Effect of platinum electrode on partial oxidation of glycerol and optimization by central composite design

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Abstract: - Global production of biodiesel around the world has caused a major surplus of glycerol as a byproduct. Intensive research on the processing of this compound has been carried out during the last years. This research approach the partial oxidation of glycerol for the generation of glycerol derivatives with special interest in achieving high selectivity to glyceraldehydes and glycerol overall conversion. A central composite design was performed to optimize the parameters (0.22 mM MnO2, stirring speed of 167 rpm and 82 °C) of the electrochemical reaction. 43% selectivity and 23% of glycerol overall conversion were obtained using a platinum electrode (0.56 cm2 surface area). Cyclic voltammetry and Multiple Pulse Amperometry were used to study the electrochemical behavior of platinum electrode in glycerol solutions with MnO2.

Key-Words: - glycerol oxidation, cyclic voltammetry, central composite design, glyceraldehyde, oxidation, optimization

1 Introduction
The growth of world biodiesel production has caused a surplus of glycerol, which is generated as a byproduct of the process. Therefore, extensive research to produce value added products using glycerol as a raw material has been carried out. Particular interest lays on the partial oxidation of glycerol, which can produce valuable compounds, namely glyceraldehyde, dihydroxyacetone, glyceric acid, glycolic acid, mesoxalic acid and tartaric acid. These chemicals find broad application in food and pharmaceutical industry. The use of electrodes such as platinum or gold to perform the partial anodic oxidation of glycerol has been reported by several authors [1-4]. In mentioned works, glyceric acid, oxalic acid, glycolic acid or formic acid were reported as the main products using platinum, gold or graphite-polystyrene composite electrodes. Even the high interest in glycerol oxidation, a few works on glyceraldehyde production are reported, mainly using strong oxidant reagents and with poor selectivity. Glyceraldehyde is a compound that finds broad application in food and pharmaceutical industry, particularly as a substituent of the carcinogen compound glutaraldehyde in some food processes. In addition, special interest starts to take place in its synthesis due to its price (1g ≈ 100 EUR), which represents nearly three times more expensive than gold itself. Its high price is precisely due to complexity of the glycerol oxidation reaction and selective synthesis. Therefore, the challenge lays precisely on the generation of these derivatives with high selectivity that are produced during the reaction, and on the selection of an environmentally friendly oxidation method that will not introduce new hazardous chemicals to the process. In this view, the electrochemical oxidation method emerges as an ecofriendly process in which electrodes provides the electron source for reduction and oxidation to take place in the cathode and anode respectively.

2 Methodology
2.1 Instrument
Analysis was carried out using a Shimadzu HPLC instrument with automatic injection. The system comprises a degassing unit DGU-20A 5R, a pump LC-20AD, an auto sampler SIL-30AC, a column oven CTO—20A, a Refractive index detector RID-10A, an UV Detector SPD-20A and a communications bus module (control unit) CBM-20A. Data analysis and acquisition was performed with LabSolutions Software. The HPLC column used was a reversed-phase Aminex HPX-87C (300mm x 7.8mm).
2.2 Voltammetric Measurements

Electrochemical experiments were performed in a three electrode glass cell of 25 mL capacity and a conventional three electrode system was used. The working and counter electrode consisted of a Pt electrode (Radiometer model P101). Ag/AgCl electrode was used as a reference electrode. The glycerol electrooxidation reaction was studied in alkaline solutions (MnO₂). Two different cyclic voltammogram analyses were performed. The first one was between -1.5 and 1.5 V at 25°C and scan rate of 50 mV/s in 62 mM glycerol solutions with MnO₂ concentration between 7 and 28 mM. The second consisted of one consisted in 14mM MnO₂ solutions with a glycerol concentration of 15-124 mM.

2.4 Optimization of glycerol partial oxidation

In search of optimum conditions that lead to improve selectivity to glyceraldehydes and overall glycerol reaction, two different statistical models were developed for the optimization of selected parameters by response surface methodology (RSM). The nature of the response surface in the optimum region was studied by performing a central composite design (CCD) with rotatable design using three factors, namely the concentration of MnO₂ (A), the stirring speed (B) and the temperature (C) at three levels. The coded and natural levels as well as the range of selected independent variables are presented in Table 1. The optimization parameters were selectivity to glyceraldehyde (Y1) and glycerol overall conversion (Y2). The number of trials required by the central composite design was based according to equation (1):

\[ N=2^k+2k + N_0 \]

Where \( k \) is the number of factors, \( 2^k \) is the number of points in the cube portion of the factorial design, 2k is the number of face-centered points and \( N_0 \) are the number of experiments performed at the center. Six center-point runs were included to determine experimental error. Therefore, the number of experiments was calculated as \( N=2^3+2(3)+6=20 \). The value for rotatability (\( \alpha \)) is function of the number of points in the factorial proportion of the design (\( \alpha=(2^k)^{1/4} \)). Therefore \( \alpha \) is equal to \( (2^3)^{1/4}=1.68 \). The analysis was carried out according to the design shown in Table 1. Experiments were performed for two hours to find the optimum conditions at this time.

Table 1. Coded and natural levels of the design factors.

<table>
<thead>
<tr>
<th>Design factors</th>
<th>Coded levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: [MnO₂] (x 10⁵ M)</td>
<td>11.86 18 27 36 42.13</td>
</tr>
<tr>
<td>B: Stirring speed (rpm)</td>
<td>32 60 100 140 167</td>
</tr>
<tr>
<td>C: Temperature (°C)</td>
<td>48 55 65 75 81</td>
</tr>
</tbody>
</table>

2.3 Oxidation at controlled potential

Glycerol partial oxidation was studied at a controlled potential by means of Multiple Pulse Amperometry during prolonged electrolysis, using a potential of 0.5V (2s) and two cleaning steps at 1.5 (1s) and -1.5 V (1s). The oxidation was performed over a 13 h period time using optimum conditions. Sample was taken every hour and the analysis of the glycerol oxidation products was performed using a reversed-phase Aminex HPX-87C (300mm x 7,8mm) column at 30°C in isocratic mode with 0.003M H₂SO₄ as a mobile phase, with a flow of 0.5mL/min. The temperature of the RI detector was set to 30°C.

3 Results

3.1 Analysis of Cyclic Voltammetric data

Figure 1 shows the cyclic voltammogram of the Pt electrode in glycerol 0.063 M and 35mM MnO₂ from where it is possible to identify six different peaks, three in the positive scan and three in the negative. Peak (I) is caused by the oxidation of adsorbed hydrogen:

\[ \text{Pt-H_ads} + \text{OH}_\text{ads} + \text{Pt} + \text{H}_2\text{O} + e^- \]

The adsorption of OH⁻ (II) starts at a negative potential (-0.3 V).

\[ \text{Pt} + \text{OH}^- \text{Pt} + \text{OH}_\text{ads} + e^- \]

\[ \text{Pt} + \text{OH}_\text{ads} + \text{OH}^- \text{Pt-OH}_2 + e^- \]

\[ \text{Pt} + \text{OH}_\text{ads} + \text{Pt} + \text{OH}_\text{ads} + \text{Pt-OH}_2 + \text{H}_2\text{O} \]
Peak (III) indicates the formation of platinum oxide layer on the catalyst surface which is reduced in peak (IV). Oxidation of glycerol continues in (V) due to dehydrogenation of organic compounds and hydrogen desorption in (VI).

**3.2 Analysis of reaction order for glycerol and MnO₂**

A cyclic voltammetry study was performed for the partial oxidation of glycerol in 14mM MnO₂ with 15-124 mM of the reagent to calculate the reaction order for glycerol by means of the analysis of the anodic current following next equation:

\[
r = \left( \frac{\partial \log I}{\partial \log [C_{3}H_{8}O_{3}]} \right) \tag{6}
\]

Figure 2 shows the plot of log current vs log glycerol concentration for the three peaks (-0.5, 0.05 and 0.7 V). Good linear correlations with an average negatives slope of \(r= -0.16\) for peaks at 0.5V and 0.05V was obtained, indicating that the glycerol oxidation is inhibited by the reagent concentration and the fractional value shows that the rate determining step involves adsorbed species generated during the reaction.

For the analysis of MnO₂ reaction order, equation (7) was taken into account:

\[
r' = \left( \frac{\partial \log I}{\partial \log [MnO_{2}]} \right) \tag{7}
\]

When varying the concentration of MnO₂ between 7 and 28 Mm and keeping constant the concentration of glycerol (62 mM), an average positive slope of \(r=0.09\) (0.05 and 0.7 V). With the maximum concentration tested (28 mM), the peak at 0.05 V presented a decreasing in current, due to oversaturation of adsorbed intermediates.

**3.3 Optimization of glycerol oxidation**

A second order polynomial equation was used to express the relationship between the three factors and each independent variable response as expressed in equation (8)

\[
Y = \beta_0 + \sum_{i=1}^{j} \beta_i x_i + \sum_{i=1}^{j} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \tag{8}
\]

Where \(x\) represents the codified variables, \(\beta\) is the regression coefficient obtained from estimation of the effects and \(\varepsilon\) is the error observed in the response. The data were analyzed using Statgraphics Centurion XVI Software (V. 16.1.11) to obtain a model which describes the relationship between the
concentration of MnO₂(A), the stirring speed (B) and the temperature (C) expressed as:

\[ Y_1 = 4.05 + 105328A - 0.42B + 0.12C - 1.73 \times 10^{8}A^2 - 300AB + 4225AC - 45.52 \times 10^{-6}B^2 + 73.87 \times 10^{-4}BC - 13.61 \times 10^{-3}C^2 \]  

(9)

\[ Y_2 = 54.55 - 58225.2A - 0.04B + 1.02C + 1.40 \times 10^{8}A^2 + 102.43AB - 1018.06AC + 39.04 \times 10^{-5}B^2 - 83.446 \times 10^{-5}BC + 11.129 \times 10^{-5}C^2 \]  

(10)

Where A, B and C represent the coded values of the test variables. The analysis of variance (ANOVA) partitions the variability in the response into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. From the ANOVA analysis for each of the different responses, it was seen that for conversion into glyceraldehyde there are 2 effects (temperature and stirring speed-temperature interaction) with P-values less than 0.05 (0.0093 and 0.0432 respectively), showing that they are statistically significantly different.

Figure 5. Estimated response surface for selectivity to glyceraldehydes at temperature equal to 65°C

Figure 6. Estimated response surface for selectivity to glyceraldehyde at stirring rate equal to 100 rpm

Figure 7. Estimated response surface for overall conversion of glycerol at temperature =65 °C

Figure 8. Estimated response surface for overall conversion of glycerol at stirring speed equal to 100 rpm.

Optimum conditions for partial oxidation of glycerol with high selectivity to glyceraldehyde during the first two hours of reaction were found to be 0.22 mM MnO₂, stirring speed of 167 rpm and 82 °C of temperature.
3.3 Oxidation at controlled potential by Multiple Pulse Amperometry

The results from partial oxidation of glycerol at controlled potential are presented in figure 4, from where it is clearly seen that the current increased constantly during the reaction time (13 h). When no cleaning step was introduced, a current decay was presented after the first hour of reaction.

Figure 9. Current vs time plot at controlled potential using Multiple Pulse Amperometry

The products formed were identified and quantified by means of HPLC, Figure 10 presents the variation of products formed in function of reaction time. Overoxidation of glyceraldehyde to glyceric acid occurred. Most probably due to formation of an oxide layer or adsorption of intermediates in the electrode surface.

Figure 10. Mass of products formed (g) vs time of oxidation. a)glycerol, b)glyceric acid, c)glyceraldehydes, d)glycolic acid, e)tartronic acid, f)mesoxalic acid

4 Conclusion

In this study, the partial oxidation of glycerol was studied by electrochemical experiments. Cyclic voltammetry and Multiple Pulse Amperometry were the techniques selected to evaluate the effect of platinum electrode to oxidize glycerol in solutions of MnO₂. A central composite design was realized to find the optimum conditions to increase selectivity to glyceraldehydes and overall glycerol conversion.

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