Optimization of electrochemical oxidation of glycerol for glyceric acid production

Juan Carlos Beltrán-Prieto, Roman Slavík, and Karel Kolomazník.

Abstract—The anodic oxidation of glycerol using platinum electrodes in alkaline solution was studied to optimize the production of glyceric acid using central composite design. The parameters under study were concentration of oxidant reagent, stirring speed and temperature of reaction. Selectivity to desired product and overall conversion of glycerol were considered as the response variables. In order to perform the electrochemical oxidation, cyclic voltammetry and multiple pulse amperometry techniques were used to study the effect of potential variation, the reaction order for glycerol and oxidant reagent, ad to perform the oxidation at controlled potential.

Keywords— glycerol oxidation, central composite design, cyclic voltammetry, optimization

I. INTRODUCTION

THE growth of world biodiesel production has caused a surplus of glycerol, which is generated as a byproduct of the process. This nontoxic and biodegradable renewable fuel is constituted by mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [1,2]. Extensive research on glycerol utilization has been realized due to the fact that this molecule is highly functionalized and widely used for the synthesis of value-added chemicals.

Glycerol is used as a component to produce polymers. For example, polyglycerol ester is used in biodegradable surfactants and lubricants; poliglycerol and polyglycerol methacrylates are used as wood treatments to improve its stability; and polyester polyols are used to produce polyurethanes, which are applied as coatings, foams and sprays. In addition it can also be used to preserve the freshness of tobacco products, and it has been used in alkyd resin production, which is an important element for surface coatings and printing inks. In paper production, glycerol is used as a plasticizer and lubricant, and in the textile industry, it is used for lubricating, sizing, and softening yarn and fabric [3].

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The most important industrial uses of glycerol are in food and beverage, personal and oral care, and tobacco [4]. Glycerol and its derivatives can be blended with gasoline [5]. Etherification of glycerol produce branched oxygen containing components, with properties for use as a fuel or solvent [6]. Glycerol is used in the production of chemicals and fuels including hydrogen [7]. Pure glycerine is widely used in pharmaceutical formulations and can be obtained from saponification reactions of soap production, microbial fermentation, petrochemical feedstock and transesterification reaction of biodiesel production. Due to its properties, it is also used for improving smoothness, providing lubrication, and as humectants. It is used in cough syrups, elixirs, expectorants, ointments, plasticizers for medicine, capsules, ear infection medicines, and as a carrier for antibiotics and antiseptics [3].

Glycerol is also an important intermediate of glucose and lipid metabolism by virtue of its ability to support glycogenesis in various systems, as well as serving as a precursor for the synthesis of triglycerides and other glycerolipids [8]. Oral administration of glycerol has been demonstrated to result in increased serum glucose levels, gluconeogenesis, or both [9], similar to the changes observed in various pathological situations such as type 2 diabetes mellitus. It has also been shown that obese subjects have increased levels of plasma glycerol and increased glycerol turnover when compared with lean individuals [10]. These observations indicate the potential importance of glycerol homeostasis in healthy individuals, as well as in patients with abnormalities in glucose or lipid metabolism who are at higher risk of coronary artery disease.

Most of the glycerin in the market today is manufactured to meet the requirements of the United States Pharmacopeia (USP) and the Food Chemical Codex (FCC). However, technical grade of glycerin that are not certified as USP or FCC are available in the market as well. The purification quality of glycerin can be identified by its grade. Accordingly it can be classified as rude glycerin (70-90% glycerin) or as refined glycerin (99.5% technical grade, 96% USP –vegetable based-, 99.5% USP -tallow based-, 99.5% USP -vegetable.based-, 99.5% USP/FCC-Kosher, and 99.7% USP/FCC-Kosher.

In search of cleaner methodologies that can have applicability at industrial level, the different catalytic methodologies (homogeneous, heterogeneous and enzymatic) have been brought to bear on organic synthesis. Homogeneous

catalysis by organometallic complexes is used in both bulk and fine chemicals and is the method of choice in e. g. carbonylations and hydroformylations [11]. Similarly, biocatalysis is widely used in fine chemicals manufacture. Heterogeneous catalysts have the advantages of recovery and recycling, therefore, they are amenable to continuous processing. Heterogeneous catalysis has, moreover, already been applied in oil refining and bulk chemicals manufacture [12]

In the past years there has been a growing demand for solid catalysts efficient in the partial oxidation of alcohols for the production of fine and specialty chemicals. The use of stoichiometric inorganic reagents, though decreasing, is still widespread. The present stringent ecological standards increase the pressure to develop new, environmentally benign methods. In many instances, homogeneous catalysis provides powerful solutions, but on an industrial scale the problems related to corrosion and plating out on the reactor wall, handling, recovery, and reuse of the catalyst represent limitations of these processes [13].

Application of solid catalysts for the gas- or vapor-phase oxidation of simple, small-chain alcohols to the corresponding carbonyl compounds is well known. An important requirement is the reasonable volatility and thermal stability of reactant and products a strong limitation in the synthesis of complex molecules. Solid catalysts active in the liquid phase under mild conditions have a much broader application range [14]. A major challenge in liquid-phase oxidation with solid catalysts is to prevent leaching of the active species. The reactants and particularly the carboxylic acid-type (by) products are frequently excellent chelating agents and accelerate dissolution and deactivation of the catalysts.

Liquid phase oxidation of alcohols in the presence of supported metal catalyst are potentially very attractive reactions for the preparations of intermediates and fine chemicals because high selectivities can be obtained with environmentally clean process. Indeed, they proceed under mild conditions, with molecular oxygen as oxidizing agent and water as solvent. Supported catalyst, based mainly on platinum-group metals, are resistant to leaching, are recyclable, and are readily available from catalyst manufacturers in various compositions and forms [15].

Oxidation of aldehydes, alcohols or carbohydrate derivatives can be performed with air in aqueous media, in the presence of palladium and platinum catalyst under mild conditions (293-353 K and atmospheric pressure). These reactions are environmentally friendly and could replace stoichometric oxidations with mineral oxidizing agents. They operate via an oxidative dehydrogenation mechanism whereby the functional groups adsorb and dehydrogenate on the metal surface, followed by oxidation of the adsorbed hydrogen atoms. This was supported by kinetic modeling of oxidation experiments and by direct observation of hydrogen evolving from aldose aqueous solutions at basic (pH >11) in the presence of platinum or rhodium catalysts. The dehydrogenation mechanism was also supported by various physical and chemical measurements. Thus, oxidation experiments of ethanol or 2-propanol conducted with ^{18}O/labeled oxygen showed that this isotope was not incorporated into reaction products. Measurements of electrode potential showed that the potential of the platinum catalysts in alcohol solutions was almost similar to that of the hydrogen electrode, i.e. Pt-surface was predominantly covered with hydrogen even though the oxidation reaction was run under 1 bar of oxygen [16].

The aqueous noble metal catalysed alcohol oxidation, resulting in ketonic, aldehydic and carboxylic acid groups, is a reaction which can profitably be applied in fine-chemistry and for carbohydrate conversion [17]. The nobel metal catalysed oxidation of alcohols, especially polyols, in aqueous phase is attractive because of the mild reaction conditions and the high selectivity that can be obtained. It is environmentally friendly process compared to classical oxidation methods, as water is the secondary product next to the oxidized alcohol. It provides useful carbonyl compounds and carboxylic acids for various applications in fine chemistry [18]

The platinum catalyzed oxidation of alcohols with molecular oxygen in aqueous medium was discovered almost two hundred years ago [19]. The method has been improved with the general development of heterogeneous catalysis. At the beginning of the last century it was found that not only platinum, but dispersed palladium was also a good catalyst for the reaction [13]. The next milestone was the promotion of platinum metals with heavy metals such as Bi or Pb to overcome the deactivation problems and change the direction (selectivity) of the reaction [13].

Selective oxidations e.g. alcohol oxidations and olefin epoxidations, are pivotal transformations in organic synthesis [20]. Many of these transformations are currently performed, both on laboratory and industrial scale, by use of stoichiometric inorganic oxidants, e.g. chromium (VI) reagents. There is an urgent need, therefore, for catalytic methods that employ O_2 or H_2O_2 as the primary oxidant and are effective with a broad range of substrates. Heterogeneous catalyst has the added benefits, compared with their homogeneous counterparts, of ease of recovery and recycling and amenability to continuous processing. Site-isolation of transition metal centers in an heterogenous system can afford catalysts with high activity [21].

A. Catalyst and reaction conditions

Pt-group metals can activate alcohols and molecular oxygen under close to ambient conditions and produce the corresponding carbonyl compounds or carboxylic acids in high yields. Today, various bi- and multimetallic catalysts are applied that are more active, more selective, and less prone to deactivation than monometallic catalysts.

The most commonly used catalysts consist of Pt or Pd as active components and Bi or Pb as promoters, on carbon and alumina supports. Ru and Rh are usually applied without promoters. Besides Bi and Pb, a variety of promoter metals

have been suggested, including Cd, Co, Cu, Se, Ce, Te, Sn, Au, and Ru. The non-noble metal promoters are inactive under reaction conditions, and their deposition onto the active sites should result in lower oxidation rates. Still, promotion of Pt or Pd may lead to a considerable rate enhancement and to a remarkable shift in the product distribution

Various strategies can be envisages for the inmobilization of redox-active elements in a solid matrix. Mixed oxides, e.g. the TiO_2-SiO_2 epoxidation catalyst, can be prepared by impregnation techniques or by the sol-gel method. The latter is analogous to the hydrothermal synthesis of zeolites and related molecular sieves. Redox metal ions can be incorporated into acidic clays or zeolites by ion exchange, and oxoanions can be similarly exchanged into hydrotalcite-like anionic clays.

Alternatively, redox metal ions can be incorporated into framework positions of zeolites and realted molecular sieves by hydrothermal synthesis or post synthesis modifications. A suitable choice of molecular sieve, with an appropriate pore size and hydrophobicity, enables one to influence which molecules can readily access the active site on the basis of their dimensions and/or their hydrophobic or hydrophilic properties. Such materials bear a resemblance to redox enzymes in which the protein mantle plays an analogous role and, for this reason, these redox molecular sieves have been referred to as mineral enzymes [22]. Redox metal centers can also be grafted on the surface of silica, or on to the internal surface of a molecular sieve, by ligand displacement with pendant silanol groups. Alternatively metal complexes can be tethered to silica or the internal surface of a molecular sieve via a spacer that is attached to the surface. This approach is analogous to the tethering of organic bases to solid surfaces referred to earlier. Metal complexes can also be attached to oxidatively stable organic polymers such as polybenzimidazole [21]. Supported noble metals widely used as hydrogenation catalysts can be used to catalyze the reverse reaction-oxidative dehydrogenation-in the presence of oxygen. This is applied, for example, in the oxidative dehydrogenation of alcohols and carbohydrates.

B. Oxidation of primary alcohols to aldehydes

The selective oxidation of primary alcohols to aldehydes is one of the most important functional group transformations in organic synthesis and industrial fine chemical productions. Conventional methods are based on chromium reagents like manganese dioxide, silver oxide, N-chlorosuccinimide [14], dimethyl sulfoxide activated by oxalyl chloride [23] and periodanes [24]. These methods are restricted to laboratory scale usage because of the toxicity or corrodibility of the reagents, and the amount of chemical waste, which is produced due to the stoichiometric nature of these processes. Other oxidation methods use stoichiometrically e.g. oxygen or hydrogen peroxide. In addition, nitroxyl radicals like 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) and its derivatives in combination with copper ions, proved to be efficient as selective catalysts in the oxidation of alcohols to the corresponding carbonyl compounds [25]. There have also

been a number of studies of glycerol oxidation using carbon-supported Pt or Pd catalyst with molecular oxygen as oxidant.

C. Glycerol oxidation

As glycerol contains two types of –OH groups i.e., primary and secondary alcoholic groups, it undergoes all reactions characteristic of these groups. In addition, it also undergoes some reactions typical of polyhydric alcohols. One of the two primary alcohol functions can be selectively oxidized in basic media to give sodium glycerate. This was best achieved with Pd/C catalysis at pH 11, glycerate selectivity was 70% at 100% conversion, tartronate and oxalate were the main by-products [26]. Although further oxidation of glycerate in the presence of palladium or platinum catalyst was slow, when oxidation was conducted with a 5% Pt-1.9% Bi/C catalyst under basic conditions (pH 10-11), 83% yield in tartronate was obtained at 85% conversion [27]. They also studied glycerol oxidation over bismuth promoted Pd and Pt catalyst and showed that the oxidation of the primary hydroxyl group to give glyceric acid was dependent upon pH and that the oxidation of the secondary hydroxyl group of glyceric acid was preferred under acidic conditions.

Patents have been issued on the oxidation of glycerol and derivatives. A 54% yield of sodium glycerate was claimed for oxidation of glycerol over Pd/C at pH 8-13 [28]. Amination of glyceric acid with NH_3 solution yielded 38% serine [29]. This amino acid was also obtained by oxidation of serinol [30], prepared by reductive amination of dihydroxyacetone [31]. They also reported that by tuning the reaction conditions with these catalysts, selectivities to products such as dihydroxyacetone could be increased and that the reaction was pH sensitive. In particular, Bi promotion or Pt was found to significantly enhance the selectivity to dihydroxyacetone.

The challenge is the relatively complex glycerol oxidation network, seven potential C_3 oxygenated products – dihydroxyacetone, hydroxypyruic acid, mesoxalic acid, glyceraldehydes, glyceric acid, tartronic acid and hydroxymethyl glyoxal, together with C_2 (oxalic acid, hydroxyethanoic acid) and C_1 products (formic acid, CO_x) – can be obtained from the oxidation reaction of glycerol. Selective versus nonselective oxidation is, therefore, the big challenge associated with these catalytic oxidation reactions.

Particular interest lays on the partial oxidation of glycerol, which can produce valuable compounds, namely glyceraldehyde, dihydroxyacetone, glyceric acid, glycolic acid, mesoxalic acid and tartronic 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 [32-35]. 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. Glyceric acid is an important compound that finds broad application in food and pharmaceutical industry. The challenge in the oxidation of

glycerol lays on the generation of 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.

D. Central composite design

Multivariable design of experiments is an important approach to analyze and find out a set of design or process variables that influence the process and therefore determine at what levels these variables must be kept to optimize the response characteristic of interest [36]. In the present research, surface response methodology via the proposal of a central composite design was used to optimize the electrochemical oxidation of glycerol considering three different parameters (temperature, concentration of oxidation agent and stirring speed) and the effect on the response variables (selectivity to glyceric acid and conversion of glycerol)

II. METHODOLOGY

A. 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). The cyclic voltammetric measurements were performed using an EmStat Potentiostat with computerized control by PSTrace Software.

B. Voltammetric Measurements

A conventional three electrode system was used and electrochemical experiments were carried out in a three electrode glass cell of 25 mL capacity. The working and counter electrode consisted of a Pt electrode (Radiometer model P101) and a Ag/AgCl electrode was selected as reference electrode. The glycerol electrooxidation reaction was studied in alkaline solutions (NaOH).
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C. Optimization of glycerol oxidation

In order to optimize the parameters (concentration of oxidant reagent, temperature and stirring speed) to improve selectivity to glyceric acid and glycerol conversion, central composite design with rotatable design was used. Table 1 presents the range of selected independent variables and the coded and natural levels. The optimization parameters were selectivity to glyceric acid (Y1) and glycerol conversion (Y2).

The number of experiments was found to be 20. This value comes from the consideration of equation (1)

$$N = 2^k + 2k + N_0 \qquad (1)$$

Considering k as 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 is the number of experiments performed at the center.

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

Design factors	Coded levels				
	-1.68	-1	0	1	1.68
A:[NaOH] ($x10^5$ M)	20	40	70	100	120
B: Stirring speed (rpm)	42	70	110	150	177
C: Temperature (°C)	40	50	65	80	90

D. Multiple Pulse Amperometry

Multiple Pulse Amperometry during 14 h was used to maintain the electrolysis. A potential of 0.017 V (2s) and two cleaning steps at 1.0 (1s) and -1.0 V (1s). The oxidation was performed over a 14 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 (300 mm x 7,8 mm) column at 30°C in isocratic mode with 3 mM H_2SO_4 as a mobile phase, with a flow of 0,5mL/min. The temperature of the RI detector was set to 30°C.

E. Quantitative analysis of products

Methodology for quantitative analysis of glycerol derivatives concentration was followed according to reference [37].

III. RESULTS

A. Analysis of Cyclic Voltammetric data

Fig.1 shows the cyclic voltammogram of the Pt electrode in glycerol 70m M and 14mM NaOH. As it can be seen, there are two peaks responsible for oxidation of glycerol at different potentials (0.015 and 2.8 V respectively).

A. 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 (2)

$$Y = \beta_0 + \sum_{i=1}^{j} \beta_i x_i + \sum_{i=1}^{j} \beta_{ii} x_i{}^2 + \sum \sum_{i<j}^{j} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

In the equation, x represents the codified variables, β is the regression coefficient obtained from estimation of the effects and ε is the response error.
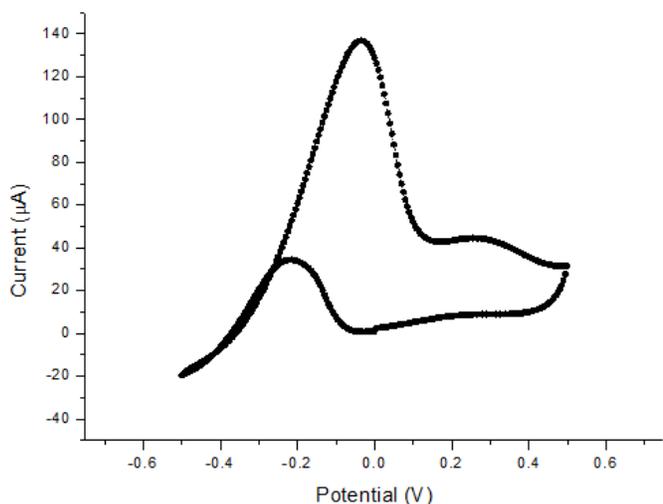
Fig.1. Cyclic voltammogram of the Pt electrode in 0.063 M glycerol solution and 35mM MnO$_2$

The Software Statgraphics Centurion XVI (V. 16.1.11) was used to analyze the experimental data and to obtain a model which describes the relationship between the parameters under study and the response variable. Table 2 shows the ANOVA results, from where A:[NaOH], B:stirring speed, and C:temperature.

Table 2. Analysis of Variance for selectivity to glyceric acid

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A	2510.96	1	2510.96	38.26	0.0001
B	144.10	1	144.10	2.20	0.1692
C	39.96	1	39.96	0.61	0.4532
AA	906.81	1	906.81	13.82	0.0040
AB	18.0	1	18.0	0.27	0.6119
AC	8.0	1	8.0	0.12	0.7342
BB	99.62	1	99.62	1.52	0.2461
BC	32.0	1	32.0	0.49	0.5009
CC	325.22	1	325.22	4.96	0.0502
Total error	656.20	10	65.62		
Total (corr.)	4576.95	19			

The ANOVA table partitions the variability in selectivity 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. In this case, 2 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level. The R-Squared statistic was found to be 85.6%, which explains the variability in selectivity.

Fig. 2 describes the effect of stirring speed and oxidant concentration on selectivity to glyceric acid and Fig. 3 shows the contours of estimated response surface. It is clearly seen from both figures, that selectivity is increased at lower concentration of NaOH (40 mM), lower stirring speed (42 rpm) and at temperature of 65 °C. By a similar study, the conversion of glycerol, (Fig. 3 and Fig. 4) was favored by higher concentration of oxidant and higher stirring speed at 65°C and at temperature of 65 °C.

Table 3 shows the analysis of variance for glycerol conversion, where 1 effect has P-values less than 0.05.
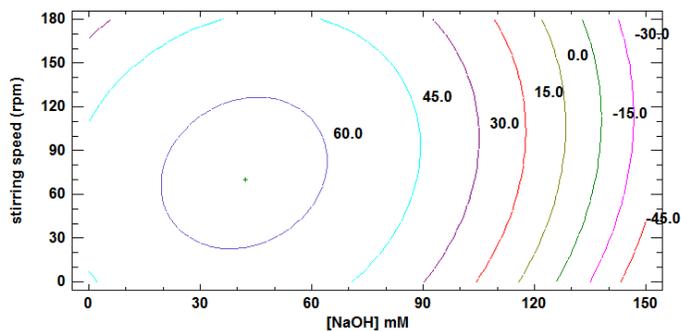
Fig. 2. Contours of estimated response surface for selectivity to glyceric acid at temperature equal to 65 °C
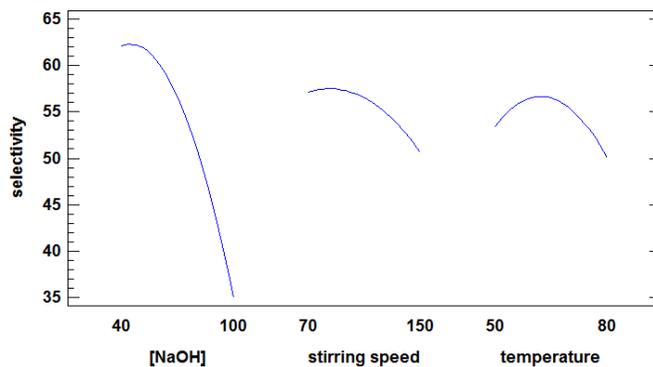
Fig. 3. Main effects plot for selectivity.
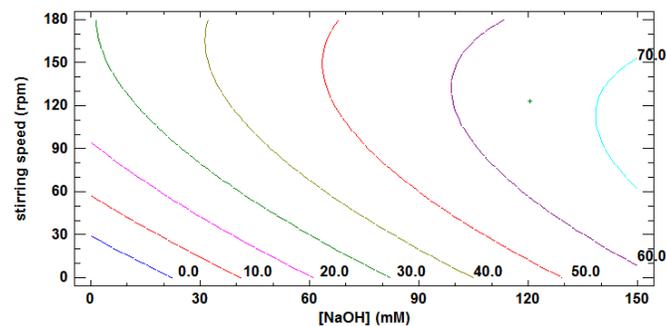
Fig. 4. Contours of estimated response surface for overall conversion of glycerol at temperature =65 °C
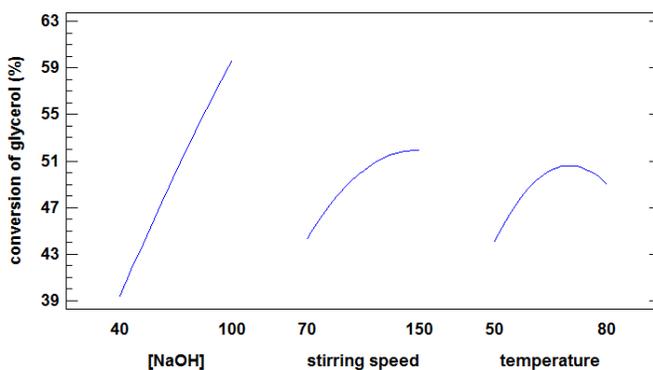
Fig. 5. Main effects plot for overall conversion of glycerol

Table 3 Analysis of Variance for glycerol conversion

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A	1402.74	1	1402.74	15.24	0.0029
B	192.83	1	192.83	2.09	0.1784
C	82.84	1	82.84	0.90	0.3652
AA	5.86	1	5.86	0.06	0.8059
AB	18.0	1	18.0	0.20	0.6678
AC	0.0	1	0.0	0.00	1.0000
BB	60.67	1	60.67	0.66	0.4358
BC	0.5	1	0.5	0.01	0.9427
CC	191.24	1	191.24	2.08	0.1801
Total error	920.58	10	92.05		
Total (corr.)	2850.55	19			

By the analysis of the data, two models were obtained that describes the relationship between the concentration of NaOH (A), the stirring speed (B) and the temperature (C) with both response variables (selectivity and glycerol conversion). The models are expressed in equations 3 and 4:

$$\text{Selectivity (\%)} = -24.43 + 0.78\,A - 0.023\,B + 2.41\,C - 0.008\,A^2 + 0.001\,AB - 0.002\,AC - 0.001\,B^2 + 0.0033\,BC - 0.021\,C^2 \quad (3)$$

$$\text{Conversion of glycerol} = -88.52 + 0.57A + 0.43\,B + 2.22\,C - 0.0007\,A^2 - 0.001*AB - 0.0012\,B^2 + 0.0004\,BC - 0.016\,C^2 \quad (4)$$

B. Oxidation at controlled potential by Multiple Pulse Amperometry

The results from partial oxidation of glycerol at controlled potential are presented in Fig. 6, 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. The products formed were identified and quantified by means of HPLC, Fig. 7 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.
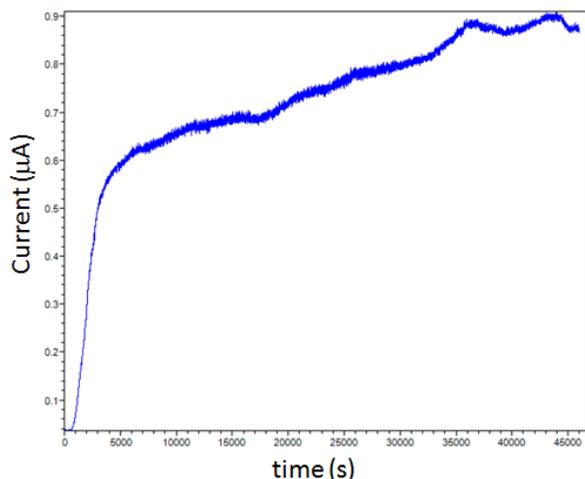
Fig. 6. Current vs time plot at controlled potential using Multiple Pulse Amperometry
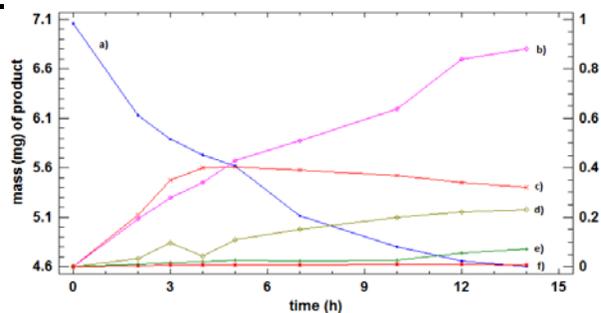
Fig. 7. Mass of products formed (mg) vs time of oxidation. a)glycerol, b)glyceric acid, c)glyceraldehydes, d)glycolic acid, e)tartronic acid, f)mesoxalic acid

IV. CONCLUSION

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

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