

Modeling and multivariate analysis of the production process of alpha-hydroxy acids and hydrogen by electro-oxidation of glycerol**Modelagem e análise multivariada do processo de produção de alfa-hidroxiácidos e hidrogênio por eletro-oxidação de glicerol**

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ABSTRACT

The electro-oxidation of alkaline solutions of glycerol to obtain alpha-hydroxy acids and hydrogen is a sustainable procedure of a renewable nature, with the raw material derived from the co-production of biodiesel. The system is composed of a stirred tank electrochemical reactor built "ad-hoc" with a cell separated by ceramic where oxygen is generated to produce acids and hydrogen. The present studies were conducted by controlling the variables: temperature (°C), molar ratio (mol/mol) and current density (mA/cm²), based on experimental design and cyclic voltammogram. The empirical model and multivariate analysis were obtained through data collected by HPLC with a refractive index detector. This analysis presents the conversion of glycerol to tartronic and oxalic acid associated with the current density corresponding to factor1. Factor2 reveals the productivity of glyceric acid and glycolic acid related to molar ratio. The accumulated percentage of the two factors were more than 75% representative. The empirical model built from experimental planning had an error of less than 5%. The best phenomenological model experienced had an average error of less than 7%. From this model, the amount of hydrogen generated in the NTP was calculated.

Keywords: glycerol electro-oxidation, alpha hydroxy acids, hydrogen, empirical and phenomenological modeling, multivariate analysis

RESUMO

A eletro-oxidação de soluções alcalinas de glicerol para obtenção de alfa-hidroxiácidos e hidrogênio é um procedimento sustentável de natureza renovável, com a matéria-prima derivada da coprodução

de biodiesel. O sistema é composto por um reator eletroquímico de tanque agitado, construído "ad-hoc" com uma célula separada por cerâmica, onde o oxigênio é gerado para produzir ácidos e hidrogênio. Os presentes estudos foram conduzidos controlando as variáveis temperatura (0C), razão molar (mol / mol) e densidade de corrente (mA / cm²), com base no delineamento experimental e no voltamograma cíclico. O modelo empírico e a análise multivariada foram obtidos através de dados coletados por HPLC com um detector de índice de refração. Esta análise apresenta a conversão de glicerol em ácido tartrônico e oxálico associado à densidade de corrente correspondente ao fator 1. O fator 2 revela a produtividade do ácido glicérico e do ácido glicólico relacionado à razão molar. O percentual acumulado dos dois fatores foi superior a 75% representativo. O modelo empírico construído a partir do planejamento experimental apresentou um erro inferior a 5%. O melhor modelo fenomenológico experimentado teve um erro médio inferior a 7%. A partir desse modelo, foi calculada a quantidade de hidrogênio gerado no NTP.

Palavras-chave: eletro-oxidação de glicerol, alfa-hidroxiácidos, hidrogênio, modelagem empírica e fenomenológica, análise multivariada

1 INTRODUCTION

In this work the electro-oxidation of glycerol was aimed to generate alpha-hydroxy acids and hydrogen as a form of use of the so-called benign echo, also called the totally green pathway (ZHOU and SHEN, 2018). This is a renewable process, adding value to the surplus of glycerol production of a co-product resulting from the production of biodiesel. Biodiesel is well established as green fuel widely marketed in the US and Latin America, especially in Brazil. It is obtained from the transesterification process of triglycerides producing 1kg of glycerin as a co-product of every 10kg of biodiesel (GARCIA, et al., 2017). The product is a subject of great research interest because it involves a high energy density triol as well as because of its high power to add value to products generated from its electro-oxidation (CIRIMINNA, et al., 2014). Thus, is possible the production of the cheapest biofuel, compared to traditional fossil fuel (FARNETTI and CROTI, 2016).

Electrocatalytic processes in most cases are conducted in an alkaline medium with a platinum electrode and have been shown to be efficient in the study of electro-oxidation of glycerol according to the research carried out by Gomes and Tremiliosi-Filho (2011). The use of oxidation of glycerol by electro-oxidation has been shown to be an alternative to catalytic, biochemical and photocatalytic processes. This adds value to the industrial process as it reduces costs because the reactions occur under lighter conditions.

The system uses a stirred electrochemical reactor to reduce the effects of electrode depletion, according to Von Fraunhofer and Banks (1972). This consists of platinum-coated titanium anode, the Ag|AgCl reference electrode, in which acids are produced. These are separated by ceramic from the graphite cathode where the hydrogen is generated. The electrodes connected to the potentiostat operate in a galvanostatic mode because the tests were conducted at constant current.

The experiments were conducted in an alkaline sodium hydroxide medium, much cheaper than potassium hydroxide, but with a higher activity coefficient of up to ten percent for low concentration solutions (SILVA and LIMA FILHO, 2016).

Considering only the reactions detected from the chromatographic analysis, the simplified mechanism of the electrochemical reactions used to obtain the glyceric, tartronic, glycolic, oxalic acids is given by Equations 1 to 4, based on the literature (ROQUET et al., 1994 and FERNANDEZ et al., 2012):



The variables analyzed in the evaluation of the electro-oxidation process were: temperature ($^{\circ}C$), current density (mA/cm^2) as a function between the intensity and the area that remained constant in this work, and the molar ratio (mol / mol) between the molar concentration of the base and glycerol. Several kinetic studies on the electro-oxidation process in alkaline solutions with glycerol have reported a first order kinetics related to the phenomenological models according to Simões et al. (2010) using conventional electrodes. Therefore, this knowledge of a kinetic model that can correctly represent the transformation of the glycerol by electro-oxidation is essential in the choice of the operative conditions in function of the researched objective. In the case of the present study, the models that best represented the experimental results were developed by Liang (2009), Gil et al. (2011), Fernandez et al. (2012) and Melle et al. (2019).

Based on the experiments carried out during the development of the glycerol electro-oxidation process, the quantitative evaluation was performed without considering the steps of forming intermediates such as glyceraldehyde. A model involving the kinetic evolution of organic acids quantified during the reaction followed the simplified phenomenological mechanism as shown in Figure 1.

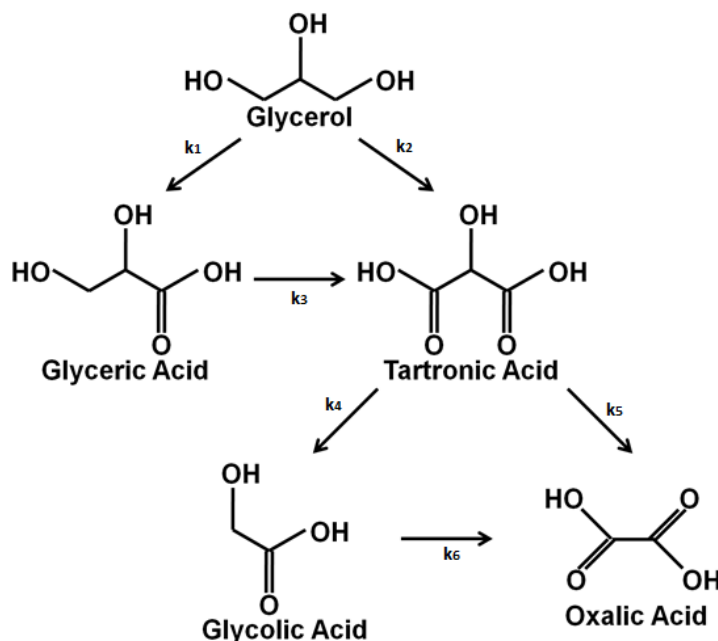


Figure 1 - Simplified phenomenological kinetic model

From the above, the system was constituted by differential equations where time is the independent variable modeled as a function of the dependent variable, in concentrations according to Equations 5 to 9:

$$dC_{GLI}/dt = -(k_1 + k_2)C_{GLI} \quad (5)$$

$$dC_{AGE}/dt = k_1C_{GLI} - k_3C_{AGE} \quad (6)$$

$$dC_{ATA}/dt = k_2C_{GLI} + k_3C_{AGE} - (k_4 + k_5)C_{ATA} \quad (7)$$

$$dC_{AGO}/dt = k_4C_{ATA} - k_6C_{AGO} \quad (8)$$

$$dC_{AOX}/dt = k_5C_{ATA} - k_6C_{AGO} \quad (9)$$

Where k_1 , k_2 , k_3 , k_4 and k_5 are the kinetic parameter constants. C_{GLI} , C_{AGE} , C_{ATA} , C_{AGO} , C_{AOX} represent the mass concentrations of the family of constituents, namely, glycerol (GLI), glyceric acid (AGE), tartaric acid (ATA), glycolic acid (AGO) and oxalic acid (AOX), respectively.

2 METHODOLOGY

In agreement with Coeuret, (1992) Figure 2 deals with an anodic curve located in the region of positive ordinates. This represents the cyclic voltammogram at a scanning speed of 50 mV/s constructed from the best conversion result. The voltammogram establishes the minimum limit of the electro-oxidation process.

This is also indicated by the coordinates of this figure obtained through the filter applied to the fast Fourier transform (FFT). The beginning of the adsorption process occurs at an electric

potential of 580.9 mV corresponding to the current intensity of 1.1 mA, where the electro-oxidation of glycerol occurs. The desorption process occurs at the platinum-coated titanium electrode at 1595.7mV and corresponds to the 333.7mA current intensity where glycerol reduction occurs (Gomes et al., 2013).

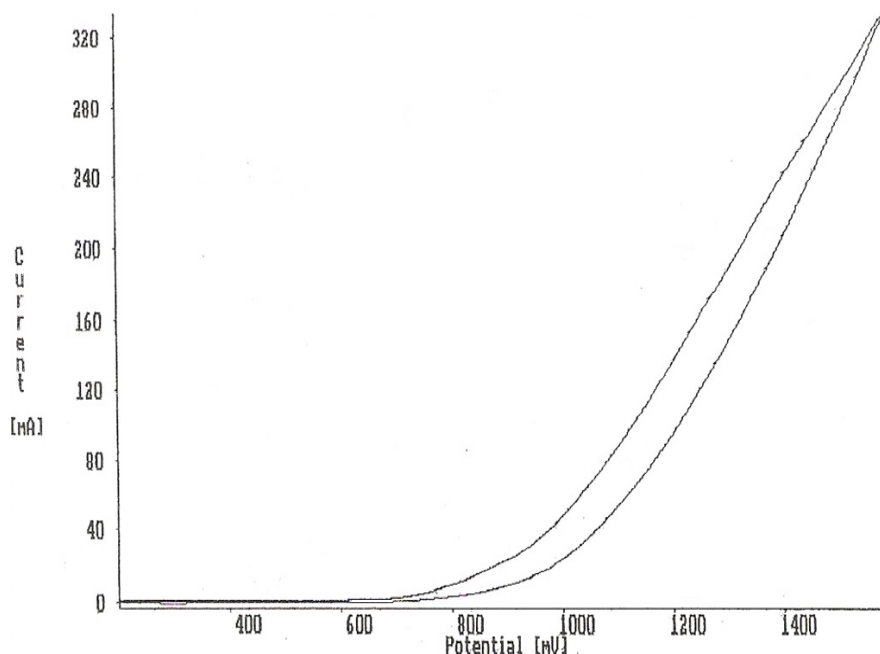


Figure 2 - Cyclic voltammogram of molar ratio 20: 1 mol / mol, temperature 323 K conducted at a scanning speed of 50.0 mV / s.

The cyclic voltammogram data establishes the initial electro-oxidation conditions for the laboratory equipment. The calculated stoichiometry values allow the design and implementation of an operating system with the objective of initiating evaluations based on experimental planning.

Table 1 below shows the experimental design for the variables under study and represents the lower and upper values that delimit the research and also the respective central points:

Table 1 - Experimental planning with molar ratio, current density and temperature.

Variable	Lower	Upper	Center
Molar ratio (mol/mol)	10	30	20
Current density (mA/cm ²)	25	75	50
Temperature (°C)	40	60	50

3 RESULTS

The limits of the factorial planning, as reported in Table 1 served to direct the procedures of preparation and analysis of the samples under study. The Pareto diagram of Figure 1 shows the main effects that each of the variables exerts on its subordinate and verifies the existence or absence of effect of the greater order created from the data in Table 2. To obtain the calculations, graphs and Figures, the StatSoft statistical program was used.

See Table 2 for the conversion values in the format described in Barros Neto et al. (2007).

Table 2 - Data resulting from the conversion of glycerol by electro-oxidation

Experiment	Ja (mA/cm ²)	T(°C)	R(mol/mol)	Cv
1	25	40	10	18.63
2	75	40	10	32.61
3	25	60	10	35.31
4	75	60	10	34.32
5	25	40	30	33.78
6	75	40	30	49.26
7	25	60	30	46.44
8	75	60	30	48.31
9	50	50	20	49.36
10	50	50	20	48.10
11	50	50	20	45.08

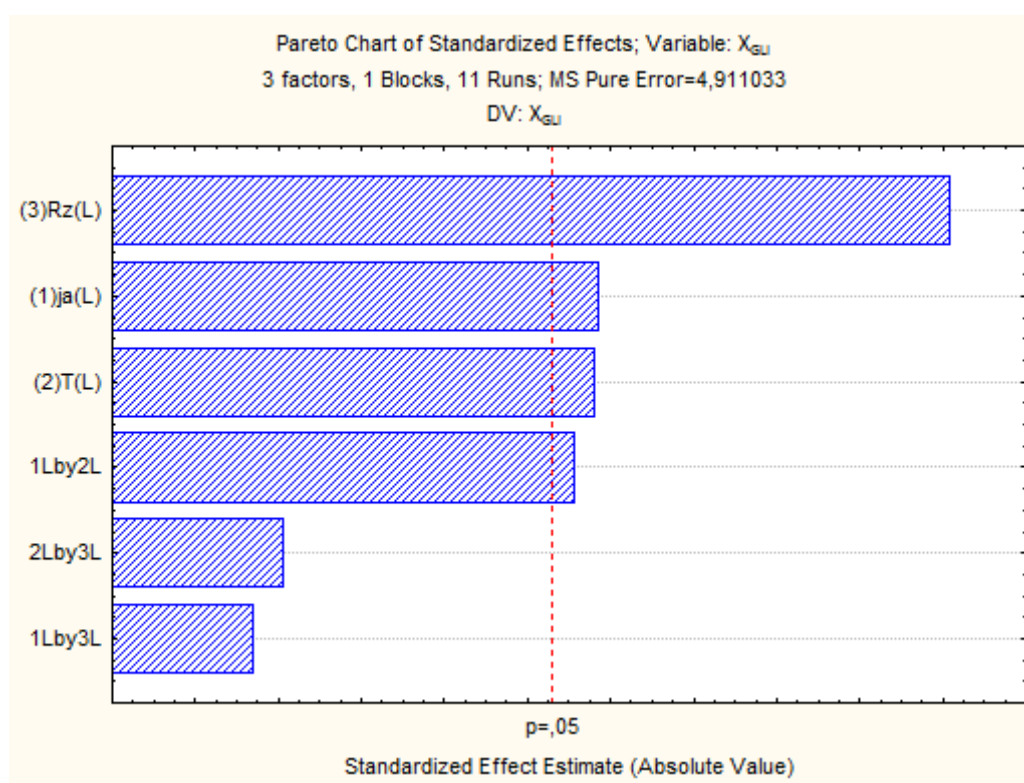


Figure 3 - Pareto diagram for molar ratio Rz, current density ja, temperature T, current density and temperature 1Lby2L, temperature and molar ratio 2Lby3L, current density and molar ratio 1Lby3L

The diagram of Figure 3 shows the molar ratio (Rz) of the variable with the greatest effect on the conversion, followed by the current density (ja) and temperature (T) respectively. These represent first order interactions in the diagram. The second-order interaction between the current density (ja) and the temperature (T) shown in the diagram by 1Lby2L complete the main effects of greater statistical significance with a level of representativity higher than 95%.

The concomitant effect of current density and temperature occurred because the reaction released heat. The other combinations of variables with second order effects were less significant and were therefore not considered in modeling. Thus, the Pareto diagram serves to show the result of the evaluation of the effects of the statistically important variables related to the production of AHA by conversion of the electro-oxidation of the glycerol.

Multivariate analysis refers to a set of statistical methods that enable the simultaneous analysis of multiple measures for each object or phenomenon observed. Thus, methods that allow the simultaneous analysis of more than two variables can be considered as part of this method of analysis.

The factor analysis is a statistical technique used to identify non-directly observable factors of the correlation between a set of observable and measurable variables. It is used to explain their relationship by simplifying these complex structures by representing revealed underlying structures that are not directly observable. The orthogonal rotation employed allows a variable to be identified by a single factor.

From the above, the corresponding load factor in Table 3, the FACTOR1 column, extracted from principal component analysis, reveals a relationship in the yield of tartronic acid (ATA) and oxalic acid (OXA) to (ja) anodic current density. Increasing current density implies increasing the electrical potential with constant resistance, thus increasing the amount of nascent oxygen in the anodic cell, allowing electro-oxidation in the primary carbon of the glycerol chain.

The FACTOR2 column in Table 3, has the glyceric acid (AGE) and glycolic acid (AGO) yields related to the effect of variable (Rz) molar ratio.

Table 3 - Load factors extracted from main components with orthogonal rotation

Variable	Factor1	Factor2
ja	0.7752	-0.4594
T	0.3536	0.0413
Rz	0.3466	0.7935
%AGE	-0.0479	0.8903
%ATA	0.9581	0.0494
%AGO	-0.1965	0.8717
%AOX	0.9255	0.0004
CGLI	0.8265	0.5317

By the factor analysis, the current density variable (ja) has a significant direct effect on the determination of all compounds obtained through electro-oxidation the current density variable (ja) results in a corresponding variation in the acquisition of the acids.

The eigenvalues of each factor expressing their individual and cumulative representativeness for yields are in Table 4.

Table 4 - Eigenvalue of each factor and respective accumulated

Factor	Eigenvalue	%Total	Accumulated	%Accumulated
1	3.399	42.491	3.399	42.491
2	2.621	32.763	6.020	75.254

It appears from the values of the two cumulative factors evaluated in Table 4, that the degree of representativeness of the system is equal to 75.25%.

The phenomenological modeling procedure proceeds by optimization considering minimizing an objective function (f_0) defined as the quadratic difference between the experimental values C_{iexp} and C_{ical} calculated from the concentrations of each component of reaction i , and is given in Equation 10:

$$f_0 = \sum [C_{iexp} - C_{ical}]^2 \quad (10)$$

The reaction constant values of the glycerol electro-oxidation process are shown in Table 5, resulting from the resolution of the differential equations 5 to 9:

Table 5 - Reaction constant of the BOX program kinetic model

k	Reaction constant
k_1	$2.10 \cdot 10^{-1}$
k_2	$4.05 \cdot 10^{-1}$
k_3	$4.26 \cdot 10^{-1}$
k_4	$1.65 \cdot 10^{-1}$
k_5	$2.56 \cdot 10^{-1}$
k_6	$4.59 \cdot 10^{-1}$

Table 6 shows an average difference of less than 7% for the calculation data compared to the experimental ones. These data correspond to the operating environment where the temperature was 323K, the molar ratio 20: 1mol / mol and the current density 0.50 Acm^{-2} .

Table 6 - Percentage concentration difference between experimental and model data

Description	Concentration difference (%)
Glycerol	5.76
Glyceric acid	6.88
Tartronic acid	6.64
Glycolic acid	6.25
Oxalic acid	7.89
Average error	6.69

Under these operating conditions, the estimated volume of hydrogen obtained was $228.325 \text{ cm}^3/\text{h}$ at CNTP and the maximum energy consumption of $108 \text{ kJ} / \text{mol}$ with an efficiency index of 57.17%.

4 CONCLUSIONS

The empirical model based on the data treatment and delimited through experimental planning presents results compatible with the values established according to Table 1. Lowering the temperature is compensated by the rise in current intensity using the same model. By the law of thermodynamics, it is impossible to use all the heat. The analysis data compared to the statistical model calculation show a significance level of 95%, and an error of 4.91% for the variables under study, as shown in Figure 3.

The experiments indicated that the increase of current intensity causes the temperature to rise concomitantly. This produces a greater amount of nascent oxygen and therefore tartronic and oxalic acid, according to Faraday, and a progression of the reaction rate according to Arrhenius. The statistical study shows this effect in the diagram in Figure 3.

Multivariate analysis revealed that the effect of current density was most significant in the glycerol electro-oxidation process and for the generation of tartronic acid and oxalic acid because higher electrode potentials facilitated the process of carboxyl formation. The molar ratio was more relevant in the production of glycolic acid and glycolic acid inherent to the higher glycerol concentration. See Table 3.

The phenomenological model obtained of the experimental planning presented reaction kinetics with an average error of 6.69% for the results and adherence higher than 93% compared to the real values obtained experimentally as shown in Table 6.

Finally, the estimated value of 228.325 cm³/h in the hydrogen NTP produced in the electrochemical reactor anode had an efficiency index of 57.17%.

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