Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Lactic Acid Production as a New Approach for Exploitation of Glycerol

S. Lux[a]; P. Stehring[a]; M. Siebenhofer[a]
[a] Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria

To cite this Article Lux, S. , Stehring, P. and Siebenhofer, M.(2010) 'Lactic Acid Production as a New Approach for Exploitation of Glycerol', Separation Science and Technology, 45: 12, 1921 — 1927
To link to this Article: DOI: 10.1080/01496395.2010.493824
URL: http://dx.doi.org/10.1080/01496395.2010.493824

Separation Science and Technology, 45: 1921–1927, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.493824

Lactic Acid Production as a New Approach for Exploitation of Glycerol

S. Lux, P. Stehring, and M. Siebenhofer
Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria

Electrochemical oxidation of glycerol, the principal by-product of biodiesel production, generally leads to multicomponent product mixtures. The aim of this project was to investigate the feasibility of a technical process for electrochemical oxidation of crude glycerol followed by catalytic conversion of the intermediates dihydroxyacetone and glyceraldehyde to lactic acid. Partial electrochemical oxidation of glycerol with diamond coated electrodes was assumed to provide a route for converting glycerol to dihydroxyacetone and glyceraldehyde. Through instant selective conversion of dihydroxyacetone and glyceraldehyde to lactic acid the major disadvantage of electrochemical conversion, cleavage of intermediates, may be limited. Continuous separation of lactic acid from the electrolyte enables acceptable current efficiency as well as yield of products. Reactive extraction with phosphoryl compounds has proven applicable for the isolation of lactic acid from the electrolyte. Based on the results of these investigations a complete process for lactic acid production from glycerol was designed.

Keywords electrochemical conversion; extraction; glycerol; lactic acid

INTRODUCTION

Lactic acid (2-hydroxypropionic acid) is a versatile commodity chemical with a wide range of utilizations. Fields of industrial use for lactic acid as well as salts and esters of lactic acid include food, beverages, personal-care, and pharmaceutical products. In the last few years the consumption of lactic acid for industrial use has surpassed the food and beverages industry as the leading market. Future growth in demand is expected to be mainly driven by lactic acid-based polymers and, to a lesser degree, lactate solvents (1). With both a hydroxyl group and a carboxylic acid group lactic acid may undergo many chemical reactions. Among the established reactions, polymerization to polylactic acid (PLA) is a profitable pathway. These polymers are highly promoted due to their environmentally-friendly properties. The viability of making biodegradable polymers out of lactic acid has attracted consumers as well as the plastics industry. A lot of research has been done in the area of production and recovery of pure lactic acid (2). Synthesis of lactic acid either through fermentation of carbohydrates or through chemical synthesis from lactonitrile are state-of-the-art routes (3). Glycerol based synthesis of lactic acid is an attractive approach in processing fats and oils.

Until now production of lactic acid is preferably based on fermentation of carbohydrates. While the chemical synthesis route produces the racemic mixture of lactic acid, enantiopure lactic acid can be isolated from fermentation broth (1). During fermentation calcium lactate is formed which is concentrated, isolated by fractionated crystallization, and reacidified with a strong mineral acid such as sulfuric acid. This conventional route consumes large amounts of acid and generates waste calcium sulfate (3).

Glycerol as the principal by-product of biodiesel production is an important industrial bulk chemical. However, crude glycerol from biodiesel production is a low-value product because of impurities. In order to make biodiesel production more economically feasible in the long term, subsequent transformation of crude glycerol into value-added products is crucial. Much effort in research and development has been focused on developing new applications for glycerol. Conversion of glycerol to lactic acid could be a promising way for utilizing crude glycerol. Whereas direct thermal conversion of glycerol to lactic acid demands extreme reaction conditions (4), conversion under moderate conditions can be achieved by a combination of oxidation with conversion and isolation. Partial electrochemical oxidation of glycerol in principle is a technical route for converting glycerol to dihydroxyacetone and glyceraldehyde which can then be catalytically converted to lactic acid. Figure 1 shows the basic outline of the overall process.

According to the overall process scheme of Fig. 1 the process steps

- anodic oxidation
- catalytic conversion
- extractive isolation

Received 19 February 2010; accepted 16 March 2010.

Address correspondence to S. Lux, Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Graz, Austria. E-mail: susanne.lux@tugraz.at

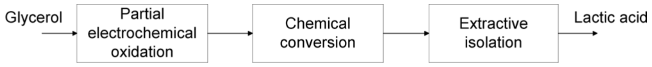

FIG. 1. Schematic outline of the overall process for conversion of glycerol to lactic acid.

were separately investigated in the first part of the project. Finally the overall process was tested in bench-scale.

Electrochemical oxidation is specified as an environmentally-friendly ("green") process because chemical oxidation agents are substituted by electrons. Electrochemical oxidation of glycerol has already been investigated in the past (5–8). Several electrode materials, electrolyte compositions, pH-regions, and temperature fields have been investigated by different research groups. To briefly summarize the results, the expected optimum set up for highly selective synthesis of a specific product has still not been found. Most electrode materials which have been tested in the past are not stable or may preferably cleave the glycerol molecule (5). Only the use of a platinum anode in combination with sodium hydroxide in excess as electrolyte provided acceptable yield of the product sodium lactate (6). Due to the high oxygen overpotential, improved yield of products was expected from oxidation with diamond coated electrodes in this project.

In the past, acids and alkali hydroxides were mainly used as electrolytes. As acids are not consumed during electrolysis and sufficient electric conductivity is provided, the use of acid-based electrolytes is recommended. Unfortunately at strong acidic conditions cleavage of glycerol is the main anodic reaction and current yield is low. The use of alkali hydroxides provides better current yield but large excess is needed as alkali hydroxides are consumed by many competitive reactions leading to complex product mixtures. Complex product composition and the huge amount of sodium hydroxide make downstream processing difficult and expensive.

To overcome the mentioned disadvantages the use of several metal salts as electrolytes has been tested in this project with the aim of obtaining dihydroxyacetone and glyceraldehyde with high yield and selectivity. Whereas the isolation of dihydroxyacetone through crystallization is laborious (9) subsequent catalytic conversion to lactic acid is beneficial.

The conversion of dihydroxyacetone or glyceraldehyde to lactic acid can either be carried out under caustic conditions (10,11) or under acidic conditions (12,13). The first reaction step is dehydration of dihydroxyacetone and glyceraldehyde to form pyruvic aldehyde. Pyruvic aldehyde undergoes further rearrangement yielding lactic acid, or lactate respectively, as the final stable reaction product. This step can be seen as a kind of intramolecular Cannizzaro reaction (14,15).

Isolation of lactic acid from the aqueous reaction mixture was investigated with phosphoryl compounds. Tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and Cyanex 923, a mixture of tertiary octyl and hexylphosphine oxides, were used as solvents.

MATERIALS AND METHODS

Chemicals

Glycerol ($\geq$99.5%, p.a., anhydrous) and $Al_2(SO_4)_3 \cdot 16\ H_2O$ ($\geq$95%, p.a.) were purchased from Carl Roth. Aqueous solutions of lactic acid (pur.) in a concentration of 1 mol/L were provided by Riedel-de Haën. Dihydroxyacetone (puriss.) and the extractant tri-*n*-butylphosphate (99%, pur.) were purchased from Merck. The extractants tri-*n*-octylphosphine oxide and Cyanex 923 (a mixture of tertiary *n*-octyl and *n*-hexylphosphine oxides) were supplied by Cytec Industries Inc. All extractants were used without further purification. The diluent Shellsol T, an isoparaffinic hydrocarbon solvent with hydrocarbons ranging from C_{11} to C_{13} and a distillation range of 187–213°C, was supplied by Shell Chemicals.

Aqueous solutions were prepared by dissolving glycerol, dihydroxyacetone, or lactic acid in deionized water.

Electrochemical Oxidation

Electrochemical oxidation was carried out in batch operation in a thin layer cell. Anode and cathode compartments were separated by an anion exchange membrane (type fumasep FAA from FuMA-Tech GmbH). Anolyte and catholyte were pumped through the cell with peristaltic pumps with a volumetric flow rate of $20\,cm^3/min$ in order to increase the mass transfer rate and to flush hydrogen from the cathode compartment of the cell. Temperature was measured with a Pt100 resistance dip thermometer and controlled via heat exchange between the pump and cell. The experimental setup for anodic oxidation of glycerol is shown in Fig. 2.

A diamond coated electrode (from Fraunhofer IST) was used as anode. The diamond coated electrode consists of a boron doped polycrystalline diamond layer on a niobium carrier. A platinum grid electrode was used as cathode. All experiments were carried out with aqueous anolyte mixtures of glycerol ($w(\text{glycerol}) = 0.17$–$0.76$) at constant current density, flow rate, and temperature. The catholyte solution was NaOH ($c(\text{NaOH}) = 10\,g/dm^3$). Cell voltage, current, and temperature were recorded. Aqueous solutions of metal salts providing different pH-regions for oxidation were used as anolytes ($w = 0.03$–0.1). $NaHSO_4$, $Al_2(SO_4)_3$ and $SnSO_4$ were used as anolytes to provide acidic conditions. K_2HPO_4 was used as a buffer for neutral conditions. Na_2CO_3, Na_3PO_4, NaOH, and $Ca(OH)_2$ were used for investigation of oxidation at caustic conditions.

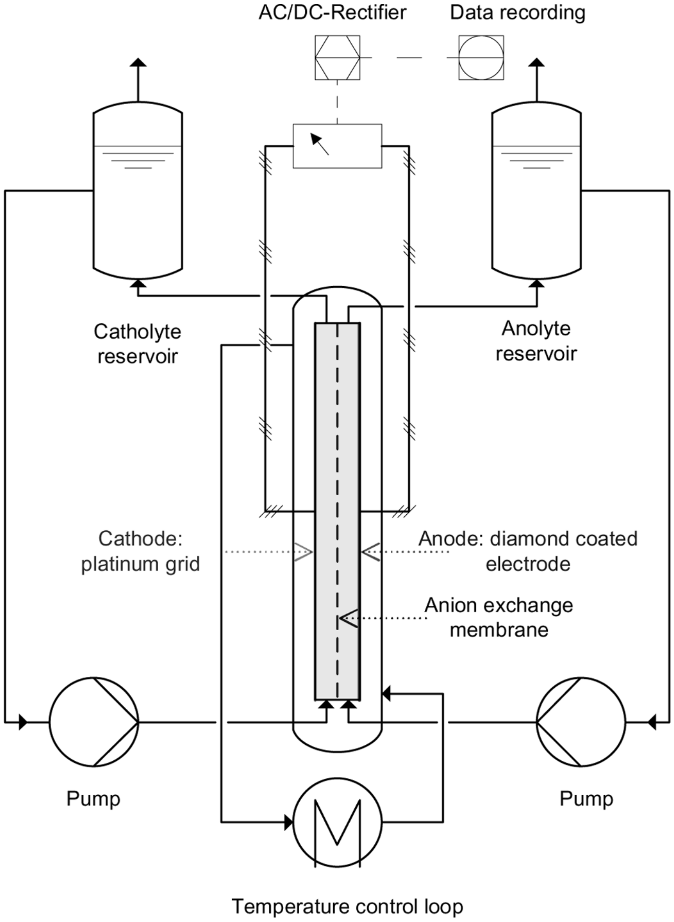

FIG. 2. Scheme of the electrolysis cell.

Investigation of the Catalytic Conversion of Dihydroxyacetone/Glyceraldehyde to Lactic Acid

All catalytic conversion experiments were carried out in batch mode in flasks equipped with a reflux condenser, heating coil, and magnetic stirrer. The concentration of dihydroxyacetone was varied between 5 and 100 g/dm^3. The reaction was started by adding the catalyst to the feed. The catalyst aluminium sulfate has proven best. The conversion reaction favors acidic conditions. The concentration of the mineral acid was varied between 0.5 and 5 mol/dm^3. The concentration of metal ions was varied between 0.06 and 0.8 mol/dm^3. The temperature was controlled and kept constant throughout the reaction.

Combination of Glycerol Oxidation and Catalytic Conversion of Dihydroxyacetone and Glyceraldehyde to Lactic Acid

A combination of electrolysis and catalytic conversion was investigated by installing a continuously stirred tank reactor in the anolyte loop. The reactor was operated at a temperature of 125°C. The electrochemical cell was operated between 50°C to 60°C.

Liquid/Liquid-Extraction of Lactic Acid

The extractants tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and Cyanex 923 were diluted with Shellsol T. Cyanex 923 was also used without dilution (16). The desired portions of the aqueous solution of lactic acid, the extractant, and the diluent were equilibrated in a temperature controlled mixing funnel. A solvent/water ratio of $V_{org}/V_{aqu} = 1{:}2$ was applied. Equilibrium was achieved within 30 minutes. Extraction experiments at elevated temperature (90°C) were carried out in flasks equipped with a reflux condenser, heating coil, and magnetic stirrer. After phase separation the concentration of lactic acid in the aqueous phase was determined by HPLC. The water content in the organic phase was determined by Karl Fischer titration. The concentration of lactic acid in the solvent phase at equilibrium was determined via mass balance.

Analytics

Several substances were analyzed by high-performance liquid chromatography (HPLC). The HPLC system Ultimate 3000 (Dionex) equipped with a Rezex ROA-Organic Acid H^+ column (Phenomenex) and the column Acclaim OA (Dionex) were used for separation. Detection was carried out with a variable wavelength UV/VIS-detector (Dionex). Elution of substances from Rezex ROA was carried out with 0.005 mol/dm^3 H_2SO_4 in ultrapure water, operated at 50°C. From Acclaim OA column substances were eluated with 0.1 mol/dm^3 Na_2SO_4 in ultrapure water. The pH-value of 2.65 was adjusted with methanesulfonic acid. The operation temperature was $T = 30°C$.

For structure determination of unidentified substances one-dimensional and multidimensional NMR spectroscopy (Bruker Avance DRX 500 MHz) was used.

RESULTS AND DISCUSSION

Electrochemical Oxidation

Diamond coated electrodes are said to have high chemical, mechanical, and thermal stability. Nevertheless, damage of the coating cannot be completely prevented during electrolysis. The main advantage of diamond coated electrodes for anodic synthesis reactions is the very high oxygen overvoltage. Formation of oxygen is therefore largely suppressed.

At the beginning of the electrolysis process the desired products glyceraldehyde and dihydroxyacetone are formed with sufficient selectivity and current yield. The ratio between glyceraldehyde and dihydroxyacetone strongly depends on the pH-value. At acidic conditions glyceraldehyde is formed, at neutral and moderate alkaline conditions mixtures of glyceraldehyde and dihydroxyacetone are formed.

But with ongoing process cleavage reactions become process controlling. Following the scheme shown in Fig. 3 glycolaldehyde and formic acid are mainly formed. On a limited scale the oxidation of glyceraldehyde to glyceric acid and the oxidation of glycolaldehyde to glycolic acid take place.

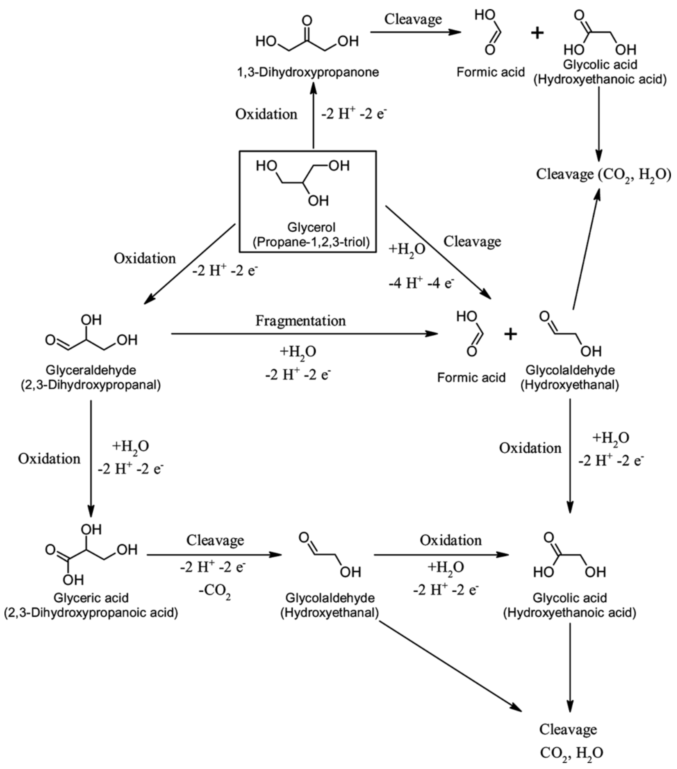

FIG. 3. Scheme of oxidation routes of glycerol and intermediates.

Under acidic conditions glyceraldehyde, glycolaldehyde, glycolic acid, and formic acid are the main reaction products of electrochemical oxidation of glycerol. Figure 4 representatively shows the product distribution. As a result of preferred cleavage during electrolysis the concentration of glyceraldehyde and dihydroxyacetone pass a maximum.

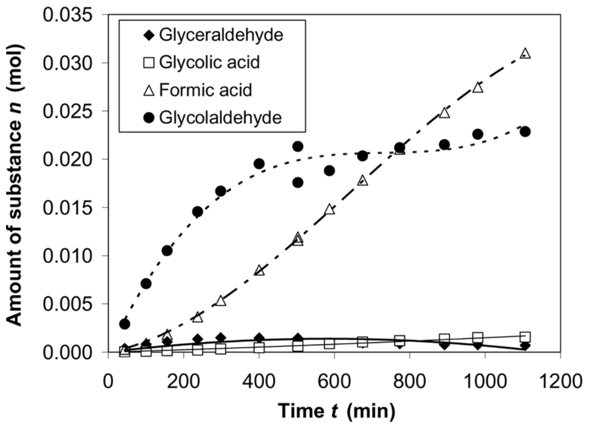

FIG. 4. Product distribution versus electrolysis time for electrochemical oxidation of glycerol; $T = 50°C$; current density $j = 60\ A/m^2$; $w(\text{glycerol}) = 0.33$; electrolyte: $Al_2(SO_4)_3$; $w(Al_2(SO_4)_3) = 3.6\%$ (error interval of data is 2%).

For anodic oxidation of glycerol the concentration of glycerol has a major impact on product formation. Anhydrous glycerol and solutions with a mass fraction of glycerol above 0.5 cause electrode fouling, interfering mass, and charge transfer and limiting the yield of desired reaction products. Aqueous solutions with a mass fraction of glycerol of less than 0.5 do not cause electrode fouling.

Catalytic Conversion of Dihydroxyacetone to Lactic Acid

Experiments were carried out under alkaline and under acidic conditions using alkali metal salts, alkaline earth metal salts, and mineral acids for catalyzing the conversion of dihydroxyacetone and glyceraldehyde to lactic acid and lactate respectively. Whereas alkali metal salts due to their high basicity effectively catalyze conversion, their use unfortunately leads to complex product mixtures. Downstream processing is laborious due to the high solubility of alkali lactate.

Strong mineral acids are capable of converting dihydroxyacetone and glyceraldehyde to lactic acid with a yield of 90%. Unlike alkaline conversion in which lactic acid formation passes a maximum at $T = 55°C$ elevated reaction temperature and high catalyst concentration are required for acid catalysis. Conversion was therefore carried out at 100°C.

Lactic acid is formed under acidic conditions in two consecutive reaction steps with the intermediate pyruvic aldehyde as shown in the mechanism scheme in Fig. 5. At high temperature and in the presence of strong acids water is eliminated from dihydroxyacetone and glyceraldehyde whereby pyruvic aldehyde is formed. Pyruvic aldehyde is not stable under strong acidic conditions. It undergoes prompt conversion to lactic acid which can be seen as a kind of intramolecular Cannizzaro reaction.

For catalysis with mineral acids conversion of pyruvic aldehyde to lactic acid is rate determining. Polyvalent metal ions are also capable of catalyzing Cannizzaro reactions (15). Mixtures of metal ions accelerate the rate determing step. Metal salts with acidic hydrolyzing properties combine the catalytic effect of metal ions for the Cannizzaro reaction with the acidic conditions necessary for dehydration. Figure 6 shows the conversion of dihydroxyacetone and glyceraldehyde to lactic acid catalyzed with aluminium sulfate.

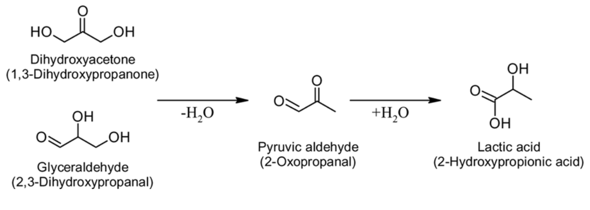

FIG. 5. Scheme of dihydroxyacetone/glyceraldehyde conversion to lactic acid.

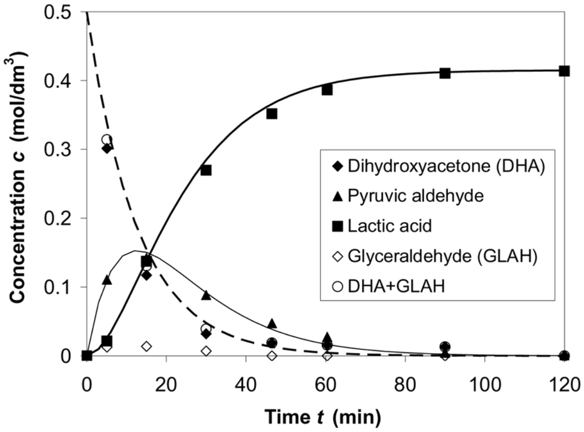

FIG. 6. Lactic acid formation through catalytic conversion of dihydroxyacetone and glyceraldehyde; catalyst: $Al_2(SO_4)_3$; $w(\mathrm{DHA}) = 0.05$; $n(\mathrm{DHA}):n(\mathrm{Al}^{3+}) = 1:1.5$; T = 99°C (uncertainty of data is 2%).

Combination of Glycerol Oxidation and Catalytic Conversion

High selectivity of lactic acid formation can be achieved through a combination of anodic oxidation of glycerol with subsequent catalytic conversion of dihydroxyacetone and glyceraldehyde with aluminium sulfate, as shown in Fig. 7. Dihydroxyacetone and glyceraldehyde, undergoing cleavage during electrolysis, can be selectively converted to lactic acid in the subsequent reaction step when combining the oxidation step with catalytic conversion. The recommended conversion of glycerol by electrolysis is 5 to 10%. For complete electrochemical oxidation of glycerol the reaction broth is passed through the electrochemical cell in recycle mode followed by catalytic conversion of dihydroxyacetone and glyceraldehyde to lactic acid, separation of lactic acid from the electrolyte solution by liquid/liquid-extraction, and recycle of glycerol after make up with fresh glycerol. Through a combination of continuous oxidation and chemical conversion, lactic acid can be obtained with sufficient selectivity. Fractional amounts of the products lactic acid, glycolaldehyde, glycolic acid, formic acid, and glyceric acid, are shown in Fig. 7. By combining anodic oxidation of glycerol with catalytic conversion of the so formed intermediates glyceraldehyde and dihydroxyacetone a maximum yield of lactic acid of 15% related to the glycerol feed was obtained.

Liquid/Liquid-Extraction of Lactic Acid

As mentioned earlier, a continuous process for converting glycerol to lactic acid needs a separation of products from the recycle electrolyte by liquid/liquid-extraction. Extraction of lactic acid from the dilute aqueous product mixture is recommended to be based on Lewis acid/Lewis base interaction with organophosphorus compounds. Therefore extraction of lactic acid was carried out with the extractant Cyanex 923. The Lewis acid/Lewis base interaction between the extractant and the acid molecule enables the acid extraction into the solvent phase according to the following reaction equation:

$$n \cdot \mathrm{HA}_{\mathrm{aqu}} + \mathrm{RPO}_{\mathrm{org}} \leftrightarrow (\mathrm{RPO(HA)}_n)_{\mathrm{org}}$$

Solubility of Cyanex 923 phosphine oxide extractant dissolved in hydrocarbon based diluent in water is as low as $0.01\ \mathrm{g/dm^3}$.

The effect of the temperature and the content of the extractant in the organic phase on the extraction of lactic acid were investigated for the extractants tributyl phosphate, trioctylphosphine oxide and Cyanex 923. Dilution

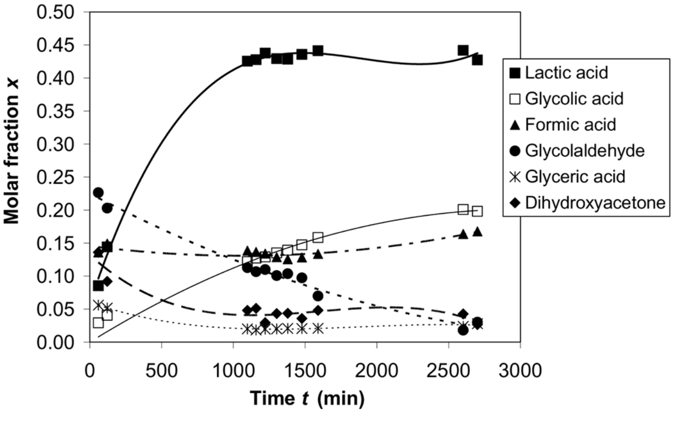

FIG. 7. Fractional amounts of products lactic acid, glycolaldehyde, glycolic acid, formic acid, and glyceric acid through electrochemical oxidation of glycerol combined with consecutive chemical conversion; electrolyte: $Al_2(SO_4)_3$; $w(Al_2(SO_4)_3) = 4.1\%$; electrolysis: T = 60°C; chemical conversion: T = 125°C (error interval of data is 3%).

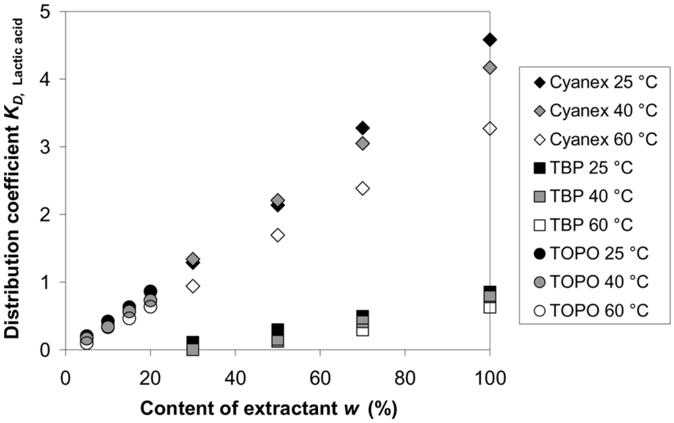

FIG. 8. Effect of temperature and extractant content of the solvent on the distribution coefficient of lactic acid; solvents: tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), Cyanex 923; $c_{\mathrm{Lactic\ acid,aqu,0}} = 2\ \mathrm{g/dm^3}$ (error interval of data is 2%).

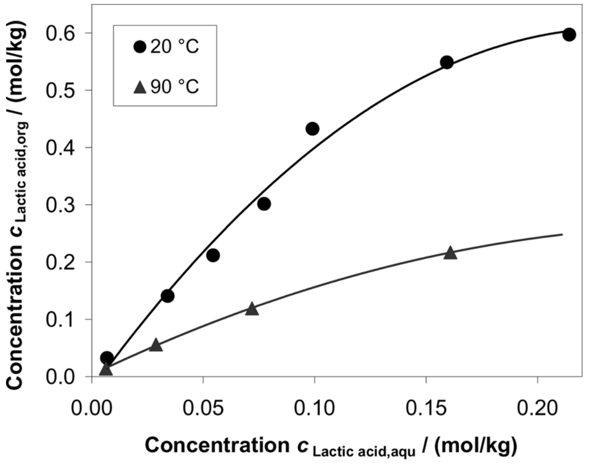

FIG. 9. Temperature dependency of phase equilibria for lactic acid extraction from aqueous solution; solvent: Cyanex 923; *c*(phosphine oxide) = 2.3 mol/dm^3 (data accuracy is within 2% of the mean).

TABLE 1
Distribution coefficients ($K_{D,\text{Lactic acid}}$) for lactic acid extraction with Cyanex 923 with and without glycerol (w(lactic acid) = 9600 ppm, w(glycerol) = 0.3, c(phosphine oxide) = 2.3 mol/dm^3, T = 20°C, V_{org}:V_{aqu} = 1:2)

	$K_{D,\text{ Lactic acid}}$
Lactic acid	4.1 ± 0.1
Lactic acid plus glycerol	5.6 ± 0.1

with Shellsol T, a high boiling hydrocarbon based diluent with less than 5% aromatics, is favorable as far as the hydrodynamic properties for mixing and phase separation are concerned. Lactic acid distribution correlates linearly with the extractant concentration of the solvent. As shown in Fig. 8 the distribution coefficient K_D is significantly temperature dependent.

At elevated temperature the solubility of lactic acid in the solvent phase decreases. Figure 9 shows the effect of temperature on the liquid/liquid-equilibrium of lactic acid between the aqueous carrier and the extractant Cyanex 923. Extraction of lactic acid and reextraction can therefore be carried out through temperature swing. Consequently the extraction step has to be carried out at ambient temperature. Reextraction of lactic acid is carried out through stripping with water at elevated temperature.

The aqueous feed solution may contain unconverted glycerol. Therefore the effect of glycerol in the aqueous phase on extraction has to be considered. Glycerol (w(glycerol) = 0.3) has a positive effect on lactic acid extraction, a beneficial property for the overall process. As can be concluded from Table 1, the distribution coefficient for lactic acid increases when glycerol is present in the aqueous phase.

The positive effect of glycerol on lactic acid extraction with Cyanex 923 underlines the advantage of the concept of implementing liquid/liquid-extraction in the glycerol conversion process.

Process Design

Based on the results of investigation of the process steps anodic oxidation, catalytic conversion, and liquid/liquid-extraction, the complete process may be designed as shown in Fig. 10.

According to Fig. 10 crude glycerol, water, and the catalyst are fed to the anodic oxidation facility. The product solution from anodic oxidation containing dihydroxyacetone

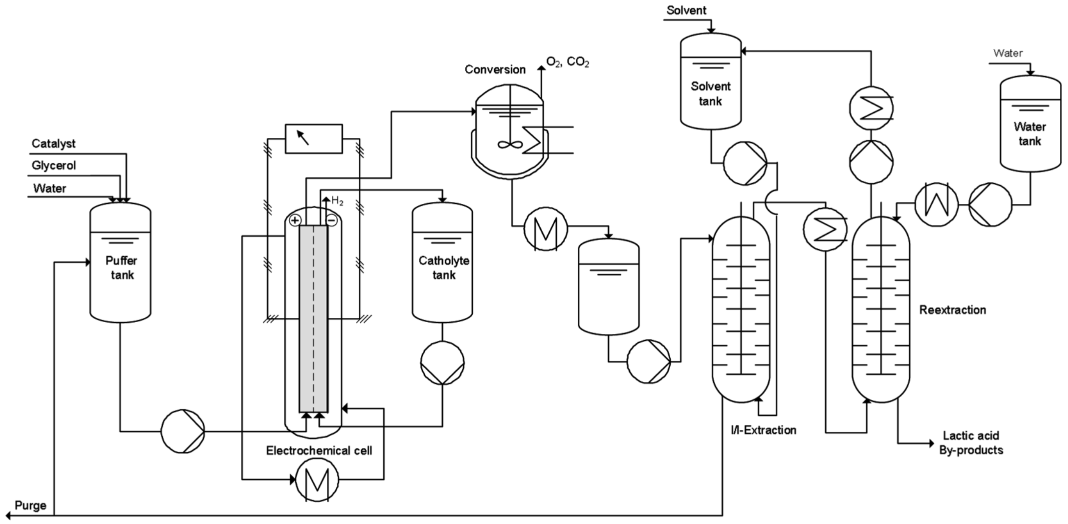

FIG. 10. Process scheme for lactic acid production from glycerol.

and glyceraldehyde is passed to the reactor for further catalytic conversion to lactic acid. Lactic acid and the by-products are separated from the aqueous product solution by liquid/liquid-extraction. Regeneration of the loaded solvent and isolation of lactic acid and by-products from the extractant phase are carried out through reexctraction with water at elevated temperature. The raffinate phase containing unconverted glycerol and the catalyst is recycled by adjusting the glycerol concentration with crude glycerol prior to feeding the mixture to the anodic compartment of the electrolysis cell.

SUMMARY

The technology of lactic acid production from crude glycerol by anodic oxidation of glycerol followed by catalytic conversion and liquid/liquid-extraction was investigated. Selectivity and yield of lactic acid formation by anodic oxidation of glycerol drop with increasing residence time due to cleavage and oxidation of intermediates. Continuous product separation from the electrolyte after catalytic conversion of dihydroxyacetone and glyceraldehyde to lactic acid followed by extractive separation of lactic acid limits cleavage during anodic oxidation.

Reactive extraction with phosphoryl compounds has proven efficient for the isolation of lactic acid from the product mixture. Extraction can be carried out with Cyanex 923, a mixture of hexyl- and octylphosphine oxides, at ambient temperature. Lactic acid and the by-products are reextracted from the solvent phase through stripping with water at elevated temperature. Based on the results of these investigations a complete process for lactic acid production from glycerol was designed. The complete process is a technical feasible approach for using renewable feedstock for industrial lactic acid production.

NOMENCLATURE

K_D	distribution coefficient
V	volume
w	weight fraction
x	molar fraction
aqu	aqueous phase
org	organic phase

REFERENCES

1. Malveda, M.P.; Blagoev, M.; Kishi, A. (2006) *Lactic Acid, Its Salts and Esters*. CEH Marketing Research Report, SRI Consulting.
2. Joglekar, H.G.; Rahman, I.; Babu, S.; Kulkarni, B.D.; Joshi, A. (2006) Comparative assessment of downstream processing options for lactic acid. *Separation and Purification Technology*, 52: 1–17.
3. Chahal, S.P.; Starr, J.N. (2006) *Lactic Acid. Ullmanńs Encyclopedia of Industrial Chemistry, Electronic Release 2009*, 7th Ed. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
4. Kishida, H.; Jin, F.; Zhou, Z.; Moriya, T.; Enomoto, H. (2005) Conversion of glycerin into lactic acid by alkaline hydrothermal reaction. *Chemistry Letters*, 34 (11): 1560–1561.
5. Weber, U. (1993) *Die elektrochemische Oxidation von Glycerin an unterschiedlichen Elektrodenmaterialien*. Ph.D. Dissertation, University of Dortmund, Germany.
6. Tkaczuk, P. (1993) *Elektrochemische Oxidation von Glycerin und Glycerinderivaten an einer Platin-Anode in verschiedenen Zelltypen*. Ph.D. Dissertation, University of Dortmund, Germany.
7. Yildiz, G.; Kadirgan, F. (1994) Behaviour of palladium electrode in alkaline medium. *Journal of the Electrochemical Society*, 141 (3): 725–730.
8. Roquet, L.; Belgsir, E.M.; Léger, J.-M.; Lamy, C. (1994) Kinetics and mechanisms of the electrocatalytic oxidation of glycerol as investigated by chromatographic analysis of the reaction products: potential and pH effects. *Electrochimica Acta*, 39 (16): 2387–2394.
9. Fakley, M.E.; Lindsay, R.J. (1978) *Process for the Isolation of Dihydroxyacetone*. European Patent 0,245,976, November 19, 1987.
10. Evans, W.L.; Hass, H.B. (1926) The mechanism of carbohydrate oxidation. VI. The action of potassium hydroxide on dl-glyceric aldehyde. *Journal of the American Chemical Society*, 48 (10): 2703–2714.
11. Evans, W.L.; Cornthwaite, W.R. (1928) The mechanism of carbohydrate oxidation. VII. The action of potassium hydroxide on dihydroxy acetone. *Journal of the American Chemical Society*, 50 (2): 486–492.
12. Prey, V.; Berbalk, H.; Steinbauer, E. (1960) Über die Bildung von Milchsäure aus Triosen durch Einwirkung von Säuren. *Chemical Monthly*, 91 (6): 1196–1198.
13. Prey, V.; Berbalk, H.; Steinbauer, E. (1962) Über die Bildung von Milchsäure aus Triosen durch Einwirkung von Säuren, 2. Mitteilung. *Chemical Monthly*, 93: 237–245.
14. Kelly, R.L. *Production of hydroxy carboxylic compounds*. European Patent 0,541,330, May 12, 1993.
15. Kiyoura, T.; Kogure, Y. (1997) Synthesis of hydroxyacetic acid and its esters from glyoxal catalyzed by multivalent metal ions. *Applied Catalysis A*, 156: 97–104.
16. *Cyanex 923 Extractant*. (2009) URL http://www.cytec.com/specialty-chemicals/PDFs/CYANEX%20923.pdf