Down Streaming of Lactic Acid from Hydrolysate of Barley after Fermentation

W. Reimann

Leibniz-Institute of Agricultural Engineering Potsdam-Bornim (ATB),
Department of Bioengineering,
Max-Eyth-Allee 100, D-14469 Potsdam-Bornim, Germany.
Email: wreimann@atb-potsdam.de

ABSTRACT

Different downstream processes were studied for the production of lactic acid after fermentation of glucose from hydrolysate of shredded barley. The fermentation broth successively passed through ultrafiltration, softening, conventional electrodialysis that operated in a two-level mode (water transport: 0.4 L/eq; current efficiency: 78%), electrodialysis with bipolar membranes (water transport: 0.17 L/eq; current efficiency: 73%), ion exchange, decolorisation, and finally evaporation. The product of the pilot plant was a concentrated lactic acid with a small portion of impurities and a concentration of up to 668 g/L. This process can be used to clean lactic acid for high grade applications in industry.

Keywords: Lactic acid, Down streaming, Ultrafiltration, Electrodialysis, Ion exchange resin

1. INTRODUCTION

The process steps required to gain the final product after fermentation are termed down streaming. Depending upon the purity requirements, several process steps are combined that exert a significant influence on the costs. The expenses for the down streaming of a bio-product, for example, cost up to 90% of the entire production costs, depending on the value of the product (Kasche, 2000). Therefore the down streaming of fermentation media is of particular importance.

Lactic acid is an organic acid with a wide area of applications, e.g. in the food industry, beverage production, pharmaceutical and chemical industries and medicine (Vick Roy, 1985; Van Velthuijsen, 1996). Exploitation of lactic acid for the production of biodegradable polymers is one of the recent applications (Datta et al., 1995). Production of these on an industrial scale is mainly achieved by means of fermentation. Several unit operations are required to obtain an acid with properties which are suitable for future use (Walter, 1998). Conventional processes are based on precipitation steps that generate large amounts of chemical effluents (Bailey and Ollis, 1986). Consequently the environmental impact and the operating costs of traditional precipitation processes can be reduced by using alternative technologies, such as two-stage electrodialysis (Glassner and Datta, 1990; Lee et al., 1998).
In the first step of desalting electrodialysis, sodium lactate is recovered, purified and concentrated. In the water-splitting or acidification step, lactic acid is generated from sodium lactate, and sodium hydroxide is recovered and purified (Kim and Moon,2001).

Membrane operations, for instance microfiltration, nanofiltration, and reverse osmosis, as well as mono-polar (EDM) and bipolar (EDB) electrodialysis, are increasingly being used as an alternative to conventional methods such as filtering, separating, crystallizing,

vaporization, drying, and ion exchange (Sirka et al., 1999). These methods provide gentle product treatment and are cost-effective, attractive in terms of energy and safety engineering, as well as being environmentally sound technologies (Paul and Ohlrogge, 1998; Schmidt et al., 1999). A complete production scheme, targeted around membrane operations for clarification, concentration and conversion of sodium lactate after fermentation, was investigated by Bailly et al. (2001). The fermentation broth is first clarified by cross flow microfiltration from biomass. This is required to obtain a fluid with appropriate properties for carrying out electrodialysis in proper conditions. Subsequently multivalent metal ions (Ca, Mg, etc.) have to be removed from the clarified broth to prevent irreversible damage to the electrodialysis membranes in the EDB stack, especially bipolar ones (Mani and Hadden, 1998). After this the target product sodium lactate is concentrated by conventional EDM electrodialysis. To some extent, EDM can also simultaneously increase the purity of the target sodium lactate, since residual sugars or other impurities can be removed (Yen and Cheryan, 1991; Madzingaidzo et al., 2002; Tang et al., 2004). After conversion of sodium lactate into lactic acid by EDB, the product is finally upgraded by ion exchange resins, whereby polluted effluents of rinsing water and consumption of regenerants are minimized.

In this paper the investigations concentrate on the down-stream processes of lactic acid in the form of sodium lactate made by fermentation of the renewable raw material barley. Glucose used for the fermentation was obtained by hydrolysis of barley pellets and contains a high proportion of inorganic salts and organic compounds. The down-stream processes were performed as reported by Bailly (2002) for the production of fermented organic acids, based on membrane processes and a final purification stage using ion exchange resins. The efficiency of each down stream process is stated.

2. MATERIAL AND METHODS

2.1 Membrane Filtration

The membrane filtration studies were carried out in a pilot plant of Messrs. UFI-TEC GmbH Oranienburg (Germany) with exchangeable modules and membranes as shown in figure 1.

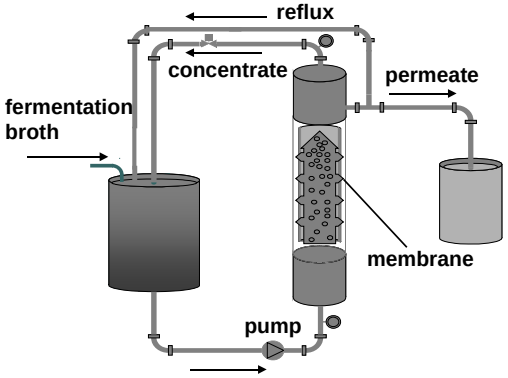


Figure 1. Test equipment for membrane filtration

The temperature was kept constant at 35° C by using a heat exchanger. In the tubular module used, capillary membranes with a membrane effective filtration area of 0.1 m² were applied. The characteristic values of the membrane UF-MD 020 UP-3N (MICRODYN Wuppertal, Germany) examined are:

- material: PES,
- number of capillaries: 48,
- inner diameter: 1.5 mm,
- pore size: 30 nm.

Samples were drawn according to a predetermined schedule for analysis of different ingredients. The temperature, the pressure in front and behind the membrane, as well as the permeate flow were recorded regularly during the experiments.

2.2 Removal of Divalent Cations

The laboratory scale ion exchange unit (IE unit) had a column, which was filled with the ion exchange resin. The column with frit (diameter of pores: 250-500 μm) from QVF Labortechnik Ilmenau, Germany, was 1750 mm high with an inner diameter of 22 mm. The bed volume (BV) of the resin was 0.5 L. Chelating resin RCH 46 (Eurodia Industrie SA, Pfullingen, Germany) was used to remove multivalent metal ions from clarified fermentation broth before the electrodialysis experiments. On the basis of the producer's specification, the following separation and regeneration procedure was applied:
Separation

1. Down-flow: 12.6 bed volumes of sodium lactate solution. Flow rate: 3 L/hr.

Regeneration

1. Down-flow: rinsing with 6 bed volumes of de-ionized water. Flow rate: 3 L/hr.
2. Up-flow: rinsing with 4 bed volumes of de-ionized water. Flow rate: 4 L/hr.
3. Down-flow: regeneration with 3 bed volumes of HCl (40 g/L). Flow rate: 3 L/hr.
4. Down-flow: slow rinsing with 4 bed volumes of de-ionized water. Flow rate: 2 L/hr.
5. Down-flow: fast rinsing with 4 bed volumes of de-ionized water. Flow rate: 4 L/hr.
6. Up-flow: regeneration with 2 bed volumes of NaOH (40 g/L). Flow rate: 2 L/hr.
7. Up-flow: slow rinsing with 4 bed volumes of de-ionized water. Flow rate: 2 L/hr.
8. Down-flow: fast rinsing with 4 bed volumes of de-ionized water. Flow rate: 4 L/hr.

Samples were drawn from the original solution at the beginning of a run, in accordance with a predetermined schedule, and at the end of a run for analysis of lactic acid and ions of Ca and Mg.

2.3 Electrodialysis

The electrodialysis experiments for mono-polar and bipolar electrodialysis were conducted using a laboratory facility with 4 cycles (fig. 2) and the membrane stack OS-ED-100 Quadro (OSMOTA Membrantechnik GmbH Rutesheim, Germany). The membranes ACS/CMS were used for the mono-polar electrodialysis and the mono-polar membranes AMX/CMX as well as the bipolar membranes of Neosepta, Tokuyama Corp., Japan, for the bipolar electrodialysis. The size of the cell frame was 15 x 15 cm with a thickness of 0.5 mm. The effective membrane area was 100 cm^2. The number of membranes used comprised 10 AMX-, 11 CMX- and 10 bipolar membranes. Each circuit was equipped with a pump and measuring devices for flow, pressure, temperature, pH-value and conductivity. Conductivity, pH and temperature were measured with a MultiLine P3pH/LF (WTW Weilheim, Germany). The power supply to the membrane stack was provided via a direct current supply unit (EA-PS 7065 – 10 A, EA Elektro-Automatik GmbH Viersen, Germany) with a controllable

voltage from 0 to 50 V and current from 0 to 10 A, designed for running with constant current and constant voltage.

The experiments were carried out in a batch mode. Four storage tanks (each 10 L) were used to hold dilute (salt), concentrated (acid), base, and electrode rinse solutions. The stock tanks were temperature-managed by thermostat to maintain the temperature between 33 and 36° C. In all stack configurations, the electrode rinse solution was re-circulated continuously to transfer the electric current and to remove gases produced by the electrode reaction during the operation of the ED. From each chamber, 10 cm³ samples were taken according to a predetermined schedule for analysis of lactic acid, inorganic and organic materials.

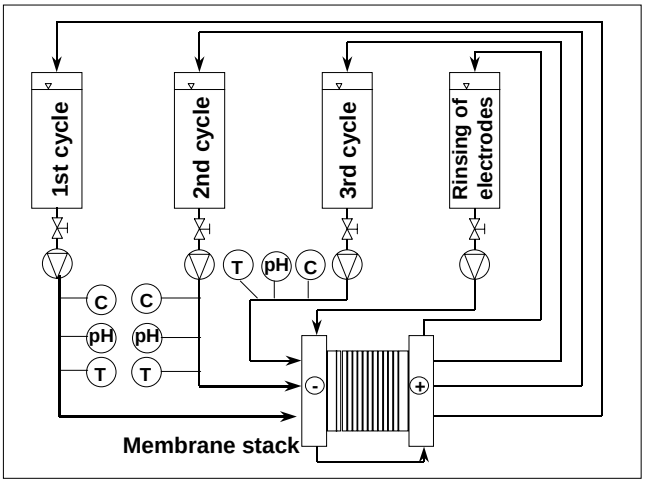


Figure 2. Apparatus for electrodialysis experiments.

2.3.1 Mono-polar Electrodialysis

The principle is illustrated in figure 3. The electrode rinse solution (Na_2SO_4 – 5 g/L), the concentrate (sodium lactate – initial concentration 6.6 g/L) and the diluate (sodium lactate – initial concentration 115 g/L) were circulated through the corresponding chambers of the stack with the flow rates in the three channels ranging from 2.5 to 3.0 L/min for each chamber. For the period of constant voltage 20 V was applied. The experiments were finished when the conductivity in the diluate dropped to 8.0 - 9.5 mS/cm (concentration of sodium lactate 8 to 10 g/L).

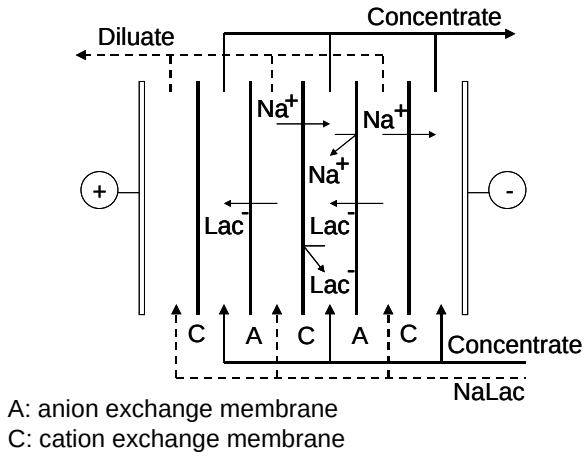


Figure 3. The process scheme of mono-polar electrodialysis.

2.3.2 Bipolar Electrodialysis

The following solutions were used for the EDB: NaOH – 9.5 g/L (electrode rinse solution), NaOH – 9.5 g/L (base stream), lactic acid – 5 g/L (acid stream). A current density of 500 A/m² was applied. The circulation flow rates in the channels ranged from 2.5 to 3.0 L/min.

The three-compartment bipolar electrodialysis unit (EDB3C**)** consisted of ten cell pairs with bipolar membranes, anion exchange membranes and cation exchange membranes, and four solution tanks (salt stream, acid stream, base stream, and electrode rinse solution). Bipolar membranes, anion exchange membranes, and cation exchange membranes were arranged alternately. During ED operation lactate ions and sodium ions in the salt compartment moved simultaneously into the acid and base compartments through anion and cation exchange membranes, respectively. Free lactic acid was formed by combination of lactate ions and hydrogen ions generated on the cation exchange layer of the bipolar membrane, while sodium hydroxide was generated simultaneously by combination of sodium ions and hydroxyl ions on the anion exchange side of the bipolar membrane (fig. 4).

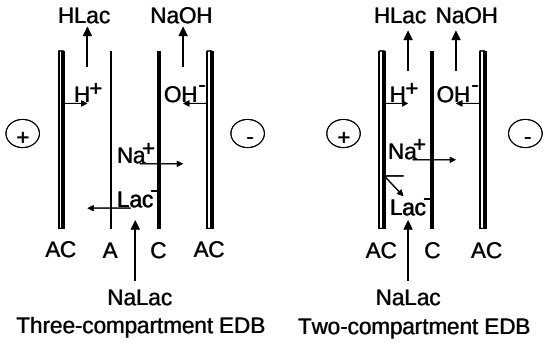


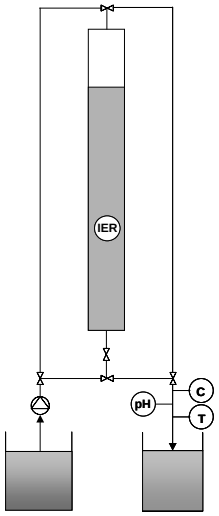
Figure 4. The process scheme of the three- and two-compartment bipolar electrodialysis EDB.

The two-compartment bipolar electrodialysis unit (EDB2C) consisted of ten cell pairs with bipolar membranes and cation exchange membranes, and three solution tanks (salt/acid

stream, base stream, and electrode rinse solution). Bipolar membranes and cation exchange membranes were arranged alternately. The cation exchange membranes allow the selective passage of sodium ions from the salt solution, but reject lactate ions.

2.4 Ion Exchange

Ion exchange (IE) is a fixed-bed separation technology using ion exchange resins (Helferich 1959). These resins have a high number of firmly attached bonds on their surfaces, which can adsorb anions and cations reversibly. The capacity of exchangeable ions is limited, however. The quantity of ions that can be separated by given quantities of resins is determined experimentally. The same applies with regard to the required amount of rinsing water and regenerant, which removes the adsorbed ions and thus regenerates the resin to its previous state. The set-up of the laboratory-scale ion exchange unit is shown in figure 5. The ion exchange resins Relite EXC08 (strongly acidic resin) and Relite EXA133 (weakly basic resin) from Residion S.R.L. Mitsubishi Chemical Corporation, Italy were used.



IER: Ion exchange resin, C: Conductivity,
pH: pH-Value, T: Temperature

Figure 5. Set-up of a laboratory scale ion exchange unit.

2.5 Analytical Methods

Lactic acid and glucose concentrations were measured by HPLC using a GYNKOTEK chromatograph, Germany (column: Eurokat H (KNAUER); 300 x 7.8 mm I.D.; eluent: 0.003 n H_2SO_4; flow rate: 0.8 mL/min; sample volume: 50 µL; temperature: 25° C; pressure: 3 MPa; detection: RI). The concentration of sodium lactate was calculated from the concentration of lactic acid. Water content of biological dry solid matter (BTS) was determined gravimetrically after drying at 105° C. Total Kjeldahl nitrogen (TKN) was analyzed using standard-method Vapodest apparatus from Gerhardt by digestion using a selenium catalyst. The colorimetric technique was used to measure total phosphorus (TP) with the molybdenum blue method. Anions and cations were determined under the following conditions using the ion chromatograph DX-120 from Dionex, Idstein: column: IonPac AS14 (4 mm) with precolumn (anions); Ion-Pac CS12A (4 mm) with precolumn (cations); eluent: 3.5 mM disodium carbonate, 1 mM sodium hydrogen carbonate (anions), 22 mM sulfuric

acid (cations)**;** flow rate: 1.12 mL/min (anions), 1.1 mL/min (cations); detection: conductivity with auto-suppression; suppressor: ASRS in the recycle mode (anions), CSRS in the recycle mode (cations); injection volume 25 µL; elution duration: 12 min (anions), 14 min (cations). Concentrations of Ca- and Mg-Ions were determined by AAS (Vario 6, analytikjena, Germany).

3. RESULTS AND DISCUSSION

3.1 Ultrafiltration

The components of sodium lactate solution after fermentation are set out in table 1. The fermentation broth from the lactic acid fermentation was filtered to remove the cells in order to prevent deposition of bacteria on the membrane surface and the creation of bacteria clusters in the space between the membranes of the electrodialysis unit. All cells of the fermentation broth were removed and cell-free permeate was obtained by ultrafiltration (UF).

Table 1. Components of sodium lactate solution after fermentation.

Components	Unit	Value
Sodium lactate	(mg/L)	130 700
Glucose	(mg/L)	1690
Biological dry solid matter BTS	(mg/L)	9300
TKN	(mg/L)	1670
TP	(mg/L)	607
Na^+	(mg/L)	33 100
K^+	(mg/L)	1520
Ca^{2+}	(mg/L)	58
Mg^{2+}	(mg/L)	159
NH_4^+	(mg/L)	97
Cl^-	(mg/L)	588
PO_4^{3-}	(mg/L)	526
SO_4^{2-}	(mg/L)	2160
NO_2^-	(mg/L)	< 5
NO_3^-	(mg/L)	< 5
pH	-	6.49
Conductivity	(mS/cm)	44.6
Extinction	(420 nm)	3.5

Owing to deposition of organic and inorganic substances on the membrane surface and in its pores (fouling and scaling), permeate flux of UF-membranes decreased within the first two hours. After this period further deposition was prevented by the overflow velocity of the solution (fig. 6). The concentration factor amounted to 19.7, equivalent to a permeate recovery rate of 95%. By rejection of biomass the concentrations of different compounds are changed, as shown in table 2. Sodium lactate was able to pass through the membrane completely.

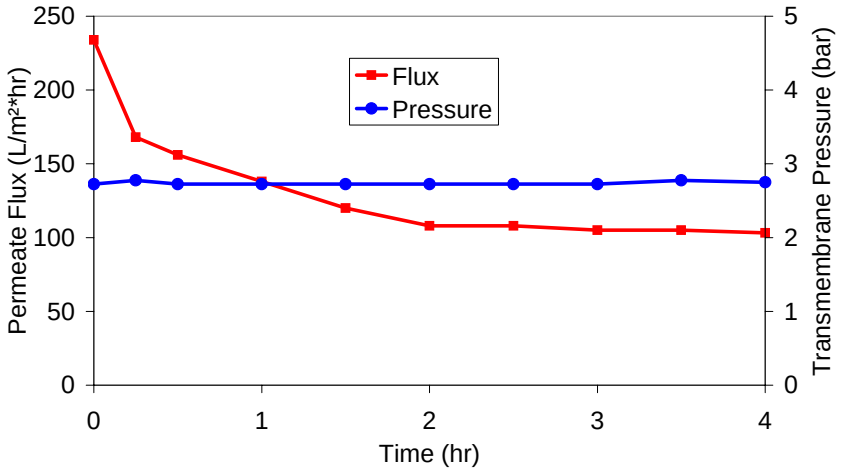


Figure 6. The time course of permeate flux and transmembrane pressure for ultrafiltration of sodium lactate after fermentation.

Table 2. Composition of initial and treated fermentation broth by ultrafiltration.

Compound	Initial fermentation broth	Treated fermentation broth	Rejection (%)
Sodium lactate (mg/L)	130 700	130 700	0
BTS (mg/L)	9300	0	100
TKN (mg/L)	1670	1130	32
TP (mg/L)	607	527	13

The quality of the solutions was based on the rejection of components. Pollution rejection R was quantified by decreasing concentrations , either total or soluble, defined by Equation (1):

$$R = [1 - (c_p / c_f)] * 100 \quad (\%) \qquad (1)$$

where c_p is the concentration of the cleaned solution and c_f is the feed concentration at a given time. The volumetric concentration factor CF_V was equal to the ratio of feed volume F to the concentrate volume C:

$$CF_V = F / C \qquad (2)$$

and the permeate recovery PR was equal to the ratio of the permeate volume P to the feed volume F, defined by equation (3):

$$PR = P / F * 100 \quad (\%) \qquad (3)$$

3.2 Removal of Multivalent Metal Ions

Multivalent metal ions (Ca, Mg etc.) have to be removed from the cell-free fermentation broth. Their concentration must be altogether lower than 1 mg/L.

According to the specification of the chelating resin RCH 46, the total exchange capacity of 1 L resin corresponds to 1 equivalent cation of heavy metals. The capacity of this resin is dependent upon the pH (alkaline pH for Mg and Ca). It is recommended that laboratory trials (column tests) be carried out to prove the process. Since the resin used was new, after preliminary tests the process was designed with 20% of the determined capacity.

These data and concentrations of Ca and Mg ions in the solution of sodium lactate resulted in a capacity of 6.2 L solution/bed volume BV resin . The solution was separated at a flow rate of 6 BV/hr. To obtain a high yield of sodium lactate in the collected solution, approximately 0.68 BV of rinsing water were necessary. The total loss of sodium lactate was 5.8%. The rejection for Ca- and Mg-ions was 99.1% and 99.9%, respectively (table 3). It is possible to control the procedure by measuring the conductivity and the pH-value of the solution after passing the column (fig. 7). The breakthrough of dissolved sodium lactate and starting point of rinsing are marked with an arrow. The sudden increase in conductivity and the sudden decrease in the pH-value mark the breakthrough and the beginning of ion exchange. Finally, the solution displaced by the rinsing solution in the column is diluted with a part of the bed volume of the rinsing solution. As a result, the concentration of sodium lactate in the solution decreases from 130.7 g/L to 115.2 g/L after processing through the column. According to the specification of 1 BV resin, 60 g HCl (pure), 40 g NaOH (pure), and 26 BV de-ionized water for rinsing were needed for the regeneration and rinsing step of a run.

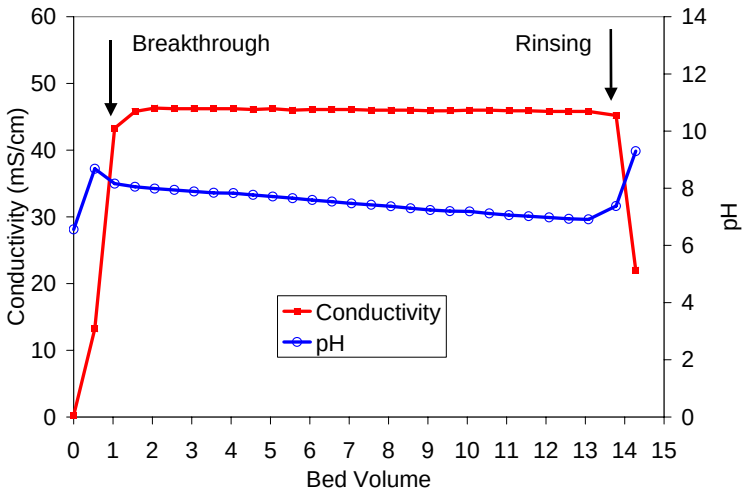


Figure 7. Conductivity and pH-value plotted as a function of throughput volumes measured in units of bed volumes using chelating resin RCH 46.

Table 3. Composition of initial and treated sodium lactate solution using chelating resin RCH 46.

Compound	Cell free fermentation broth	Treated fermentation broth	Rejection (%)
Sodium lactate (mg/L)	130 700	115 200	11.8
Ca^{2+} (mg/L)	58	0.5	99.1
Mg^{2+} (mg/L)	159	0.1	99.9

3.3 Conventional Electrodialysis (EDM)

The product sodium lactate is concentrated and purified by conventional EDM electro-dialysis. The value of the concentration is a very important factor for the subsequent lactic acid recovery step of electro-conversion. The degree of concentration (the ratio of the final concentration in the concentrate to the initial diluate concentration) can be influenced by the ratio of the initial diluate volume to the initial concentrate volume. For the trials the degree of concentration was limited by a minimal value of 1 L in the concentrate. The electrodialysis was therefore operated in two-level mode.

The results of the experiments using electrodialysis are presented as current efficiency, CE (%), and specific energy consumption, SEC (kWhr/kg). The current efficiency CE was calculated using the equation:

$$CE = t_{th} / t_{exp} = [((NaL_{in} - NaL_{fin}) / EW) * F / (I * CP * t_{exp})] * 100 \quad (\%) \quad (4)$$

where t_{th} is the theoretical and t_{exp} the experimental time, NaL_{in} and NaL_{fin} represent, respectively, the initial and final amount of sodium lactate in the feed reservoir (i.e. the diluted one), EW is the equivalent weight of sodium lactate, F is Faraday constant, I is the current (A), and CP the cell pairs in the stack.

The specific energy consumption, SEC, was calculated using the equation:

$$SEC = \int_0^{t_{fin}} (U * I) * dt / (NaL_{in} - NaL_{fin}) \quad (kWhr/kg) \quad (5)$$

where U is the voltage (V), I is the current (A), and t the run duration time (hr). Since U and I can change during a run (depending on the power supply conditions), the integral in Equation 5 has to be evaluated numerically on the basis of experimental data.

Figure 8 shows the time course of the conductivity in the diluate and concentrate circuit as well as the power required to transport ions for a constant voltage period of 20 V for the two-level electrodialysis with the sodium lactate solution. Performance parameters for two-level electrodialysis are listed in table 4 and show that an increase of sodium lactate in the concentrate by two-level electrodialysis does not affect water transport (the volume of water passed to the equivalent of the transported sodium lactate), current efficiency or specific energy consumption considerably.

Since only charged particles are transported in the electric field during the electrodialysis, purification was carried out for the concentrate solution of uncharged particles. This led to glucose and uncharged compounds of nitrogen remaining in the diluate solution (table 5).

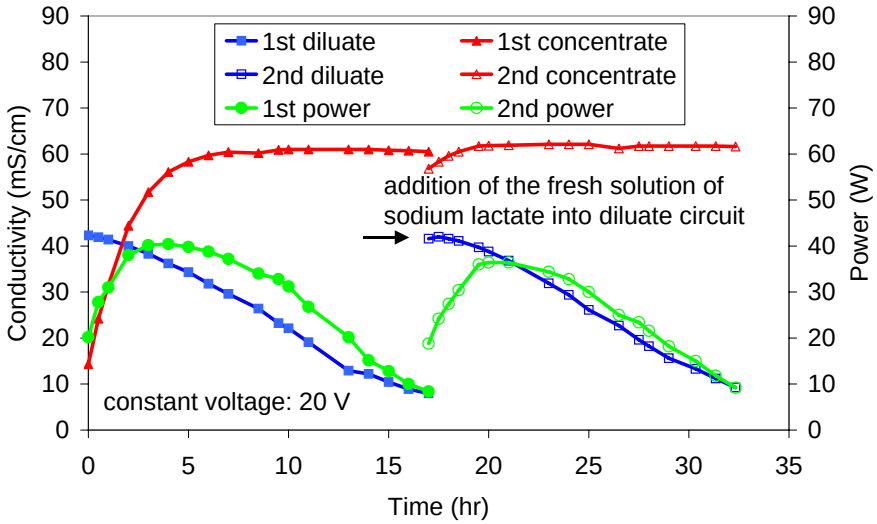


Figure 8. Evolution of conductivity and power vs. time during the two-level concentration of solution of sodium lactate by conventional electrodialysis.

Table 4. Parameter during two-level conventional electrodialysis of sodium lactate solution.

Parameter	Stage of experiment	
	1st stage	2nd stage
Operating time (hr)	17	15.33
Voltage (V)	20	20
Current density (A/m²)	140	130
Initial volume of diluate (L)	8	7
Initial volume of concentrate (L)	1	3.677
Initial concentration of diluate (g/L)	115.2	115.2
Final concentration of diluate (g/L)	8	10
Initial concentration of concentrate (g/L)	6.6	209
Final concentration of concentrate (g/L)	209	236
Water transport (L/eq)	0.39	0.4
Current efficiency (%)	76	78
Specific energy consumption (kWhr/kg)	0.63	0.62

Table 5. Concentrations of selected ingredients in the diluate and concentrate solution after two-level conventional electrodialysis of sodium lactate solution.

Compound	Diluate solution	Concentrate solution	Rejection (%)
Sodium lactate (mg/L)	115 200	236 000	-
Glucose (mg/L)	1500	0	100
TKN (mg/L)	1000	389	61

3.4 Bipolar Electrodialysis (EDB)

The bipolar electrodialysis was investigated using a two- and three-compartment membrane stack configuration. For the first configuration the two-compartment stack

consisted of base and salt compartments and was assembled using alternating bipolar and cation exchange membranes. Anion exchange membranes were not used because of their short lifetime. The three-compartment membrane stack consisted of anion exchange, cation exchange and bipolar membranes to allow three streams to flow, i.e. acid, base, and salt streams.

3.4.1 Two-Compartment Bipolar Electrodialysis (EDB2C)

The experiment was carried out in a constant current mode (5 A). Figure 9 shows the time course of the EDB2C. The trial was stopped when, after a decrease, the electrical conductivity of the salt-/acid-stream increased again . Experimental results are summarized in table 6. A final lactic acid concentration of about 188 g/L, corresponding to 95% conversion, was obtained. The specific energy consumption for the recovery of 1 kg of lactic acid was 1 kWhr and the current efficiency was 57%.

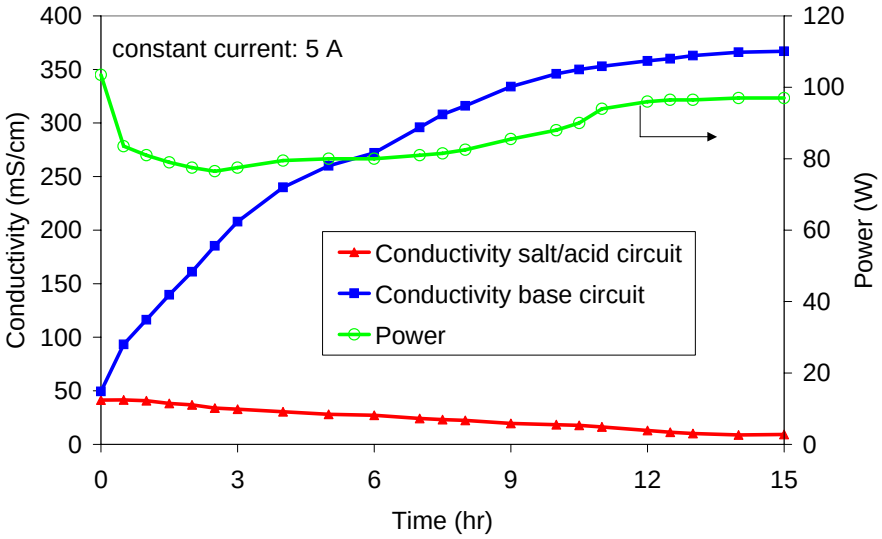


Figure 9. Evolution of conductivity in the salt/acid and base circuit as well as of power vs. time during the two-compartment bipolar electrodialysis of solution of sodium lactate.

Table 6. Parameters during the two-compartment and three-compartment bipolar electrodialysis (EDB) of sodium lactate solution.

Parameter	Two-compartment EDB	Three-compartment EDB
Operating time (hr)	15	11.5
Average voltage (V)	18	31
Current density (A/m²)	500	500
Initial volume of NaL (L)	8	8.5
Initial volume of HLac (L)	-	5.3
Initial volume of NaOH (L)	5.1	6.1
Initial concentration of NaL (g/L)	236	236
Final concentration of NaL (g/L)	9	13.2
Initial concentration of HLac (g/L)	-	11.5
Final concentration of Hlac (g/L)	188	183
Initial concentration of NaOH (g/L)	5.2	5.2

Final concentration of NaOH (g/L)	104	84
Rate of conversion (%)	95	95
Water transport (L/eq)	0.066	0.17
Current efficiency (%)	57	73
Specific energy consumption (kWhr/kg)	1	1.24

The purity of the lactic acid and sodium hydroxide produced is determined by the amount of organic and inorganic compounds in the recovered acid and base solution. In two-compartment bipolar electrodialysis, only cations from the salt solution can pass the cation exchange membranes (table 7).

Table 7. Concentrations of selected ingredients in the sodium lactate solution and in the lactic acid solution after two-compartment and three-compartment bipolar electrodialysis (EDB).

Compound	Sodium lactate solution (mg/L)	Lactic acid solution		Rejection	
		Two-compartment EDB (mg/L)	Three-compartment EDB (mg/L)	Two-compartment EDB (%)	Three-compartment EDB (%)
TKN	389	269	81	31	79
K^+	2500	108	26	96	99
NH_4^+	88	1.4	7	98	92
Cl^-	886	855	851	4	4

3.4.2 Three-Compartment Bipolar Electrodialysis (EDB3C)

The experiment was carried out in a constant current mode (5 A) like two-compartment electrodialysis. Figure 10 shows the time course of the EDB3C. The trial was stopped at an electrical conductivity of 5 mS/cm in the salt solution. Experimental results are summarized in table 6. A final lactic acid concentration of about 183 g/L, corresponding to 95% conversion, was obtained. The specific energy consumption for the recovery of 1 kg of lactic acid was 1.24 kWhr and the current efficiency was 73%.

By comparison with three-compartment electrodialysis, the two-compartment electrodialysis has a much lower water transport, a lower current efficiency and a lower specific energy consumption for the same rate of conversion. By contrast, higher purity of the lactic acid is obtained with three-compartment electrodialysis (table 7). Consequently the EDB2C is unsuitable for purification of lactic acid.

3.5 Final Purification Stages

Impurities of inorganic and organic compounds, which still remain in the concentrated lactic acid after both electrodialysis steps (mono- and bipolar), were almost completely eliminated by anion and cation exchange resins. The course of the conductivity and pH-value dependence on the throughput volumes is shown in figure 11. The start and the end of the ion exchange (“Breakthrough” and “Rinsing” in figure 11) are indicated, in each case, by a change of conductivity and pH-value. Decolorisation of the lactic acid occurred at the same time in the cation interchanger. The results listed in table 8 were achieved after concentration of the purified lactic acid by vacuum evaporation.

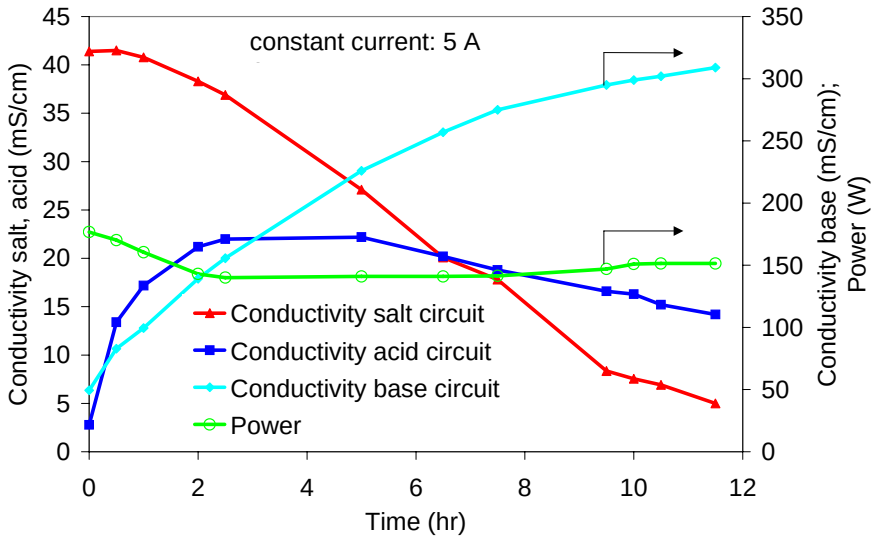


Figure 10. Evolution of conductivity in the salt, acid and base circuit as well as of power vs. time during three-compartment bipolar electrodialysis of solution of sodium lactate.

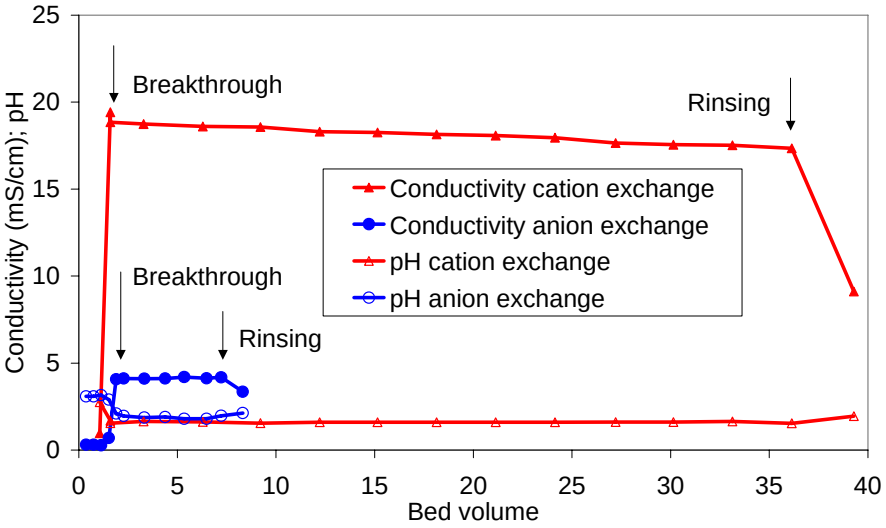


Figure 11. Conductivity and pH-value plotted as a function of throughput volumes measured in units of bed volumes by the up-flow desalting step for the anion and cation exchange.

Table 8. Concentrations of selected ingredients in the lactic acid solution before and after desalting by cation and anion exchange resin as well as concentration by evaporation.

Compound	Initial concentration	Final concentration	Rejection (%)
HLac (mg/L)	183 200	668 400	-
Na^+ (mg/L)	359	18.4	95
K^+ (mg/L)	26	1.75	93
Ca^{2+} (mg/L)	< 0.1	1.8	-
Mg^{2+} (mg/L)	< 0.1	0.37	-
NH_4^+ (mg/L)	7	0.2	97

Cl^- (mg/L)	851	56.1	93
SO_4^{2-} (mg/L)	2 350	< 30	99
PO_4^{3-} (mg/L)	805	58.8	93
TKN (mg/L)	81	99	-
TP (mg/L)	723	143	-
pH	1.5	1.07	-
Conductivity (mS/cm)	16.8	0.74	-
Extinction (420 nm)	0.04	0.004	-

4. CONCLUSIONS

The complete downstream process for the production of lactic acid after fermentation of glucose from hydrolysate of shredded barley was investigated in this work. By using the steps of down streaming ultrafiltration, softening, electrodialysis, ion exchange and evaporation, a concentrated lactic acid with only a small portion of impurities is produced. Ultrafiltration and softening of the sodium lactate solution are required in order to operate the electrodialysis properly. All suspended solids are removed by ultrafiltration, and the concentration of multivalent cations is reduced to less than 1 mg/L by softening. Sodium lactate was purified and concentrated by mono-polar electrodialysis up to 236 g/L. Subsequent purification with bipolar electrodialysis yielded good performance parameters with water transport rates of 0.17 L/eq (three-compartment electrodialysis). As a result free lactic acid concentration reached 183 g/L and chemical impurities such as inorganic cations and compounds of nitrogen were considerably reduced. Additional de-colorisation and de-ionization process steps using ion exchange resins were integrated to polish the free lactic acid for high-grade applications in industry (biodegradable plastics, basic chemicals for further synthesis, biofuels) and agriculture (acidification, cleaning and preservation agents, disinfectants). This reduced the concentrations of the remaining ingredients by 93 to 99%.

5. REFERENCES

Bailey, J. E. and D. F. Ollis. 1986. *Biochemical Engineering Fundamentals.* Singapore: MacGraw-Hill.

Bailly, M. 2002. Production of organic acids by bipolar electrodialysis: realizations and perspectives. *Desalination* 144:157-162.

Bailly, M., Balmann, H. Roux-de, Aimar, P., Lutin, F. and M. Cheryan. 2001. Production processes of fermented organic acids targeted around membrane operations: design of the concentration step by conventional electrodialysis. *Journal of Membrane Science* 191:129-142.

Datta, R., Tsai, S. P., Bonsignore, P., Moon, S. H. J. R. Frank. 1995.Technological and economic potential of poly(lactic) and lactic derivates. *FEMS Microbiology Reviews.* 16:221-231.

Glassner, D. A. and R. Datta. 1990. Process for production and purification of lactic acid. EP 0393818 A1.

Helferich, F.1959. *Ionenaustauscher*. Weinheim/Bergstrasse: Verlag Chemie GmbH.

Kasche, V. 2000. Achema-Berichte: Aufarbeitung von Bioprodukten. *Chem. Ing. Tech.* 72:1448-1448.

Kim, Y. H. and S.-H. Moon. 2001. Lactic acid recovery from fermentation broth using one-stage electrodialysis. *J. Chem. Technol. Biotechnol.* 76:169-178.

Lee, E. G., Moon, s. H., Chang, Y. K., Yoo, Ik-K. and H. N. Chang. 1998. Lactic acid recovery using two-stage electrodialysis and its modelling. *Journal of Membrane Science* 145:53-66.

Madzingaidzo, L., Danner, H. and R. Braun. 2002. Process development and optimisation of lactic acid purification using electrodialysis. *Journal of Biotechnology.* 96:223-239.

Mani, K. N. and D. K. Hadden. 1998. Process for the recovery of organic acids and ammonia from their salts. American Patent no. 5814498.

Paul, D. and K. Ohlrogge. 1998. Membrane separation processes for clean production. *Environ. Prog.* 17:137-141.

Schmidt, M., Mirza, S., Schubert, R., Rodicker, H., Kattanek, S. and J. Malisz. 1999. Nanofiltration membranes for separation problems in organic solutions. *Chem.-Ing.-Tech.* 71:199-206.

Sirka, K. K., Shanbhag, P. V. and A. S. Kovvali. 1999. Membrane in a reactor: A functional perspective. *Ind. Eng. Chem. Res*. 38:3715-3737.

Tang, V. H., Koschuh, W., Kulbe, K. D., Kromus, S., Krotscheck, Ch. and S. Novalin. 2004. Desalination of high salt content mixture by two-stage electrodialysis as the first step of separating valuable substances from grass silage. *Desalination* 162:343-353.

Van Velthuijsen, J. A. 1994. Lactic acid production and utilization. In *Carbohydrate Organic Raw Materials III, Workshop*, ed. H. van Bekkum, H. Roeper, 129-140. Weinheim: Wiley-VCH.

Vick Roy, T. B. 1985. Lactic acid. In *Comprehensive Biotechnology*, ed. M. M. Young, 761-775. New York: Pergamon Press Ltd.

Walter, K. J. 1998. In *Bio-separations and Bio-processing, A Handbook*, ed. G. Subramanian, vol. 2. Weinheim: Wiley-VCH.

Yen,Y. H. and M. Cheryan. 1991. Separation of lactic acid from whey permeate fermentation broth by electrodialysis. *Trans. IchemE* 69:200-205.