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Synthesis of Lactic Acid by Alkaline Hydrothermal Conversion of Glycerol at High Glycerol Concentration

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The synthesis of lactic acid by alkaline hydrothermal conversion of glycerol at high glycerol concentrations under autogenous pressure is described. Temperature (250–290 °C), NaOH/glycerol molar ratio (1.1–1.75), glycerol concentration (2.5–3.5 M), and reaction time (30–250 min) have been the variables studied with temperature and NaOH/glycerol molar ratio having the major influence. An 84.5% lactic acid (as sodium lactate) yield is obtained at 280 °C and 90 min with a 2.5 M glycerol concentration and a 1.1 NaOH/glycerol molar ratio. The same yield is obtained starting from crude glycerol from biodiesel production as raw material. Sodium acrylate, oxalate and formate, and sodium carbonate have been identified as the main byproducts with carbonate being the major one. Several conversion routes based on the experimental results are proposed. A process for lactic acid separation based on electrodialysis is outlined.

1. Introduction

In recent years there has been growing interest in the chemical industry for developing new synthetic routes based on renewable raw materials. Glycerol is a main candidate to be used as a building block in chemical synthesis. It is currently obtained as a byproduct in the biodiesel industry in such a way that its annual production from biodiesel has tripled from 1995 to 2006¹ from 200 000 to 600 000 tonnes. In fact, glycerol has been selected by the U.S. Department of Energy as one of the 12 top building block chemicals that can be produced from biomass and subsequently converted into a number of high-value biobased chemicals or materials.²

Lactic acid is one of the most useful chemicals which can be obtained from glycerol. Currently, it is used as a precursor of green solvents such as ethyl lactate and in the synthesis of poly(lactic acid), which is increasingly used for producing biodegradable packaging. However, the use of lactic acid is limited by its high price because 95% of the lactic acid world production is based on fermentative pathways.³

Hydrothermal conversion of biomass components has been shown to be a good technique for obtaining low molecular weight organic acids.^{4–7} The synthesis of lactic acid by hydrothermal conversion of biomass wastes has been reported by several research groups^{7,8} although with low yields. Bicker et al.⁹ reported the lactic acid synthesis from carbohydrates using Co(II), Ni(II), Cu(II), and Zn(II) catalysts. A 53% yield is obtained starting from sucrose. Recently, Yuksel et al. reported the hydrothermal alkaline electrolysis of glycerol at low glycerol concentration (0.1 M) and 280 °C both in a batch reactor¹⁰ and in a continuous flow one.¹¹ The best results are obtained in the batch reactor, but although conversion of glycerol is 92%, lactic acid yields are low, with the maximum yield being 34.7%.

Much better lactic acid yields are obtained by alkaline hydrothermal conversion of glycerol. Kishida et al.¹² reported yields of 90% starting from 0.33 M glycerol solutions with a

NaOH concentration of 1.25 M at 300 °C. Shen et al.¹³ studied the influence of different alkali-metal and alkaline-earth-metal hydroxides in the yield of lactic acid on alkaline hydrothermal conversion of glycerol into lactic acid starting from 0.33 M aqueous solutions of glycerol. A 90% yield was obtained using KOH and NaOH at 300 °C. The work of Shen et al.¹³ is focused on the effect of alkali-metal and alkaline-earth-metal hydroxides as well on the influence of metal ions on lactic acid yields and reaction mechanism.

The routes studied by Kishida et al.¹² and Shen et al.,¹³ while showing the high industrial potential of this reaction, have an important drawback for industrial development because of the very low glycerol concentration in the reactor. Assuming a 90% yield, the lactic acid concentration obtained at a starting glycerol concentration of 0.33 M is 26.7 g/L is too low for an economically feasible chemical process and even much lower than that obtained in the currently used fermentative route to lactic acid. At such low concentration, the low space-time yield of the process leads to a low productivity. Much higher lactic acid concentrations are needed to develop an industrially feasible process for manufacturing lactic acid from glycerol. On the other hand, before industrial development a deeper study about the influence of other reaction parameters, such as temperature, reaction time, and glycerol/alkali molar ratio, is necessary.

This paper is focused on these last two items. Thus, the hydrothermal alkaline conversion of glycerol into lactic acid is studied at 10-fold glycerol concentration higher than the one reported by Shen et al.¹³ by analyzing the influence of temperature, reaction time, and glycerol/alkali molar ratio on reaction yields and byproduct formation. Likewise, the alkaline hydrothermal conversion routes of glycerol, lactic acid, and reaction intermediates are discussed, and an isolation procedure is proposed.

2. Materials and Methods

2.1. Materials. Glycerol (99%), glyceraldehyde (95%), and pyruvaldehyde (99%) were obtained from Sigma-Aldrich (Madrid, Spain). Sodium hydroxide (98%), orthophosphoric acid (85%), lactic acid (92%), acrylic acid (99%), oxalic acid (99%), formic

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acid (98%), and barium chloride (99%) were supplied by Panreac (Madrid, Spain). Deionized water was used in all experiments.

CH₄, CO, CO₂, and H₂, all of them 99.99% pure, were supplied by Air Liquide (Spain) and used as standards for identification of gas products by mass spectrometry.

2.2. Experimental Setup. Reactions were carried out in a 400 mL stainless steel high-pressure reactor fitted with temperature and pressure measurement devices, a magnetic stirrer, a Watlow Band Heater ThinBand of 110 mm in diameter and 80 mm in width (Watlow Ibérica, Madrid, Spain) made of stainless steel with mica insulation able to work up to 540 °C, and an EZ-ZONE temperature controller (Watlow Ibérica, Madrid, Spain).

2.3. Reaction Procedure. A 100 mL amount of an aqueous solution composed of glycerol and sodium hydroxide at the concentrations and molar ratios specified in section 3 were introduced into the reactor. After closing the reactor, the reaction mixture was heated at 9 °C/min up to the selected reaction temperature while stirring at 500 rpm. As the influence of temperature was studied between 250 and 290 °C, the heating time was ranged between 25.5 and 30 min. The reported reaction times do not include the corresponding heating times. However, as the reaction proceeds slowly below 250 °C, the influence of heating time on the results is very low. Once reaching the desired temperature, the reaction was kept for the desired time under autogenous pressure ranging from 35 to 70 bar depending on the mixture composition and temperature. Then, the reaction mixture was quickly cooled and an aliquot was taken for analysis.

The initial glycerol and NaOH concentrations reported are the ones prepared at room temperature. Considering that the 400 mL autoclave was loaded with 100 mL of reactant mixture, 300 mL of the reactor volume is available for the vapor phase and consequently a relatively large amount of water could move to the gas phase during the reaction, modifying dramatically the reported concentrations. However, as shown below, this does not happen and initial nominal concentrations are close to the reported ones. The maximum amount of water in the gas phase was estimated by using the ideal gas equation under experimental conditions leading to both the maximum and the minimum amount of water in the gas phase: 70 atm, 290 °C and 35 atm, 250 °C, respectively. In both cases, the worst situation with respect to changes in concentrations was assumed, that is, the reaction pressure was solely due to gaseous water, which is only true just at the beginning of the reaction because the pressure always remained constant with time, meaning that the water partial pressure, and therefore the water amount in the gas phase, decreases with reaction time while the total pressure remains constant as a consequence of the H₂ produced. Calculations show that the decrease in solution volume was between 4.4% and 8.2%. Therefore, real initial glycerol and sodium hydroxide concentrations were 4.4–8.2% higher than the nominal ones, depending on experimental conditions.

2.4. Analysis. Lactic acid, oxalic acid, formic acid, and acrylic acid were analyzed by HPLC with a Hewlett-Packard apparatus model 1100, fitted with a Diode Array UV detector Agilent series 1100 and a Synergi C18 column. Chemicals were detected at 210 nm. Samples for analysis were prepared by diluting aliquots of the reaction mixture in an aqueous solution of H₃PO₄, pH 2.0. The dilution factor was 1:100. The injection volume was 5 µL, and the column temperature was 25 °C. An aqueous solution of H₃PO₄, pH 2.0, was used as the mobile phase, and samples were eluted at a flow rate of 1 mL/min.

Before analysis, samples were filtered thorough 0.45 µm nylon syringe filters. Quantification of reaction products was carried out using calibration curves. Taking into account the reaction stoichiometry, lactic acid yields in percent were calculated by dividing the amount of lactic acid moles by the number of starting moles of glycerol and multiplying the result by 100. Glycerol was analyzed by HPLC in the same conditions described above but using a refractive index detector Agilent Series 1100 instead of an UV detector. Glycerol conversions were calculated as a percentage of the initial glycerol moles reacted.

Gas products were analyzed by mass spectrometry using an OmniStar GSD 301 C mass spectrometer (Pfeiffer Vacuum) previously calibrated with CH₄, CO, H₂, and CO₂. Samples of the gaseous phase were taken by means of a Tedlar bag of 3 L at the end of reactions.

Carbonate content was analyzed by an acid–base titrimetric method as follows: 1 mL of reaction mixture was diluted in 100 mL of deionized water. A 10 mL amount of this solution was poured into a 200 mL Erlenmeyer flask, and the solution was boiled. Then, an excess of 20% w/w aqueous barium chloride solution was added while boiling. The precipitate consisting of barium hydroxide and barium carbonate was filtered off and washed with hot water. The solid was dispersed on deionized water. A 0.1 N hydrochloric acid solution was added up to pH 8 in order to convert barium hydroxide to water and barium carbonate to barium hydrogen carbonate. Hydrogen carbonate was titrated with 0.1 N hydrochloric acid using methyl orange as an indicator. Then, the carbonate molar concentration in mol/L was calculated as 1

$$\text{CO}_3^{2-}(\text{mol/L}) = (N_{\text{HCl}} V_{\text{HCl}} f) / 2V_s = V_{\text{HCl}} / 2 \quad (1)$$

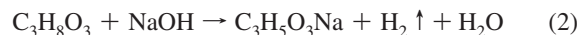
where N_{HCl} is the normality of HCl (0.1 N), V_{HCl} is the volume in mL of 0.1 N hydrochloric acid consumed, f is the dilution factor (100), and V_s is the volume of diluted sample taken for analysis (10 mL).

Metal contents in the reaction medium were determined by inductively coupled plasma (ICP) spectrometry in a Thermo Jarrell Ash Iris HR spectrometer.

3. Results and Discussion

All reactions were carried out with NaOH in excess with respect to the stoichiometric amount. Then, at the end of the reactions both lactic acid and other acidic chemicals synthesized as byproduct were obtained as sodium salts. However, as the target molecule must be marketed as its free acid form, the acid forms of all chemicals have been used for expressing the results and for discussion, with the exception of sodium carbonate which is expressed as carbonate ion.

3.1. Alkaline Hydrothermal Conversion Routes of Glycerol, Lactic Acid, and Intermediates. As shown by Kishida et al.,¹² the alkaline (NaOH) hydrothermal conversion of glycerol to lactic acid (lactate) proceeds through the following stoichiometric reaction



A HPLC chromatogram of the reaction mixture for a reaction carried out at 280 °C, 1.33 NaOH/glycerol molar ratio, 3 M glycerol concentration, and 90 min is shown in Figure 1. As it can be seen, lactic acid was the main reaction product but oxalic acid, formic acid, and acrylic acid were also detected. Carbonate was detected by titration as well. At glycerol concentrations

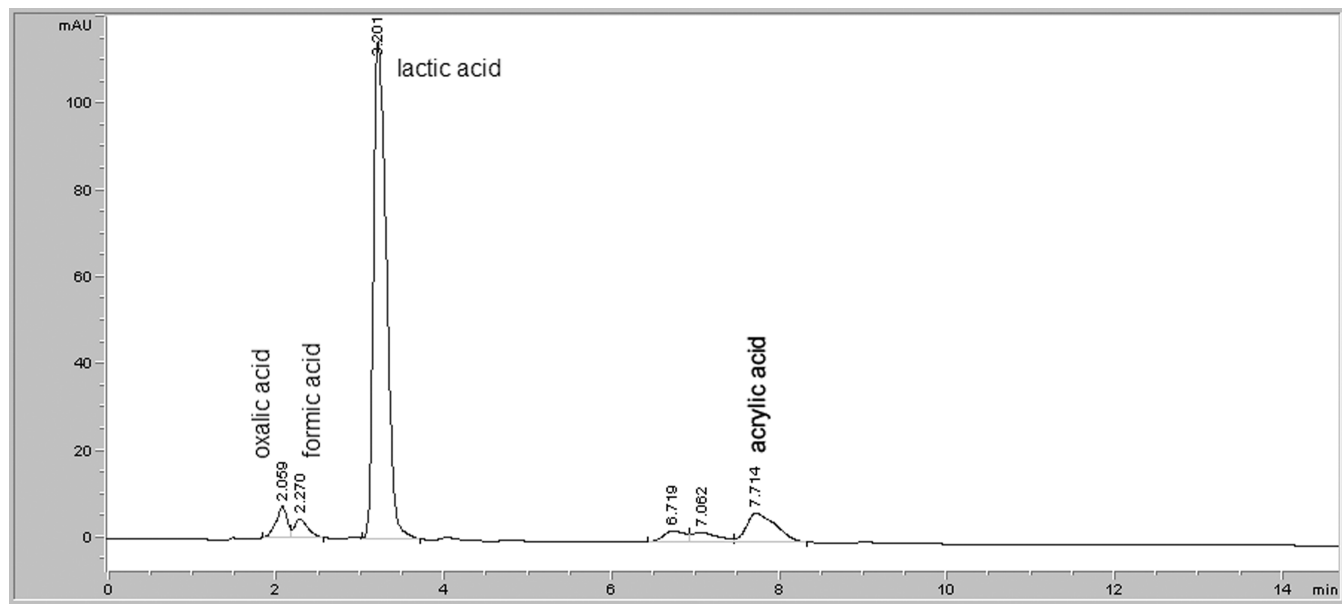


Figure 1. HPLC chromatogram of reaction products at 280 °C. NaOH/glycerol molar ratio, 1.33; glycerol concentration, 3 M; reaction time, 90 min.

Table 1. Alkaline Hydrothermal Conversion of Glycerol, Lactic Acid, Glyceraldehyde, and Pyruvaldehyde^a

substrate	substrate conversion (%)	lactic acid yield (%)	oxalic acid/lactic acid (mol/mol)	formic acid/lactic acid (mol/mol)	carbonate/lactic acid (mol/mol)
lactic acid	4.3		1.7×10^{-4}	0.025	0.23
glycerol	100	89.9	9.7×10^{-3}	0.049	0.23
glyceraldehyde	100	43.5	1.0×10^{-4}	0.010	0.02
pyruvaldehyde	100	65.5	3.1×10^{-4}	0.560	0.46

^a Experimental conditions: 280 °C, 90 min reaction time, 1.33 NaOH/starting product molar ratio, and 1 M substrate concentration.

10–100-fold lower than the ones used in this work, Shen et al.¹³ detected formic acid, acrylic acid, and acetic acid and Kishida et al.¹² also detected pyruvaldehyde and pyruvic acid in addition of those acids, but both research teams have not reported neither oxalic acid nor carbonate. According to Kishida et al.,¹² glyceraldehyde, 2-hydroxypropenal, and pyruvaldehyde are intermediates in the alkaline hydrothermal glycerol conversion to lactate. In order to elucidate the conversion products of these chemicals, several reactions were carried out starting from glycerol, lactic acid, glyceraldehyde, and pyruvaldehyde. Experimental conditions and results are reported in Table 1. Acrylic acid (not shown in Table 1) was detected, but acetic acid was not. As it can be seen from Table 1, lactic acid is very stable under the reaction conditions with formic acid and carbonate being the main conversion products. For the other three chemicals lactic acid is the main conversion product with formic acid and carbonate being the main byproduct, especially for pyruvaldehyde conversion.

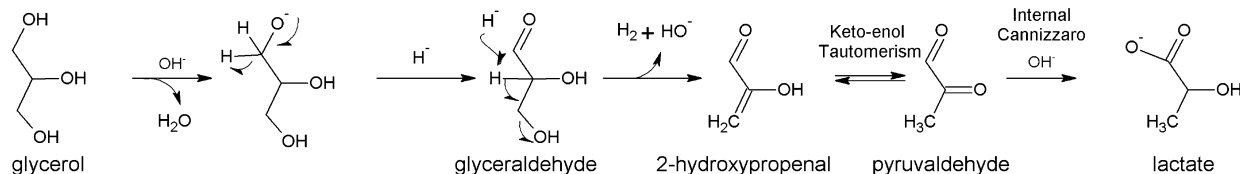
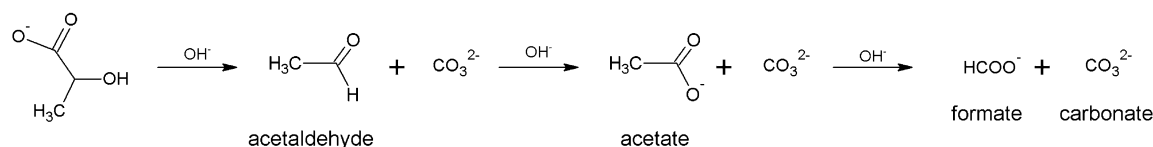
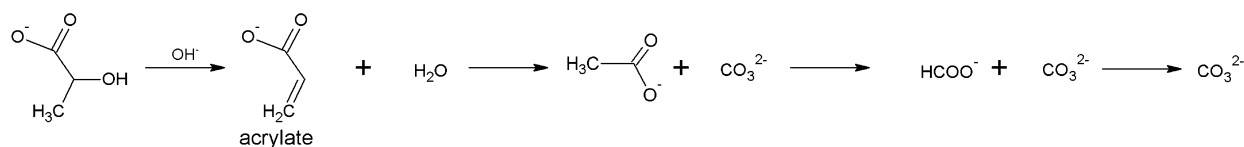
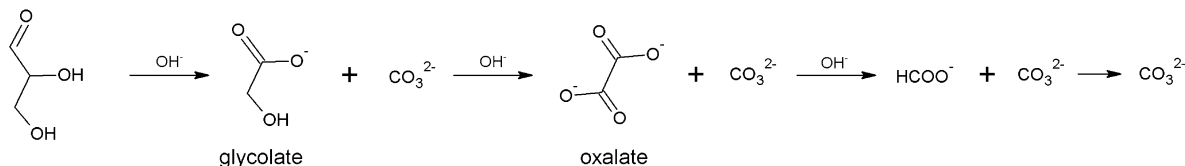
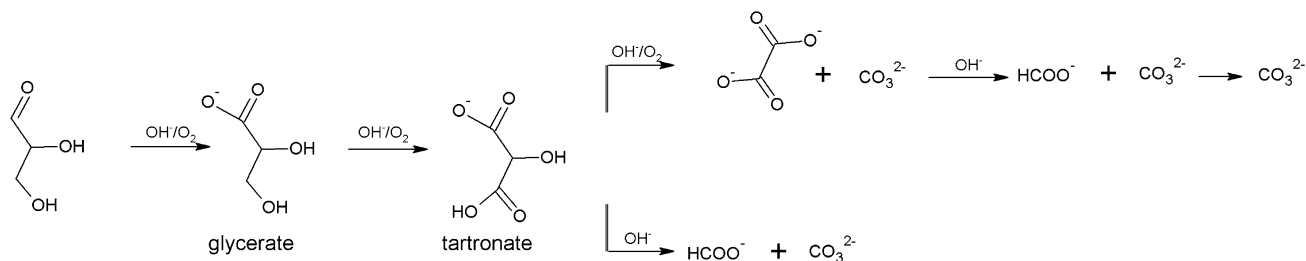
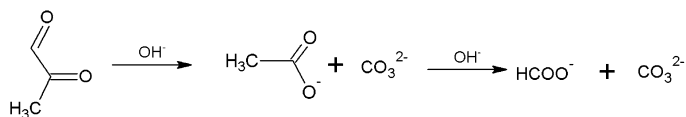
According to all these findings several alkaline hydrothermal conversion routes of glycerol, lactic acid, and reaction intermediates can be envisioned, which are given in Scheme 1. These routes are not intended to be the only ones existing but several of the more probable. Route 1 is the desired pathway for alkaline hydrothermal conversion of glycerol to lactic acid with NaOH as proposed by Kishida et al.:¹² glycerol reacts with NaOH to give sodium glyceroxide, which evolves to glyceraldehyde by releasing a hydride ion, which in turn attacks the hydrogen at the C2 atom, yielding 2-hydroxypropenal and hydrogen. By keto–enol tautomerism, 2-hydroxypropenal is converted into

pyruvaldehyde, which in basic medium yields finally sodium lactate through an internal Cannizzaro reaction.

An issue to consider is whether or not water has a role in this reaction due to the high pressures and temperatures used. It has been reported that water in supercritical conditions and subcritical ones close to the critical point could play a role as catalyst, for example, mainly because its dissociation constant as it approaches the critical point is about 3 orders of magnitude higher than it is for ambient liquid water.¹⁴ However, we think that water plays no role in the reaction herein reported because, on one hand, our more stringent experimental conditions have been 290 °C and 70 bar, far away from the critical point of water (374.4 °C and 218.3 bar), and, on the other hand, the reaction only proceeds in the presence of sodium hydroxide as shown by Kishida et al.¹² In our opinion, high temperatures are needed for overcoming the energetic barrier of some intermediate step(s) and the corresponding high pressures are required for keeping the reaction medium in a liquid state. For instance, glyceraldehyde formation requires that glyceroxide ion undergoes a rearrangement releasing a hydride ion. This step probably needs a high energy input to proceed because at lower temperatures glyceroxide ion is stable as shown, for instance, by the fact that calcium glyceroxide has been obtained by reacting glycerol and CaO in MeOH at reflux by Kouzu et al.¹⁵ and by ourselves (85% isolated yield, results not published).

Route 2 is the oxidative cleavage of lactic acid under alkaline conditions leading mainly to carbonate through acetaldehyde, acetate, and formate as intermediates. Route 3 is the dehydration of lactate to acrylate and the acrylate oxidative cleavage to carbonate also through acetate and formate as intermediates. According to the results given in Table 1, routes 2 and 3 are not very active below 90 min and 280 °C. Acetic acid was not detected by HPLC, perhaps because it is formed at the early stages of reaction since it was not detected at a reaction time of 30 min. Route 4 is the oxidative cleavage of glyceraldehyde under alkaline conditions leading to glycolate, oxalate, formate, and carbonate. Glycolate was not detected by HPLC but must be an intermediate to oxalic acid which was detected. This possibility is supported by Yuksel et al.,¹¹ who detected glycolaldehyde, a precursor of glycolate, in the hydrothermal alkaline electrolysis of glycerol at 280 °C.

Scheme 1. Alkaline Hydrothermal Conversion Routes of Glycerol, Lactate, and Intermediates

Route One: Hydrothermal conversion of glycerol to lactate**Route Two: Oxidative cleavage of lactate under alkaline conditions****Route Three: Lactate dehydration to acrylate and acrylate oxidative cleavage****Route Four: Oxidative cleavage of glyceraldehyde, under alkaline conditions****Route Five: Glyceraldehyde oxidation and dehydration under alkaline conditions****Route Six: Oxidative cleavage of pyruvaldehyde under alkaline conditions**

pyruvaldehyde

The results given in Table 1 show that route 4 is not important under the experimental conditions used. Route 5 is another oxidative pathway of glyceraldehyde under alkaline conditions through glycolate and tartronate as intermediates to give ultimately oxalate, formate, and carbonate. It cannot be very active because it requires oxygen in a stoichiometric amount as shown by Carrettin et al.¹⁶

If routes 4 and 5 do not significantly proceed under the experimental conditions used and lactic acid is only produced in a 43.5% yield from glyceraldehyde, then another conversion route for glyceraldehyde must exist to account for the remaining 56.5% conversion. However, no significant peak was observed

by HPLC under the analytical conditions used. A possible explanation could be related to the fact that in alkaline solutions glyceraldehyde isomerizes reversibly to dihydroxyacetone. Both compounds are in equilibrium. Consequently, the fraction existing as glyceraldehyde evolves to lactic acid, whereas the one existing as dihydroxyacetone does not. It has been reported that under alkaline conditions hydrothermal conversion of dihydroxyacetone runs over C₆-adducts as primary intermediates.¹⁷ Thus, it is possible that under our experimental conditions the hydrothermal conversion of dihydroxyacetone stops at this level. Further research is necessary to confirm this assumption. Obviously, the results in Table 1 indicate that this does not

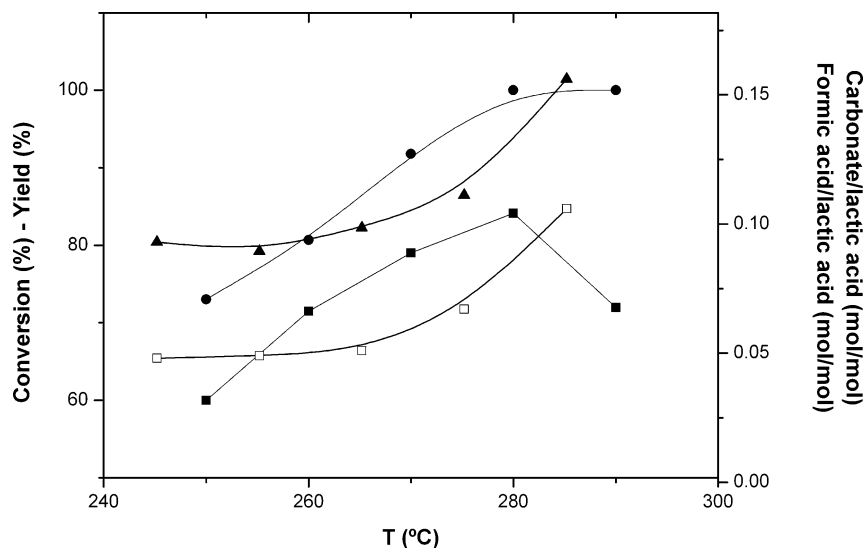


Figure 2. Influence of temperature. NaOH/glycerol molar ratio, 1.33; glycerol concentration, 3 M; reaction time, 90 min. (●) Glycerol conversion; (■) Lactic acid yield; (□) formic acid/lactic acid molar ratio; (▲) carbonate/lactic acid molar ratio.

happen when glycerol is the raw material (route 1), probably because in this case glyceraldehyde is formed from glyceroxide ion, generating at the same time a hydride ion, which quickly attacks glyceraldehyde to give 2-hydroxypropenal, which is transformed into pyruvaldehyde by keto–enol tautomerism. The reaction of this nascent hydride ion (a strong nucleophilic agent) with glyceraldehyde is much faster than the isomerization of glyceraldehyde to dihydroxyacetone, and consequently, glyceraldehyde is converted into pyruvaldehyde and subsequently into lactic acid in high yields. Another possibility is that when glyceraldehyde is the starting raw material it undergoes also a hydroxide-catalyzed aldol condensation to yield a hexose. This reaction would hardly occur starting from glycerol because the strong nucleophilic character of the nascent hydride ion would favor the conversion of glyceraldehyde into pyruvaldehyde. However, no hexose peak was detected by HPLC using the refractive index detector under the analytical conditions used.

Finally, route 6 is the oxidative cleavage of pyruvaldehyde under alkaline conditions, yielding formate and carbonate in high yields according to results in Table 1. Because under the reaction conditions given in Table 1 the only byproduct obtained with significant yields independently on the starting material are formate and carbonate and taking also into account that both are only formed in high yields when pyruvaldehyde is the raw material, we can conclude that this last chemical is the key intermediate in the synthesis of lactic acid from glycerol under alkaline conditions. Depending on the reaction conditions, pyruvaldehyde can evolve to lactate, the desired reaction, or to formate and carbonate, the undesired byproduct. The results in Table 1 also show that starting from glycerol a lactic acid yield close to 90% is obtained while a much lower 65.5% yield is obtained starting from pyruvaldehyde due to oxidative cleavage of pyruvaldehyde to formate and carbonate. Therefore, it is obvious that under the reactions conditions given in Table 1 pyruvaldehyde is almost exclusively converted into lactate when glycerol is the starting material while conversion to formate and carbonate is an important competitive route when pyruvaldehyde is the raw material, probably because once it has begun to be formed from glycerol the remaining NaOH concentration is lower than that when pyruvaldehyde is the starting material because NaOH is being employed in transforming unreacted glycerol to glyceroxide ion.

3.2. Influence of Temperature. The influence of reaction temperature between 250 and 290 °C on glycerol conversions, lactic acid yields, as well as formic acid/lactic acid and carbonate/lactic acid molar ratios was studied at 90 min, 3 M glycerol concentration, and 1.33 NaOH/glycerol molar ratio. The results are depicted in Figure 2. Formic acid and carbonate ion results were chosen to be plotted because they were the main byproducts detected. In all reactions reported in this paper, oxalic acid and acrylic acid concentrations were 3–10-fold lower than formic acid ones.

Lactic acid yield peaks close to 85% at 280 °C, a temperature at which glycerol conversion reaches its maximum value of 100%. Above 280 °C, lactic acid yield decreases quickly. On the contrary, formic acid and carbonate yields, as expressed by the corresponding molar ratios relative to lactic acid, are very low and practically constant up to 260–270 °C, but above 270 °C both increase dramatically. According to the discussion in section 3.1 we must conclude that above 280 °C conversion routes of lactic acid and pyruvaldehyde to formate and carbonate are activated. For instance, lactic acid oxidative cleavage to formic acid and carbon dioxide (carbonate) as well as dehydration to acrylic acid are favored above 265 °C in alkaline medium by the presence of an α -hydroxy group.^{18–20} The lower yields below 280 °C are due to incomplete conversion of glycerol as can be seen from Figure 2.

3.3. Influence of NaOH/Glycerol Molar Ratio and Glycerol Concentration. The influence of the NaOH/glycerol molar ratio between 1.1 and 1.75 at two glycerol concentrations (2.5 and 3.5 M) on glycerol conversions, lactic acid yields, as well as formic acid/lactic acid and carbonate/lactic acid molar ratios was studied at 90 min and 280 °C. The results are depicted in Figure 3.

First, conversions increase with glycerol concentration for molar ratios below 1.3, indicating that the reaction rate also increases with this variable. However, conversion is independent of glycerol concentration and equal to 100 above a molar ratio of 1.3. This means that the reaction rate depends on both glycerol and NaOH concentrations.

At a low molar ratio of 1.1, the same lactic acid yield (85%) is obtained at both concentrations studied. However, above a molar ratio of 1.1 lactic acid yield decreases, mainly at the higher glycerol concentration, with NaOH/glycerol molar ratio, while

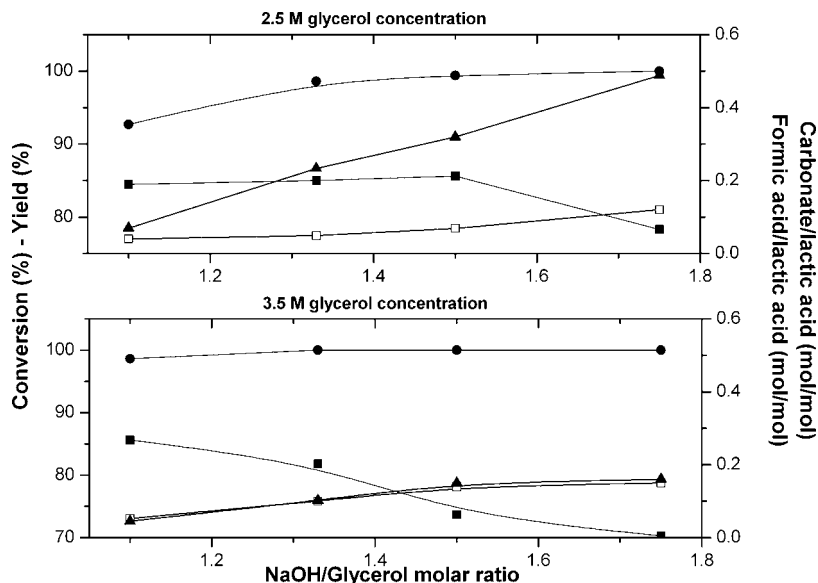


Figure 3. Influence of glycerol concentration and NaOH/glycerol molar ratio at 280 °C. Reaction time: 90 min. (●) Glycerol conversion; (■) lactic acid yield; (□) formic acid/lactic acid molar ratio; (▲) carbonate/lactic acid molar ratio.

Table 2. Formic Acid/Lactic Acid and Oxalic Acid/Lactic Acid Molar Ratios As a Function of Starting Glycerol Concentration^a

[glycerol] (M)	oxalic acid/ lactic acid (mol/mol)	formic acid/ lactic acid (mol/mol)	total amount (mol/mol)
2	2.0×10^{-3}	19.7×10^{-3}	21.7×10^{-3}
2.25	1.8×10^{-3}	33.4×10^{-3}	35.2×10^{-3}
2.5	3.2×10^{-3}	41.7×10^{-3}	44.9×10^{-3}
3.5	4.4×10^{-3}	53.5×10^{-3}	57.9×10^{-3}

^a Experimental conditions: 280 °C, 90 min reaction time, and 1.1 NaOH/glycerol molar ratio.

formic acid/lactic acid and carbonate/lactic acid molar ratios show an inverse trend, indicating a higher prevalence of the lactic acid or intermediates degradation routes at high NaOH/glycerol molar ratios. The results must be attributed to the high NaOH amount in excess, which activates the conversion routes of pyruvaldehyde and lactate to carbonate and formate. Likewise, an increase in the glycerol concentration has a negative influence on lactic acid yields which decrease between 5 and 7 points depending on the NaOH/glycerol molar ratio, probably because an increase in the glycerol concentration involves an increase in intermediates and lactic acid concentrations, causing in turn an increase in the reaction rates of their conversion routes to formic acid and carbonate (routes 2, 3, 4, and 6 in Scheme 1).

Moreover, as shown in Table 2, glycerol concentration has an important influence on the yields of organic acids other than lactic acid. The total amount of oxalic acid and formic acids with respect to lactic acid decreases by 62.5% when glycerol concentration decreases from 3.5 to 2.5 M. This is a relevant aspect from the standpoint of final lactic acid purity. After acidification of the reaction mixture, carbonate is converted into CO₂, which leaves the solution as a gas. However, salts of organic acids obtained as byproduct are transformed into the free acids, which remain in the final lactic acid solution. Then, the important role that glycerol concentration plays in both lactic acid yield and byproduct generation can be used, on one hand, to achieve a trade off between a high glycerol concentration, necessary for an industrially feasible process, and a low byproduct formation, needed for some applications, and, on the other hand, for simplifying the lactic acid separation and purification operations by decreasing byproduct generation.

On the other hand, it is worth mentioning that on comparing the results (lactic acid yields and byproduct nature) obtained at high glycerol concentrations herein given with those reported by Kishida et al.¹² and Shen et al.¹³ at low glycerol concentration (0.33 M) we must conclude that glycerol concentration has no influence on reaction pathways at least between 0.3 and 3.5 M. In both cases, the main product obtained is by far lactic acid with carbonate and formate being the major byproduct. Very small amounts of other organics such as oxalic acid and acrylic acid are also obtained, although the maximum yield obtained at high concentrations (84.5%) is 5.5 points lower than that at low concentration (0.33 M, 90%).

3.4. Influence of Reaction Time. The influence of reaction time at three glycerol concentrations (2, 2.5, and 3.5 M) on glycerol conversion, the lactic acid yield, as well as the formic acid/lactic acid and carbonate/lactic acid molar ratios was studied at a 1.1 NaOH/glycerol molar ratio and 280 °C. The results are plotted in Figure 4.

As it can be seen, lactic acid yield shows a peak for each concentration in the starting glycerol concentration range studied. Peak yields (about 85%) are not dependent on the concentration, but the reaction time needed for reaching the maximum yield decreases with concentration: 120, 90, and 60 min at 2, 2.5, and 3.5 M, respectively, meaning that the reaction rate depends on the initial glycerol concentration. Below the peak, lower yields are due to incomplete glycerol conversion, as can be seen in Figure 4. However, above the peak, lactic acid yields decrease steadily in all cases following a similar pattern while, conversely, byproduct formation increases steadily with time. Taking into account that lactic acid is largely the main product at the three concentrations, it must be concluded that the decrease in yield above the peak is basically due to lactic acid degradation (routes 2 and 3 in Scheme 1).

3.5. Gaseous Products. H₂, water–gas, CO₂, CO, and CH₄ were analyzed by mass spectrometry in the vapor phase in two reactions, both carried out at 280 °C, 90 min, and 1.1 NaOH/glycerol molar ratio, but the first one at a glycerol concentration of 2.5 M and the second one at a glycerol concentration of 3.5 M. According to eq 2, 1 mol of H₂ is produced by 1 mol of lactic acid. Water–gas comes from partial evaporation of water liquid. As shown in the above sections, sodium carbonate is

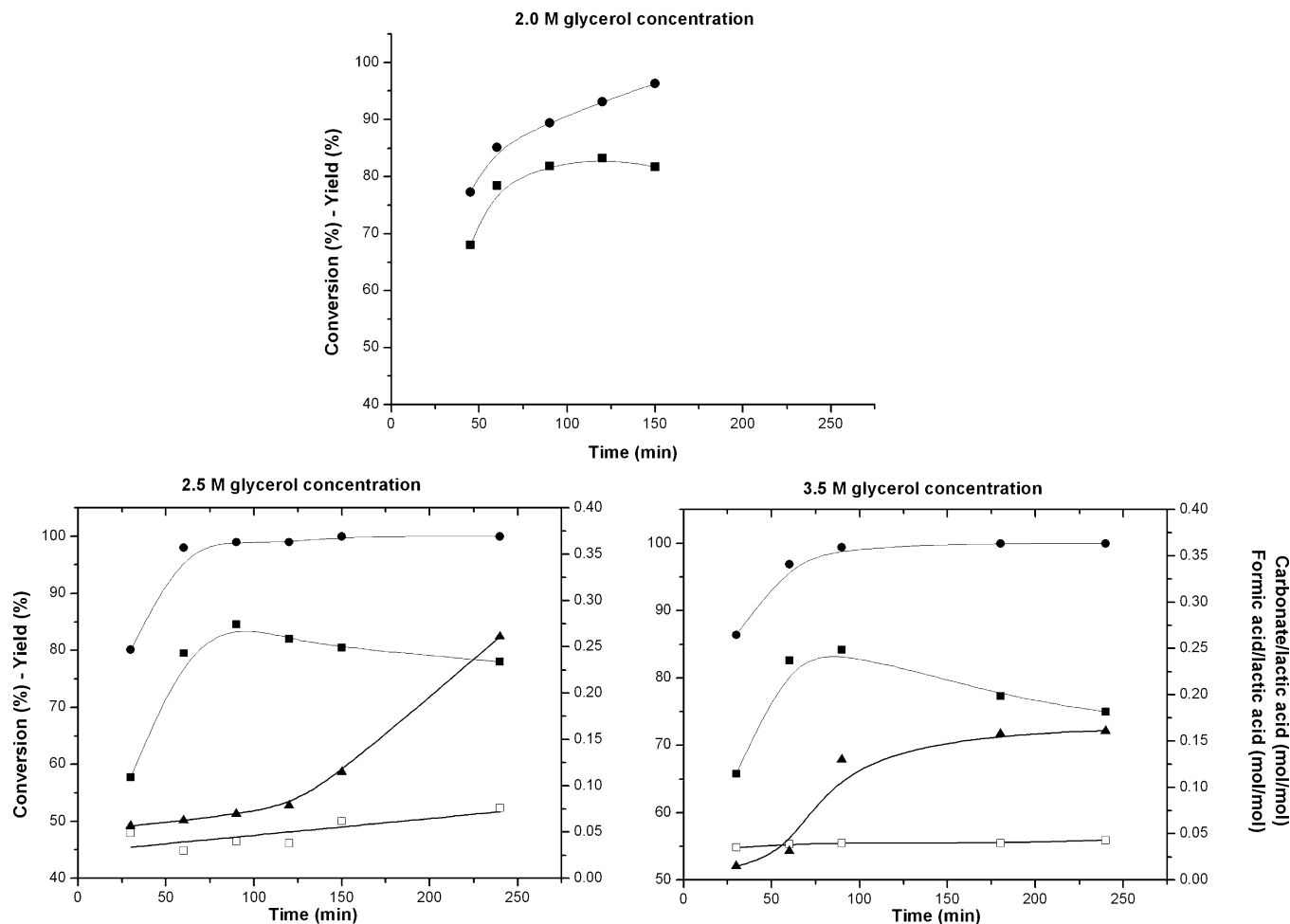


Figure 4. Influence of reaction time for a 1.1 NaOH/glycerol molar ratio at 280 °C at three glycerol concentrations. (●) Glycerol conversion; (■) lactic acid yield; (□) formic acid/lactic acid molar ratio; (▲) carbonate/lactic acid molar ratio.

obtained in all reactions by reaction of the CO_2 produced by oxidation of products with NaOH; therefore, if the absorption of CO_2 by NaOH is not complete, some CO_2 could remain in the gas phase. CO could be formed by reduction of unabsorbed CO_2 through the reverse water–gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) catalyzed by metals (Fe, Cr) present in trace amounts as a consequence of reactor corrosion (see section 3.7) and CH_4 could be formed, for instance, by reduction of formic acid in the strong reductive atmosphere due to the presence of H_2 . The only gaseous products detected were H_2 and water–gas: 62.2% v/v of H_2 and 37.8% v/v of water in the reaction at a glycerol concentration of 2.5 M and 85% v/v of H_2 and 15% v/v of water in the reaction at a glycerol concentration of 3.5 M. No trace amount of CH_4 , CO_2 , or CO was detected, indicating that CO_2 is completely adsorbed by NaOH as also confirmed by the final pHs of the reaction liquors, which were between 12.7 and 13.1 in all reactions herein reported. It is apparent that a reduction catalyst is necessary so that H_2 could act as a reductive agent under the experimental conditions used in this work.

3.6. Crude Glycerol from Biodiesel As Raw Material. In order to test if crude glycerol from biodiesel production could be used as a substitute of pure glycerol for synthesizing lactic acid, a reaction using a crude glycerol (85% pure, 100.5 g/L NaCl, balance water, pH 5.7, tan color, residual methanol < 0.05%, soaps < 0.05%, fats < 0.05%) obtained by transesterification of vegetable oils with methanol using sodium methoxide as catalyst and kindly supplied by Desmet Ballestra España (Madrid, Spain) was carried out in the following conditions:

crude glycerol concentration, 2.5 M; NaOH/glycerol molar ratio, 1.1; reaction time, 90 min; temperature, 280 °C. An 85.5% lactic acid yield was obtained, equal to the one (84.5%) obtained with pure glycerol within experimental error. The lactic acid concentration was 192.5 g/L, oxalic acid/lactic acid molar ratio 2.67×10^{-5} mol/mol, formic acid/lactic acid molar ratio 0.05 mol/mol, and carbonate/lactic acid molar ratio 0.0852 mol/mol. This result indicates that crude glycerol can be substituted for pure glycerol as a raw material.

3.7. Reactor Corrosion and Its Effects. An important problem for industrial implementation of the process is reactor corrosion. It is known that stainless steel is corroded at high temperature in an alkaline medium such as the one used in this study. Thus, two questions must be considered: first, the corrosion rate related to the lifetime of the reactor and, second, the effect on product yields of reactor materials (Ni, Fe, Cr) introduced in the reaction medium as a consequence of the reactor corrosion.

In order to determine the extent of corrosion, the metal contents in the reaction liquor of a reaction carried out at a 2.5 M glycerol concentration for 90 min at 250 °C and a 1.1 sodium hydroxide/lactic acid molar ratio were measured by ICP with the following results: molybdenum 6 ppm, chromium 19 ppm, iron 70 ppm, manganese 2.5 ppm, and Ni below the quantification limit (0.001 ppm). The maximum iron concentration expected due to the iron content in NaOH is 1.1 ppm; therefore, results reveal the existence of corrosion. Taking into account the dimensions of our reactor and assuming 8000 h/year of operation, the corrosion rate is 0.49 mm/year, which will be

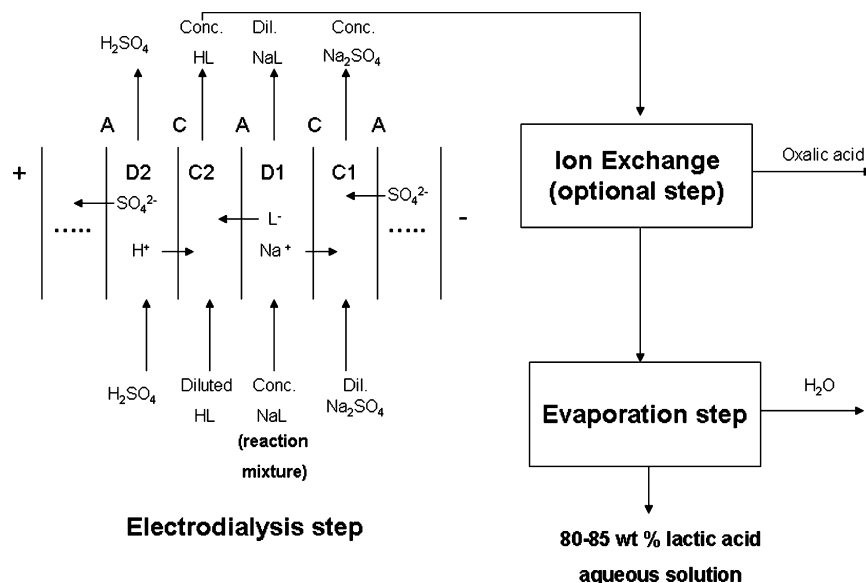


Figure 5. Proposed lactic acid isolation process: (A) anion exchange membrane; (B) cation exchange membrane. NaL: sodium lactate. HL: lactic acid.

obviously higher at the optimum reaction temperature of 280 °C. A solution could be to line the internal walls of the reactor with Teflon.

Relating now to the second item, we have not explored whether or not the metals introduced in the reaction medium by corrosion of the reactor walls influence the product distribution, but this possibility has been investigated by Shen et al.¹³ by using a Teflon-lined batch reactor with and without the addition of a little amount of SUS 316 scraps. Their results show that the materials of the SUS reactor have no significant effect on the hydrothermal conversion of glycerol into lactic acid.

3.8. Lactic Acid Isolation. Lactic acid isolation has not been studied. However, in this section a feasible procedure is proposed. A typical composition of a reaction mixture obtained for a 90% lactic acid yield is as follows: sodium lactate, 252 g/L; sodium carbonate, 21.5 g/L; total other organic acid salts (sodium oxalate, sodium formate, sodium acrylate) < 6 g/L. Then, the process depicted in Figure 5 could be used for obtaining an 80–85 wt % lactic acid aqueous solution, the form in which it is marketed.

The isolation procedure consists of the following steps. (1) Electrodialysis of the reaction mixture. This step is similar to the one developed by Ochoa-Gómez et al.²¹ for isolating iminodiacetic acid from an aqueous solution of its sodium salt by using an electrodialysis stack of several (usually up to 100) four-compartment cells formed by alternating anion and cation exchange membranes between an anode and a cathode. The reaction mixture and an aqueous solution of diluted (25–50 g/L) sulfuric acid as a source of hydrogen ions are fed by diluted compartments D1 and D2, respectively, whereas a concentrated sodium sulfate aqueous solution and another one of concentrated (up to 200 g/L) lactic acid are produced in the concentrated compartments C1 and C2, respectively, under an applied electric field. Sodium carbonate and sodium salts of the other minor organic acids in the reaction mixture are converted into carbon dioxide and free organic acids, respectively, at the same compartment in which lactic acid is produced, C2. If crude glycerol from biodiesel is used as a raw material, HCl is formed at compartment C2 together with lactic acid. Taking into account that HCl is a strong acid and lactic acid a weak one, both can be easily separated by means of an electrodialysis stack of two-compartment cells (not shown in the figure). Alternatively, HCl

could be at least partially separated by evaporation in step 3 below. Preliminary experiments carried out with a laboratory cell of 20 cm² unit membrane area show that working at 300 A/m² with Neosepta AMX and Neosepta CMX (both from Tokuyama Asia Pacific) as anion and cation exchange membranes, respectively, a very promising 70% current efficiency for lactic acid separation in compartment C2 can be achieved starting from a reaction mixture consisting of 247.5 g/L sodium lactate, 18.9 g/L sodium carbonate, 5.9 g/L sodium formate, 0.9 g/L disodium oxalate, and 9.8 g/L sodium hydroxide (excess used in the synthetic step with respect to the stoichiometric amount for a 1.1 NaOH/glycerol molar ratio). As expected, formic and oxalic acids were also formed in compartment C2 while the concentrations of their sodium salts in compartment D1 decreased to zero. Further improvements in current efficiency can be achieved if byproduct generation, mainly sodium carbonate, could be diminished and NaOH/glycerol molar ratio could be decreased below 1.1, which it is at first possible according to the variation pattern of lactic acid yields with NaOH/glycerol molar ratio depicted in Figure 3. (2) If needed, ion exchange of lactic acid concentrated stream with a weakly basic ion exchange resin, such as Amberlite CR 5550 from Rhom & Haas, for removing traces of organic acids stronger than lactic acid ($pK_a = 3.86$), such as oxalic acid ($pK_{a1} = 1.27$). Formic acid and acrylic acid have a similar pK_a to lactic acid and cannot be removed in this way. They will remain in the final commercial lactic acid aqueous solution. All the same, this step is optional and only needed if a very pure lactic acid is demanded. For most applications it can be likely avoided by decreasing the byproduct generation by carrying out the reaction at a glycerol concentration lower than 2.5 M but still high enough for keeping a high productivity. (3) Evaporation of concentrated lactic acid aqueous solution to afford the final 80–85 wt % lactic acid aqueous solution. In this process, sodium sulfate is obtained as a byproduct. An advantage of this procedure is that by substituting KOH for NaOH in the reaction medium a potassium sulfate aqueous solution instead a sodium sulfate one is obtained in the electrodialysis step. Both can be marketed because they are valuable chemicals. As shown by Shen et al.,¹³ lactic acid yield is not affected by using KOH instead NaOH. Therefore, both alkaline hydroxides can be

indistinctly used in order to suit the byproduct production to the market situation.

4. Conclusions

A process for obtaining lactic acid in high yields by alkaline hydrothermal glycerol conversion at high concentrations has been developed. The yield shows a peak at 280 °C, 90 min, 2.5 M glycerol concentration, and a 1.1 NaOH/glycerol molar ratio. Above these values a fast decrease in yield is observed due to activation of conversion routes to byproduct such as oxalic, formic, and acrylic acids and sodium carbonate. The yield remains practically unchanged by using crude glycerol from biodiesel as a raw material. Lactic acid yield and concentration in reaction liquor are high enough for industrial process feasibility.

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