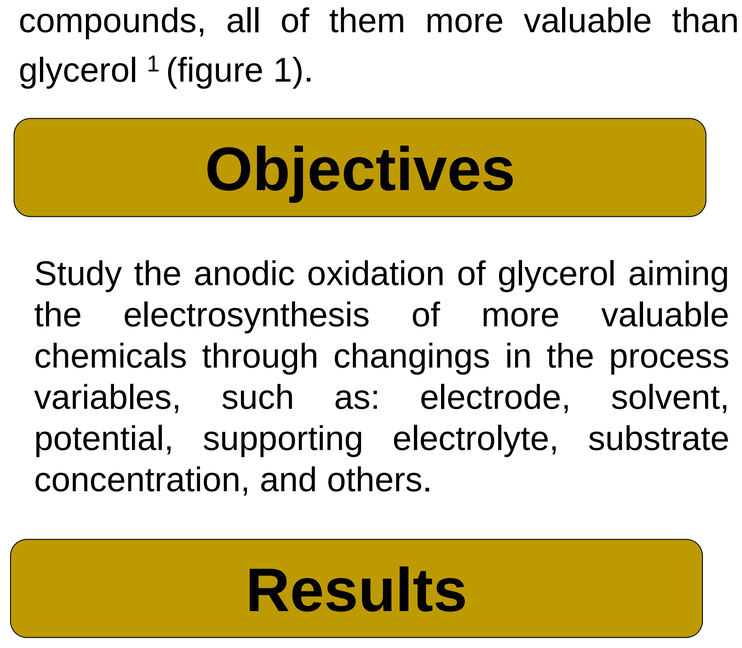

Figure 1: C_3 products obtained by electrooxidation of glycerol.

The main product in both electrodes is glyceric acid, however other products, tartronic, glycolic and oxalic acids are also detected. The yield and distribution can vary by changing reaction conditions, for example, using high concentration of KOH, supporting electrolyte, higher conversion rate is observed, also, using Pt as working electrode at lower potentials more products of C_3 chain is observed.

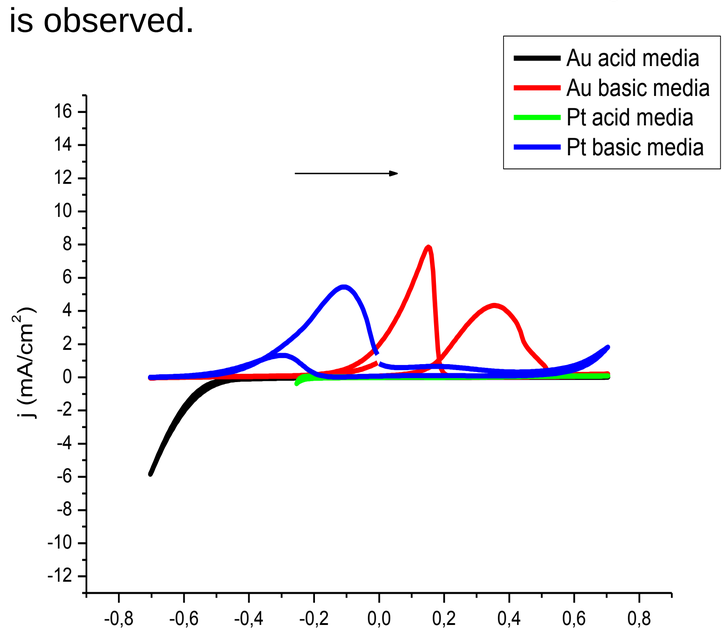

Figure 2: Voltammograms to glycerol 0,2 M in KOH 0,5 M and $HClO_4$ 0,5 M, on Au and Pt electrodes.

Different from the most works published in this area, capillary electrophoresis (CE) was used as analytic technique. The electrolyte used was H_3BO_3/LiOH, which reacts with 1,2 and 1,3 diols providing charge to neutral analytes, what makes possible the simultaneous analysis of ions and neutrals compounds [3]. Through CE is possible follow the ionic products formed during the reaction (figure 3).

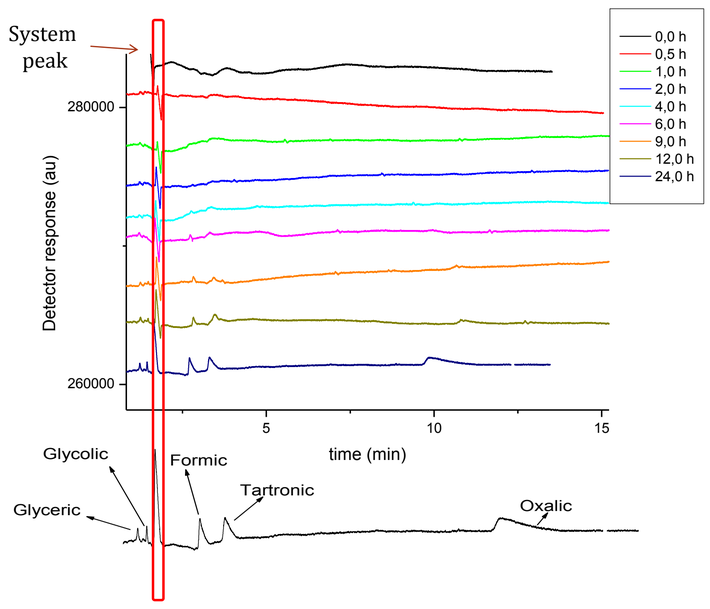

Figure 3: Electropherograms of samples collected during reaction time.

Through coulometric studies the number of transferred electrons can be estimated (figure 4), however, due to water oxidation, probably, the calculated value is higher than real one.

On Pt electrode the conversion rate was around 50%, being glyceric acid the main product, around 70 % of detectable ones, the number of electron transferred, n, was approximately 6, which is according to estimated weighted average.

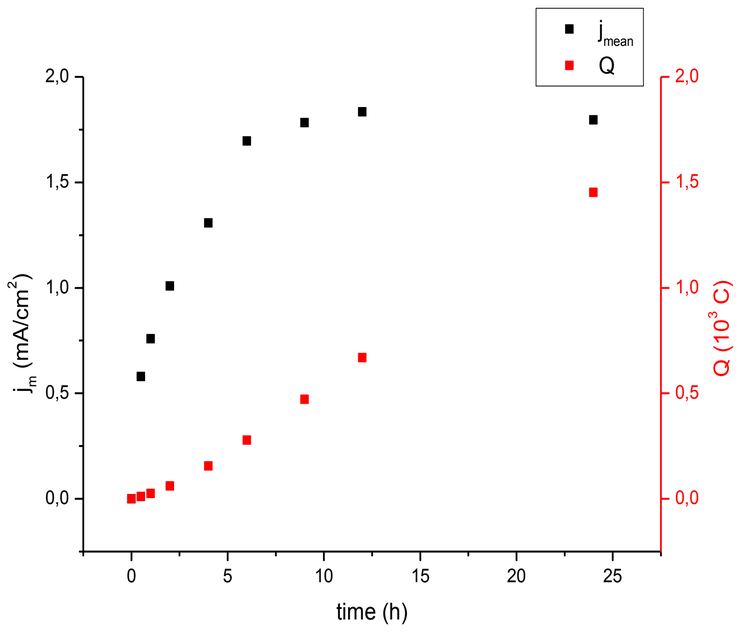

Figure 4: Mean current density and accumulated charge during the electrolysis.

Conclusions

The electrochemical via has shown to be a satisfactory method to oxidize glycerol to carboxylic acids. It was also observed that undivided cell, without atmospheric control, aqueous media and high pH are efficient ways to do it, leading to a simpler and cheaper process.

Aknowledges

To CNPq for the scholarship supporting.

References

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[3] P. Tuma, K. Málková, Z. Wedellová, E. Samcová, K. Stulík. “The use of capillary electrophoresis with contactless conductivity detection for monitoring of glycerol in adipose tissues during a sporting performance”. Electrophoresis, 31, 2037, 2010.