LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
School of Engineering Science
Degree Program in Chemical Engineering

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CONCENTRATION OF LACTIC ACID BY FORWARD OSMOSIS

Examiners: Professor Mika Mänttäri
D.Sc. (Tech.) Hanna Kyllönen

ABSTRACT

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Master's thesis

2016

91 pages, 31 figures, 12 tables, and 2 appendices

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Keywords: concentration, fermentation, filtration, forward osmosis, lactic acid, membrane

The demand of lactic acid is growing each year due to its novel uses in the production of biodegradable plastics. However, its cost-effective production by fermentation remains an unsolved challenge. The recovery of lactic acid from the fermentation broth can account for up to 50 % of the total processing costs. Calcium hydroxide precipitation is the conventional recovery method, but formation of low-value gypsum and chemical consumption have made the process economically and ecologically unattractive. Accordingly, alternative solutions are being developed.

Concentration is an essential part of all the lactic acid recovery schemes. Forward osmosis (FO) is an osmotically driven membrane process that has potential to be applied in the concentration of lactic acid. Its advantages include simplicity, selectivity, reduced chemical usage, and low energy requirement.

This study investigated the suitability of FO for concentration of lactic acid. Laboratory experiments were conducted with glucose as draw solution. The effect of feed and draw solution temperatures on the FO water flux was determined, and two different membranes were compared. The feed solution temperature was identified as the dominating factor affecting the water flux across the membrane: the higher its temperature, the higher the water flux. There was a significant difference in the performance of the two membranes.

The most favorable feed–draw solution temperature combination and membrane were used to concentrate lactic acid. A good water flux and a water recovery of up to 84 % were obtained, which corresponds to a concentration factor of 6.5. However, because the membrane presented a rejection of only 56 % for lactic acid, the real concentration factor was 4.0. The poor rejection lowers significantly the final yield of lactic acid and makes the process infeasible on a larger scale. The FO filtration conditions need further optimization in terms of feed solution pH, filtration temperature, and membrane selection.

Finally, a concept for incorporation of FO into the downstream processing of lactic acid was suggested. In the concept, the diluted glucose-based draw solution after FO is utilized as the carbohydrate source of lactic acid fermentation. Hence, the requirement for regeneration of the draw solution can be eliminated, and the energy-effectiveness of the process is enhanced.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
School of Engineering Science
Kemiantekniikan koulutusohjelma

Henna Ihalainen

Maitohapon konsentrointi forward osmosis -tekniikalla

Diplomityö

2016

91 sivua, 31 kuvaa, 12 taulukkoa ja 2 liitettä

Tarkastajat: Professori Mika Mänttäri
TkT Hanna Kyllönen

Hakusanat: fermentointi, forward osmosis, konsentrointi, maitohappo, membraani, suodatus

Maitohapon kulutus kasvaa vuosittain johtuen sen käytöstä uudenlaisten, biohajoavien muovien valmistuksessa. Maitohapon kustannustehokas tuotanto fermentoimalla on kuitenkin ongelmallista, sillä sen erotus fermentointiliemestä saattaa kattaa jopa 50 % koko tuotantokustannuksista. Maitohappo erotetaan tyypillisesti saostamalla se kalsiumhydroksidilla, mutta menetelmä kärsii suuresta kemikaalikulutuksesta ja sivutuotekipsin muodostumisesta. Vaihtoehtoisia ratkaisuja pyritäänkin kehittämään.

Kaikkia maitohapon talteenottoprosesseja yhdistää tarve konsentroinnille. Forward osmosis (FO) on osmoosiin perustuva membraanitekniikka, jota on mahdollista soveltaa maitohapon konsentrointiin. Tekniikan hyötyihin lukeutuvat yksinkertaisuus, selektiivisyys sekä vähentynyt kemikaali- ja energiankulutus.

Tässä työssä tutkittiin FO:n soveltuvuutta maitohapon konsentrointiin. Laboratoriossa suoritettiin kokeita, joissa käytettiin glukoosia vetoliuoksena. Syötteen ja vetoliuoksen lämpötilojen vaikutus membraanin läpi kulkevaan vesivuohon määritettiin sekä kahta erilaista membraania verrattiin. Syötteen lämpötilan havaittiin säätelevän veden vuota: mitä korkeampi lämpötila, sitä korkeampi vuo. Membraanit myös toimivat huomattavan eri tavoin eri olosuhteissa.

Suotuisinta syötteen ja vetoliuoksen lämpötilayhdistelmää sekä membraania käytettiin maitohapon konsentroinnissa. Kokeessa saavutettiin hyvä vesivuo sekä 84 %:n veden talteenotto, joka vastaa konsentrointikerrointa 6,5. Membraanin maitohapporejektio oli kuitenkin vain 56 %, minkä vuoksi todellinen konsentrointikerroin oli 4,0. Huono rejektio heikentää merkittävästi maitohapon saantoa ja tekee prosessista sellaisenaan kannattamattoman. FO:n suodatusolosuhteet, kuten suodatuslämpötila ja -pH sekä käytettävä membraani, vaativat vielä optimointia.

Lopuksi työssä esitettiin konsepti FO:n liittämiseksi maitohapon tuotantoketjuun. Konseptissa FO-suodatuksen jälkeinen laimentunut glukoosiliuos hyödynnetään hiilihydraattilähteenä maitohapon fermentoinnissa. Näin voidaan välttää tarve vetoliuoksen regeneroinnille ja parantaa prosessin energiatehokkuutta.

ACKNOWLEDGMENTS

This thesis was conducted at the Technical Research Centre of Finland (VTT) in Jyväskylä during the year of 2016. I would like to express my gratitude to Hanna Kyllönen, the instructor of my master's thesis, for giving me the opportunity to carry out this study at VTT and for introducing me the topic of forward osmosis. I would like to thank her for her continuous support, encouragement, and dedicated attitude when she guided me through this project. I would also like to acknowledge Professor Mika Mänttäri for his participation and valuable feedback.

I would like to thank Jorma Ihalainen for his guidance and advice in the experimental work and Veli-Pekka Heiskanen for taking the time to help me with the heat transfer calculations. Many thanks to Juha, Antti, Eliisa, and Minna for the inspiring working atmosphere, and also to the other personnel at VTT who always kindly helped me whichever problem I happened to encounter.

This thesis concludes the most stressful but also rewarding chapter of my life. I have been lucky to have made a bunch of such great friends while my studies in Lappeenranta. You have made the time worthwhile! I would also like to thank my high school friends for sticking with me through these years and providing the encouragement, laughs, and (ugly) postcards when most needed.

Finally, I would like to express my most sincere thanks to my parents and sisters for their persistent support and understanding in my decisions and pursuing my goals throughout my life.

Lievestuore, 5th of December, 2016

Henna Ihalainen

TABLE OF CONTENTS

NOMENCLATURE

Greek letters

Δ	difference operator	–
ε	porosity of the support layer	–
π	osmotic pressure	mmol/kg, bar
ρ	density	kg/m^3
σ	reflection coefficient	–
τ	tortuosity of the support layer	–
φ	osmotic pressure coefficient	–

Latin letters

A	water permeability coefficient	m^3/(m^2 s Pa)
A_m	membrane active area	m^2
B	solute permeability coefficient	m^3/(m^2 s)
C	concentration	kg/m^3, g/L
CF	concentration factor	–
C_P	specific heat capacity	kJ/(kg °C)
D	solute diffusion coefficient	m^2/s
i	van't Hoff factor	–
J	flux	L/(m^2 h), g/(m^2 h)
K	solute resistivity to diffusion	s/m
K_D	distribution coefficient	–
M	molar concentration	mol/L
m	mass	kg
$\dot{m}$	mass flow rate	kg/min
P	hydraulic pressure	bar
R	gas constant	8.314 J/(K mol)
R	rejection	%
S	structural parameter of the support layer	m
T	temperature	K, °C
t	time	h
t_s	thickness of the support layer	m

V	volume	L
w	mass fraction	%
WR	water recovery	%
Y	yield	%

Subscripts

D	draw solution
F	feed solution
f	final
Glc	glucose
i	initial
LA	lactic acid
P	permeate
S	solute
W	water

Abbreviations

BED	bipolar electrodialysis
CED	conventional electrodialysis
ECP	external concentration polarization
FO	forward osmosis
HPLC	high-performance liquid chromatography
ICP	internal concentration polarization
MF	microfiltration
NF	nanofiltration
PRO	pressure retarded osmosis
RO	reverse osmosis
TFC	thin film composite
UF	ultrafiltration

1 INTRODUCTION

1.1 Background

Ever since start of its industrial production in the 1880s, lactic acid has been used in a variety of applications mainly in food-related industry but also in pharmaceutical, cosmetic, and chemical industries. Its demand has been growing rapidly over the last decade because of its novel, large-volume uses in the synthesis of a biodegradable plastic called polylactic acid. (Vijayakumar, Aravindan, & Viruthagiri, 2008, p. 258.) In 2015, polylactic acid had the second highest production volume in Europe among all biodegradable plastics (Kaeb, Aeschelmann, Dammer, & Carus, 2016). Therefore, lactic acid has potential to become a high-volume commodity chemical, but its cost-effective production still remains a challenge to be solved.

The production of lactic acid is based on carbohydrate fermentation. However, the downstream processing to purify and concentrate lactic acid from the dilute and complex fermentation broth is the bottleneck of the process and can account for up to 50 % of the total processing costs. The traditional downstream processing method for recovery of lactic acid is calcium hydroxide precipitation, but formation of low-value gypsum and chemical consumption have made the process economically and ecologically unattractive. (Wasewar, 2005, p. 159.) For this reason, alternative separation techniques are being developed, including adsorption, extraction, distillation, membrane separation, etc., to intensify the production process and meet the growing demand of lactic acid.

Membrane separation has gained attention because of its simplicity, selectivity, reduced chemical usage, and low energy requirement (Cho, Lee, & Park, 2012, p. 10208). Even though other membrane processes have been recognized and successfully applied for concentration of lactic acid or other carboxylic acids, only few studies considering forward osmosis (FO) as an alternative have been reported. FO is an osmotic process which advantages compared to other membrane processes include lower energy consumption because of operation under no or low hydraulic pressure, high rejection for contaminants, high water recovery, low fouling tendency, and easy fouling removal (Abousnina & Nghiem, 2013, p. 571). This study investigates the suitability of FO for concentration of lactic acid.

1.2 Objectives and restrictions

The objective of this study was to evaluate feasibility of FO for concentration of lactic acid from a fermentation broth. This study consists of a literature review and experimental measurements. In the literature review, the properties, applications, and traditional production processes of lactic acid were first described briefly. The downstream processing scheme and the most commonly used techniques for recovery and purification of lactic acid from a fermentation broth were then reviewed. The advantages and disadvantages of the techniques were also evaluated. Finally, the principle of FO and different variables affecting its performance were introduced in detail. The literature considering FO for concentration of carboxylic acids was also reviewed, and the process was compared to reverse osmosis used for concentration of lactic acid to evaluate its feasibility.

In the experimental part, concentration of lactic acid by FO with glucose as draw solution was studied. Purification of lactic acid, although being very essential, was not included in the experimental study. The effect of filtration conditions on FO water flux was determined by conducting short filtrations with two different membranes under varying feed and draw solution temperature combinations. After identifying the most favorable conditions, a longer concentration run was carried out to evaluate the performance of the process and to find out the extent of water recovery that can be obtained by FO. Finally, a concept for utilization of FO in the downstream processing of lactic acid was introduced and the feasibility of the process was evaluated.

2 LACTIC ACID

Lactic acid (2-hydroxypropanoic acid) is the simplest and most widely occurring hydroxycarboxylic acid and an important factor in various biochemical processes (Datta & Henry, 2006, p. 1119). It is a chiral compound and exists in two optical isomers: L-(+)-lactic acid and D-(−)-lactic acid, both of which are illustrated in Figure 1. L-(+)-lactic acid is biologically the more significant isomer as it occurs naturally in blood and numerous fermentation products. (Chahal, 2000, p. 1; Datta, 2004, p. 1.) Some chemical and physical properties of lactic acid are listed in Table I.

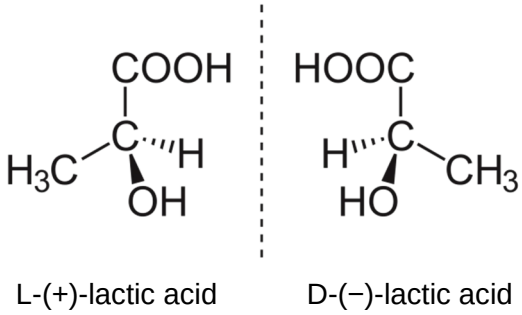

Figure 1. L- and D-isomers of lactic acid (Ren, 2010, p. 4).

Table I. Physical and chemical properties of lactic acid (Chahal, 2000, pp. 2–3; Groot, van Krieken, Sliekersl, & de Vos, 2010, p. 5; Lide, 2008, p. 318; Ren, 2010, p. 5).

Property	Value
Molecular formula	$CH_3CH(OH)COOH$ ($C_3H_6O_3$)
Molar mass	90.078 g/mol
Solid density	1.33 g/mL (20 °C)
Liquid density	1.18 g/mL (20 °C)
Melting point	L: 53 °C D: 53 °C D/L: 16.8 °C
Boiling point	122 °C (12 mmHg)
Dissociation constant (K_a)	1.38×10^{-4} (25 °C)
Physical form	White crystalline solid or clear liquid
Solubility	Very soluble in water and ethanol Slightly soluble in diethyl ether
Specific heat	Liquid: 2.34 J/(g K) (25°C) Crystalline: 1.41 J/(g K) (25°C)

The chemical behavior of lactic acid is determined by its three properties: 1) asymmetric optical activity, 2) acidic character in aqueous medium, and 3) bifunctional reactivity due to the contribution of both carboxylic acid and hydroxyl groups (Castillo Martinez et al., 2013, p. 71). Hence, lactic acid can participate in a number of chemical reactions including reduction, oxidation, esterification, condensation, substitution, etc. (Datta, 2004, p. 2).

Lactic acid is a weak acid, which means that it dissociates incompletely in water. In its dissociation reaction, lactic acid loses a proton from its carboxyl group, yielding anionic lactate (Ren, 2010, p. 5):

$$CH_3CH(OH)COOH \rightleftharpoons H^+ + CH_3CH(OH)COO^-. \quad (1)$$

Depending on the pH of the solution, lactic acid is present either as acid or its lactate salt. It forms salts with most metals, ammonia, and a large number of organic bases. The pH at which 50 % of the acid is dissociated is referred to as pK_a, which for lactic acid is 3.86 at 25 °C. (Chahal, 2000, pp. 2, 7.) Figure 2 illustrates the relative abundance of lactic acid and lactate under varying pH values.

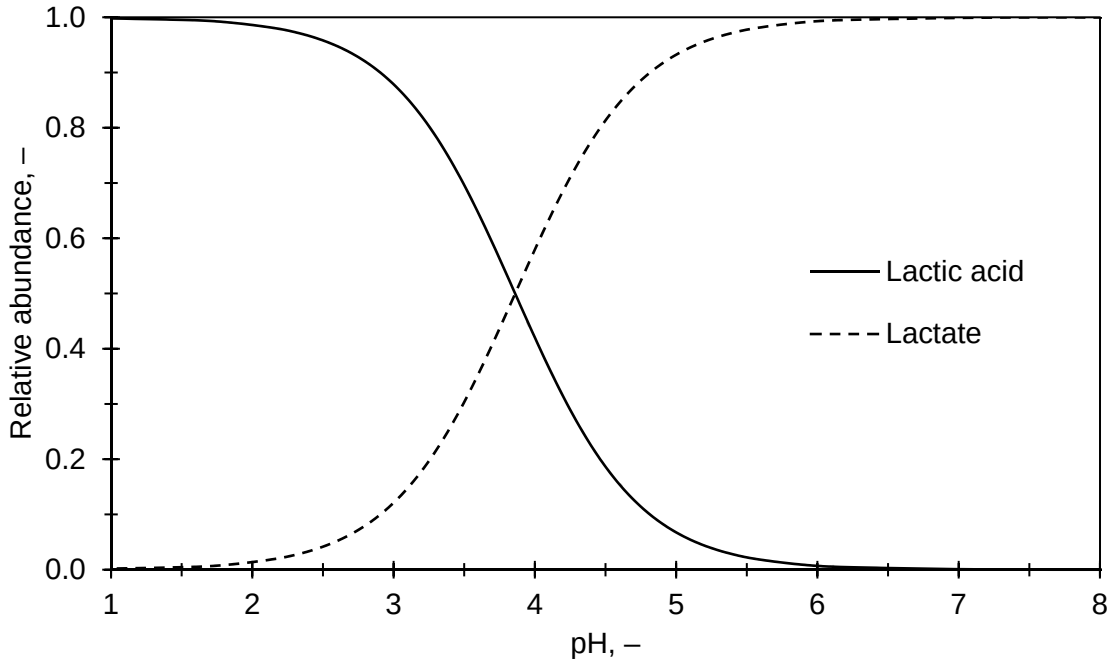

Figure 2. Relative abundance of lactic acid and its dissociated fraction (lactate) at varying pH values in an aqueous solution at 25 °C. The pK_a value of lactic acid is 3.86. (Adapted from López-Garzón & Straathof, 2014, p. 870.)

Lactic acid is used in various applications of which food and food related applications account for approximately 85 % and the rest 15 % comes from non-food industrial applications (Vijayakumar et al., 2008, p. 258). Possible uses in different industries are compiled in Table II.

Due to lactic acid's properties and natural occurrence in many food products, it is a versatile and widely used ingredient in the food industry, for instance in the production of dairy, bakery and meat products, confectionery, pickles, and wine. The non-food applications include uses in pharmaceutical, cosmetic, and chemical industries. (Vijayakumar et al., 2008, pp. 258–259.) Having both hydroxyl and carboxylic acid groups, lactic acid can participate in a number of chemical reactions. This feature makes it a potential feedstock monomer in the chemical manufacturing of a range of products, such as other chemicals, biodegradable polymers, and green solvents. (Pal, Sikder, Roy, & Giorno, 2009, p. 1549.)

Table II. Applications and commercial uses of lactic acid and its salt (Datta & Henry, 2006, p. 1120; Vijayakumar et al., 2008, pp. 258–261; Wee, Kim, & Ryu, 2006, p. 169).

Food industry	- Production of cheese and yoghurt - Acidulant, preservative, pH regulator, flavor enhancer, pickling agent, antimicrobial agent, emulsifying agent
Cosmetic industry	- Moisturizing, skin-lightening, skin-rejuvenating, or anti-acne agent, pH regulator in skin care products - Anti-caries agent in oral hygiene products
Pharmaceutical industry	- Drugs against osteoporosis, anemia, hypertension - Dialysis solutions - Biopolymers for controlled drug delivery
Chemical industry	- Solvent, pH regulator, descaling agent, cleaning agent, neutralizer, chiral intermediate, antimicrobial agent, slow acid-release agent
Chemical feedstock	- Acetaldehyde, acrylic acid - Biodegradable polymers (polylactic acid) - Green solvents (ethyl, propyl, butyl lactates) - Oxygenated chemicals (propylene glycol)

The production of lactic acid has been growing rapidly over the last decade because of its novel, large-volume uses in the synthesis of polylactic acid. The global production capacity of lactic acid was estimated to be 714,000 tons in 2013, which is still expected to grow and reach 1,960,000 tons by 2020. (Grand View Research, Inc., 2014.)

3 CONVENTIONAL METHODS OF LACTIC ACID PRODUCTION

There are two main routes for the production of lactic acid: chemical synthesis and carbohydrate fermentation, both of which have been used on a commercial scale. However, nowadays all lactic acid is produced by fermentation because of the many limitations concerning the synthetic route. (Datta & Henry, 2006, p. 1123.)

3.1 Chemical synthesis

The chemical synthesis of lactic acid is based on lactonitrile which is a by-product of acrylonitrile industry. In the process, lactonitrile is produced by adding hydrogen cyanide to acetaldehyde in the presence of a base catalyst (Datta, 2004, pp. 5–6):

$$CH_3CHO + HCN \xrightarrow{\text{catalyst}} CH_3CH(OH)CN. \qquad (2)$$

The reaction takes place in a liquid phase under a high pressure. The crude lactonitrile is recovered and purified by distillation. Concentrated hydrochloric or sulfuric acid is then added to hydrolyze lactonitrile to lactic acid, producing ammonium salt as a by-product (Datta, 2004, pp. 5–6):

$$CH_3CH(OH)CN + 2\,H_2O + \frac{1}{2}\,H_2SO_4 \rightarrow CH_3CH(OH)COOH + \frac{1}{2}\,(NH_4)_2SO_4. \qquad (3)$$

Finally, pure lactic acid is obtained by esterification-hydrolysis method which is described in more detail in Chapter 4.2.3. The block diagram of the synthetic route of lactic acid production is presented in Figure 3.

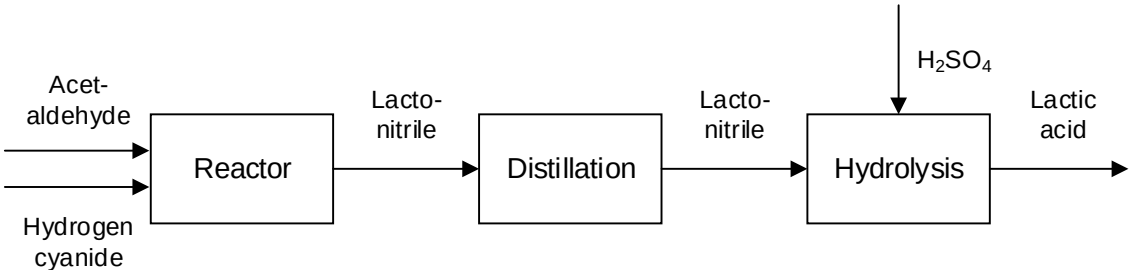

Figure 3. Production of lactic acid by chemical synthesis using acetaldehyde feed (adapted from Pal et al., 2009, p. 1550; Datta, 2004, pp. 5–6).

The synthetic route of lactic acid production has several drawbacks, which is why it is no more used on a commercial scale. The drawbacks include limited capacity because of the dependence on acrylonitrile industry for the raw material, high manufacturing and raw material costs, and impurity of the product. In addition, the synthetically produced lactic acid is a racemic mixture of L-(+)- and D-(−)-lactic acid, whereas in most cases only the L-(+)-isomer is the desirable product. (Pal et al., 2009, p. 1550.)

Other routes for lactic acid production include base-catalyzed degradation of sugars, oxidation of propylene glycol, reaction of acetaldehyde, carbon monoxide, and water under high temperatures and pressures, hydrolysis of chloropropionic acid, nitric acid oxidation of propylene, etc. None of these techniques has been implemented on a large scale because of their technical and economical unviability. (Castillo Martinez et al., 2013, p. 71; Chahal, 2000, p. 5.)

3.2 Fermentation

In the fermentative production of lactic acid, carbohydrates are anaerobically broken down by microorganisms and converted into lactic acid. Homolactic bacteria, such as *Lactobacillus delbrueckii*, *L. bulgaricus*, and *L. leichmanii*, or yeasts, such as *Saccharomyces cerevisae*, are commonly used. (Datta, 2004, p. 6.) The selection of suitable microorganism allows selective production of either L-(+)- or D-(−)-lactic acid or their racemic mixture as well as improved fermentation of carbohydrates from varying sources (Castillo Martinez et al., 2013, p. 72; Pal et al., 2009, p. 1551).

A variety of carbohydrate sources can be used, including e.g. sugars, molasses, whey, and starches (Datta, 2004, p. 6). Glucose, sucrose, and lactose are the most commonly used sugars for production of lactic acid. The selection of raw materials is done on the basis of their cost, purity, availability, pre-treatment requirements, fermentation rate, and yield for lactic acid. In addition, the raw materials affect considerably the downstream processing requirements of the fermentation broth. That is worth taking into account in their selection since purification of lactic acid from the fermentation broth is the costliest part of the production process. (Datta, 2004, p. 6; Pal et al., 2009, p. 1550.)

The process is typically run batchwise, but fed-batch, repeated fermentation, and continuous cultures are also operated (Abdel-Rahman, Tashiro, & Sonomoto, 2013, p. 885). The different operating modes are described in Table III. In the batch process, the bacterial

culture is first grown in an inoculation vessel and then transferred to the fermentation vessel which contains sugar solution and nutrients (Castillo Martinez et al., 2013, p. 71; Ghaffar et al., 2014, p. 224). The essential nutrients include soluble proteins, ammonium salts, and phosphates, which can be provided by yeast extract, soy hydrolysate, etc. (Chahal, 2000, p. 4; Datta, 2004, p. 6). Different microorganisms prefer different fermentation conditions, so it is important to choose the most favorable nutrients, pH, temperature, aeration, agitation, etc. in each occasion (Castillo Martinez et al., 2013, p. 71).

Table III. Operating modes of fermentation processes (Abdel-Rahman et al., 2013, p. 885).

Fermentation mode	Characteristics
Batch fermentation	The simplest and most commonly used method: no carbon substrates or other components are added during fermentation, only neutralizing agents for pH control + High product concentration − Low productivity, inhibition of microorganisms
Fed-batch fermentation	Nutrients are fed continuously or sequentially to the fermentation broth + High productivity and product concentration − Inhibition of microorganisms
Repeated fermentation	Done with batch or fed-batch: repeated cycles by inoculating a part or all the cells from a previous run into the next run + Increased yield, time and labor saving, etc. − Requirement of special devices or connection lines
Continuous fermentation	Fermentation broth is withdrawn and fresh medium is added to the fermentation + High productivity − Incomplete utilization of the carbon source

As lactic acid is formed in the fermentation according to the reaction

$$C_6H_{12}O_6 \xrightarrow{\text{fermentation}} 2\ CH_3CH(OH)COOH, \quad (4)$$

the pH of the fermentation broth starts to fall affecting the productivity of the microorganisms (Pal et al., 2009, p. 1551). Typically, yeasts are more resistant to low pH values than lactic acid bacteria (Ghaffar et al., 2014, p. 225). Calcium hydroxide or carbonate is added to the fermenter to neutralize the acid and maintain the pH at around 5–6 in order to keep the process viable. Such a high pH, however, leads to dissociation of lactic acid and formation

of calcium lactate as the pK_a value of lactic acid is 3.86. (Pal et al., 2009, p. 1551.) The obtained lactate yield is approximately 90 wt% based on the initial sugar concentration. The final concentration of lactate in the fermentation broth is about 10 wt%. (Datta, 2004, p. 6; Ghaffar et al., 2014, p. 224.) Because the broth contains impurities and the total lactic acid/lactate concentration is low, the broth then proceeds to concentration and purification stages.

4 SEPARATION OF LACTIC ACID FROM FERMENTATION BROTH

After fermentation, the broth has to go through a full downstream processing scheme to meet the purity requirements of the final product. Lactic acid is normally supplied in 50−90 wt% solutions of varying qualities: technical grade, food grade, pharmaceutical grade, and plastic grade. Pharmaceutical and food grades are considered as the most important ones with such quality specifications as listed in Table IV. (Vijayakumar et al., 2008, p. 257.)

Table IV. Quality specifications of lactic acid (Chahal, 2000, p. 6).

Quality	Pharmaceutical grade	Typical food grade
Assay, %	88.0	80
Chloride, %	0.008	0.02
Sulfate, %	0.02	0.05
Arsenic, ppm	4	0.2
Heavy metals, ppm	33	10
Iron, ppm	10	10
Ash, %	0.1	0.1
Calcium, %	0.02	

The crude fermentation broth contains approximately 10 wt% of lactic acid or its lactate salt and a number of impurities including microbial cells as the main impurity, other organic acids, unconverted carbohydrate sources, color, nutrients (such as yeast extract, ammonium salts, potassium, phosphorus), proteins, and water (Pal et al., 2009, p. 1551). This dilute and complex nature of the broth makes the separation of lactic acid complicated and expensive, which is why downstream processing can account for up to 50 % of the total production costs (Wasewar, 2005, p. 159).

Lactic acid is typically separated from the broth removed from the fermenter, but it can also be recovered in situ. The downstream processing can be roughly divided into three main steps (Figure 4): 1) fermentation broth is first pretreated to remove the major impurities, 2) lactic acid is then recovered from the broth, and 3) finally, lactic acid is concentrated and purified to obtain the final product. The steps can overlap each other or be combined. (López-Garzón & Straathof, 2014, p. 875.)

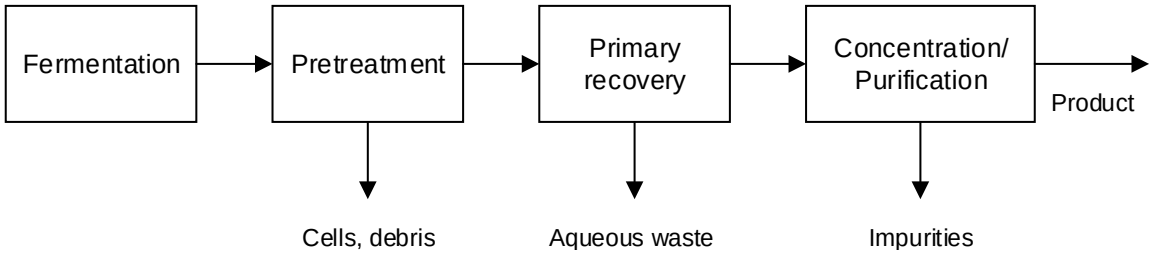

Figure 4. Downstream processing of lactic acid (adapted from López-Garzón & Straathof, 2014, p. 875).

Calcium hydroxide precipitation is the conventional recovery method, but formation of gypsum has made the process economically and ecologically unattractive (Wasewar, 2005, p. 160). For this reason, alternative separation techniques are being developed, including adsorption, extraction, membrane separation, distillation, etc. The different steps of the downstream processing of lactic acid are introduced in the following chapters.

4.1 Pretreatment of the fermentation broth for removal of main impurities

Before further separation of lactic acid, the fermentation broth must go through a pretreatment procedure to remove the main impurities that are large particles such as microbial cells, their debris, and proteins. Typically, the broth is first heated to approximately 70 °C to kill the microorganisms. A subsequent pH control can follow. (Chahal, 2000, p. 5.) Coagulation followed by flocculation can be used to improve the separation of microorganisms. A coagulant, such as a metal salt, is added to the broth to neutralize the surface charges of the microorganisms and form a colloidal suspension. A flocculating agent, such as a polyelectrolyte, is then added to aggregate the colloids into flocs. (Hansen, Jørgensen, & Bundgaard-Nielsen, 2008, pp. 538–539.)

The clarification of the broth is carried out by sedimentation, centrifugation, or filtration. Membrane processes such as microfiltration (MF) and ultrafiltration (UF) are often used. MF membranes have the average pore size of 0.1–0.2 µm, which is sufficient for retention of microbial cells. UF membranes have a smaller average pore size, 0.01–0.1 µm, and they can separate also proteins. (Pal et al., 2009, pp. 1551–1552.) MF and UF modules are typically operated under pressures of < 2 bar and 1–4 bar, respectively (Jiang, Wang, & Xu, 2016, p. 139; Li, Shahbazi, & Kadzere, 2006, pp. 576–577).

After clarification, the broth may still contain color besides other impurities. Activated carbon can be used to remove the coloring matters to prevent fouling in the subsequent purification steps or the product from having an unattractive appearance. (Huang, Xu, Zhang, Xue, & Chen, 2007, p. 8.)

4.2 Primary recovery of lactic acid

After pretreatment of the fermentation broth, the aqueous lactic acid solution still contains impurities such as sugars, salts, proteins, other carboxylic acids, and waste products from the cell decay. In the primary recovery, lactic acid is removed from the bulk aqueous solution and impurities by selectively transferring the product to another phase. Possible methods including adsorption, extraction, precipitation, and several membrane-based processes, such as nanofiltration, reverse osmosis, and electrodialysis, are introduced in the following chapters. (López-Garzón & Straathof, 2014, p. 875.)

4.2.1 Precipitation

Calcium hydroxide precipitation with subsequent esterification and hydrolysis is the conventional method for lactic acid purification on an industrial scale. The fermentation broth is first pretreated with filtration to remove impurities and then concentrated to 20–30 wt% of lactate by evaporation to obtain the mother liquor. (Li et al., 2016, p. 2; Wasewar, 2005, p. 161.) Calcium hydroxide or carbonate is then added to the mother liquor to precipitate lactic acid as calcium lactate (Datta, 2004, p. 6):

$$2\ CH_3CH(OH)COOH + Ca(OH)_2 \rightarrow (CH_3CH(OH)COO^-)_2Ca^{2+} + 2\ H_2O. \quad (5)$$

Calcium lactate is filtered off and treated with sulfuric acid to reconvert the salt into lactic acid (Datta, 2004, p. 6):

$$(CH_3CH(OH)COO^-)_2Ca^{2+} + H_2SO_4 \rightarrow 2\ CH_3CH(OH)COOH + CaSO_4. \quad (6)$$

The acid then proceeds to further purification, such as esterification and hydrolysis (Li et al., 2016, p. 2).

Calcium hydroxide precipitation is a well-established method that is highly selective and gives a high product purity. Conversely, there are drawbacks that have made the method

economically and ecologically unappealing. For each mole of lactic acid, equal amounts of calcium hydroxide/carbonate and sulfuric acid are consumed, and for each ton of lactic acid, up to one ton of low-value and difficultly disposable gypsum is formed. (Li et al., 2016, p. 2.) The salt issue can be somewhat alleviated by carefully selecting the cations and anions to form a co-product salt of higher value, such as ammonium sulfate, as demonstrated with the price comparison data in Table V (López-Garzón & Straathof, 2014, p. 896).

Table V. Market prices of co-product salts and the constituting acids and bases (López-Garzón & Straathof, 2014, p. 895).

Co-product salt	Approximate price, €/kg	Costs of acid + base, €/kg
Na_2SO_4	0.09	0.15
K_2SO_4	0.62	0.45
$CaSO_4 \cdot 2\ H_2O$	0.08	0.07
$MgSO_4$	0.13	0.16
$(NH_4)_2SO_4$	0.13	0.12

4.2.2 Reactive extraction

Because of lactic acid's hydrophilicity, it is poorly extractable by traditional extraction. Reactive extraction, however, is one of the most studied methods for separation of lactic acid from an aqueous solution and has proven to be a promising alternative. In reactive extraction, the aqueous lactic acid reacts with the extractant forming a complex or chemical compound that is solubilized into the organic phase. The extractant should ideally have a low solubility in water, a high distribution coefficient for lactic acid, and a low distribution coefficient for impurities. (López-Garzón & Straathof, 2014, pp. 884–885.) The distribution coefficient (K_D) is defined as the ratio of a solute's concentration in the organic phase to a solute's concentration in the aqueous phase (Joglekar, Rahman, Babu, Kulkarni, & Joshi, 2006, p. 3):

$$K_D = \frac{[\text{solute}]_{org.}}{[\text{solute}]_{aq.}}. \quad (7)$$

Extractants can be divided into amine-based, ionic, and neutral on the basis of the extraction mechanism (López-Garzón & Straathof, 2014, pp. 884–885). Typically, at least one

organic solvent (n-butanol, kerosene, 1-octanol, etc.) that is not miscible in water, or a mixture of an organic solvent with a long-chain tertiary amine (e.g. Alamine 336) is used in the reactive extraction of lactic acid (Ren, 2010, p. 9; López-Garzón & Straathof, 2014, p. 885; Ghaffar et al., 2014, p. 228).

Reactive extraction is conducted in three main steps (Figure 5): 1) extraction, 2) back-extraction, and 3) regeneration. In the first step, lactic acid is extracted from the aqueous, clarified fermentation broth into organic phase. Impurities are left behind in the aqueous phase. Secondly, lactic acid is back-extracted from the loaded organic phase into an aqueous phase by using, for instance, temperature or pressure swing or acid replacement. Finally, the two phases are separated, and the organic solvent is regenerated before recycling. (López-Garzón & Straathof, 2014, p. 886.) The aqueous lactic acid in its acid or lactate form can be further purified by other means such as ion-exchange (Ren, 2010, p. 9).

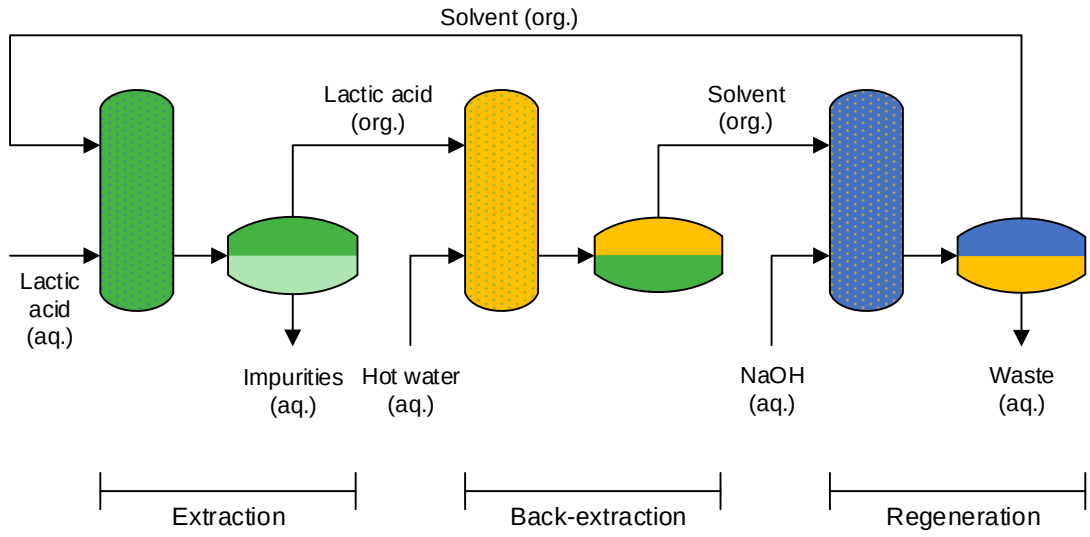

Figure 5. Reactive extraction of lactic acid (adapted from López-Garzón & Straathof, 2014, p. 886).

Extraction is affected by several factors including pH, temperature, mixing time, initial concentration of lactic acid, and volume ratio between aqueous and organic phases. The pH of the lactic acid solution influences considerably the extraction process: with a decrease in pH, the degree of extraction and distribution coefficient increase improving the separation. Initial lactic acid concentration and temperature are also important factors. The distribution coefficient has been reported to decrease with an increase in lactic acid concentration or an increase in temperature. (Ghaffar et al., 2014, p. 228; Joglekar et al., 2006, pp. 4–5.)

Therefore, reactive extraction is used only under low lactic acid concentrations to remove lactic acid from the impurities.

Reactive extraction gives high product purity and high yield with simple operation. It can also be used for solutions with low solute concentrations. (Hong et al., 2001, pp. 386–387.) However, the obtained lactic acid product is of dilute concentration, as well, and a large quantity of water has to be subsequently removed from the solution with additional energy costs. Furthermore, the operation requires use of costly solvents, and the handling and separation of liquid phases require large equipment and demanding operations with solvent losses. (López-Garzón & Straathof, 2014, p. 879.)

4.2.3 Esterification-hydrolysis and reactive distillation

Esterification with subsequent hydrolysis is a method to obtain highly pure lactic acid. Its usage requires prior concentration of the clarified fermentation broth to a lactic acid concentration of 20–30 wt% (Komesu, Martins Martinez, Hoss Lunelli, Maciel Filho, & Wolf Maciel, 2015, p. 26; Sun, Wang, Zhao, Ma, & Sakata, 2006, p. 46). In this method, crude lactic acid is esterified with methanol under heating to produce methyl lactate as

$$CH_3CH(OH)COOH + CH_3OH \rightarrow CH_3CH(OH)COOCH_3 + H_2O. \quad (8)$$

Methyl lactate is recovered and purified by distillation. It is then hydrolyzed with water under acid catalysts, yielding methanol and highly pure lactic acid:

$$CH_3CH(OH)COOCH_3 + H_2O \xrightarrow{\text{catalyst}} CH_3CH(OH)COOH + CH_3OH. \quad (9)$$

Finally, methanol is recovered by distillation and recycled back to the esterification step. The block diagram of the esterification-hydrolysis method is presented in Figure 6. Lactic acid can be separated from the aqueous solution, for instance, by evaporation crystallization. (Datta, 2004, pp. 5–6; Vijayakumar et al., 2008, p. 257.) When the above-described esterification, distillation, and hydrolysis steps take place in a single unit, the process is called reactive distillation (Litchfield, 2009, p. 371).

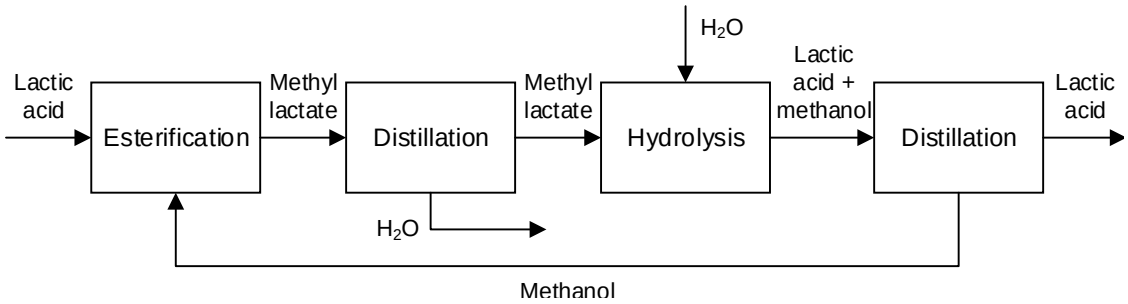

Figure 6. Esterification-hydrolysis process for recovery of lactic acid (adapted from Datta, 2004, pp. 5–6).

Esterification-hydrolysis and reactive distillation are well-established and reliable processes which advantages include high product purity and easy scale-up of the process. They are also the only separation methods that can successfully separate lactic acid from other organic acids. (Joglekar et al., 2006, p. 12.) High-boiling esters and dimers of lactic acid can, however, be formed during the process (Wasewar, 2005, p. 169). The utility and energy costs of both processes are also high, but the equipment and energy costs can be decreased when operating as reactive distillation (Litchfield, 2009, p. 371; Eggeman & Verser, 2005, p. 608). Moreover, the obtained lactic acid product is of dilute concentration, and a large quantity of water has to be subsequently removed from the solution with additional energy costs (Litchfield, 2009, p. 371).

4.2.4 Nanofiltration and reverse osmosis

Nanofiltration (NF) is a pressure-driven membrane process that is used for purification of lactic acid. It can remove impurities, such as cells, proteins, nutrients, salts, color, and unconverted carbon sources, from the fermentation broth. (Pal et al., 2009, p. 1551.) The average pore size of an NF membrane is 1 nm, allowing permeation of water and somewhat larger molecules including lactic acid. (Pal et al., 2009, p. 1551.) Rejection of lactic acid depends on the cut-off value of the membrane and the filtration conditions (Dey, Linnanen, & Pal, 2012, p. 54). Most of the commercial NF membranes are fabricated of negatively charged polyamide for which reason charge repulsion is an important separation mechanism besides size sieving and diffusion. Dissociation of lactic acid, therefore, affects considerably its separation: NF membranes can reject more efficiently negatively charged lactate than neutral lactic acid. NF is typically operated under a pressure range of 5–15 bar. (Sikder, Chakraborty, Pal, Drioli, & Bhattacharjee, 2012, pp. 130, 136.)

Reverse osmosis (RO) is another pressure-driven membrane process that can be used for concentration of lactic acid e.g. after NF purification. The separation mechanism in RO is based on diffusion rather than on size sieving, so the membranes reject also lactic acid. (Cho et al., 2012, p. 10208.) In RO, hydraulic pressure is used to overcome the osmotic pressure of the feed solution in order to force water molecules to permeate to the other side of the membrane. The used hydraulic pressures in RO are usually higher than those in NF, depending on the osmotic pressure of the feed solution. (Pal et al., 2009, p. 1551.) RO membranes have a tighter porous structure than NF membranes and they can also be fabricated of negatively charged polyamide (Cho et al., 2012, p. 10208). Therefore, the RO membranes' rejection towards lactic acid is also affected by the filtration conditions, such as pH of the feed solution (The Dow Chemical Company, 2016).

The advantages of NF and RO include simple operation and easy scale-up of the processes. However, the yield, purity, and low concentration of the recovered lactic acid are major concerns of both techniques. (López-Garzón & Straathof, 2014, p. 890.) The membranes are also subject to fouling, for which reason UF or MF, for example, should be used as a pretreatment step (Pal et al., 2009, p. 1551). Accordingly, neither NF nor RO seems like a feasible option for primary recovery of lactic acid.

4.2.5 Electrodialysis

Electrodialysis is a process in which ions are transported through ion-exchange membranes from one solution to another under the driving force of an electric potential (Wasewar, 2005, p. 162). It is one of the most promising methods for demineralization and concentration of lactic acid. The treatment is most feasible and economically competent when conducted in two steps: 1) conventional electrodialysis (CED) for separation and concentration of lactate salts, and 2) bipolar electrodialysis (BED) for conversion of lactate salts into lactic acid. (Datta & Henry, 2006, p. 1125.) That way, the lactate salt is converted into lactic acid and a corresponding base without addition of any extra chemicals (Jiang et al., 2016, p. 145).

The schematic diagrams of CED and BED processes are presented in Figures 7 and 8. In the CED step, the feed solution containing lactate salt is fed between cation and anion exchange membranes. Due to the electric potential in the electrodialysis cell, the monovalent anions and cations (lactate salt) diffuse to opposite directions passing cation and anion exchange membranes, respectively, while multivalent ions and neutral components are rejected. This leads to removal of impurities and concentration of lactate salt by twofold from

an initial concentration of 8–10 wt% to 20 wt%. (Joglekar et al., 2006, p. 11.) CED has a very high recovery yield (>95 %) for lactate salt, and it can remove multivalent cations by 98–99 %. The following BED step is extremely sensitive to multivalent cations, such as Mg^{2+} and Ca^{2+}, that form precipitates on the surface of the bipolar membrane. The intolerance limit is only 1 ppm, while fermentation broths contain often concentrations of up to 1000 ppm. Therefore, the removal of multivalent cations by CED or chelating resins is of utmost importance. CED lowers the concentration of multivalent ions to the range of 5–10 ppm and reduces the need for chelation by >95 %. (Datta & Henry, 2006, p. 1125.) NF has also been used as a pretreatment step prior to electrodialysis because it can retain Mg^{2+} and Ca^{2+} ions (Pal et al., 2009, p. 1551).

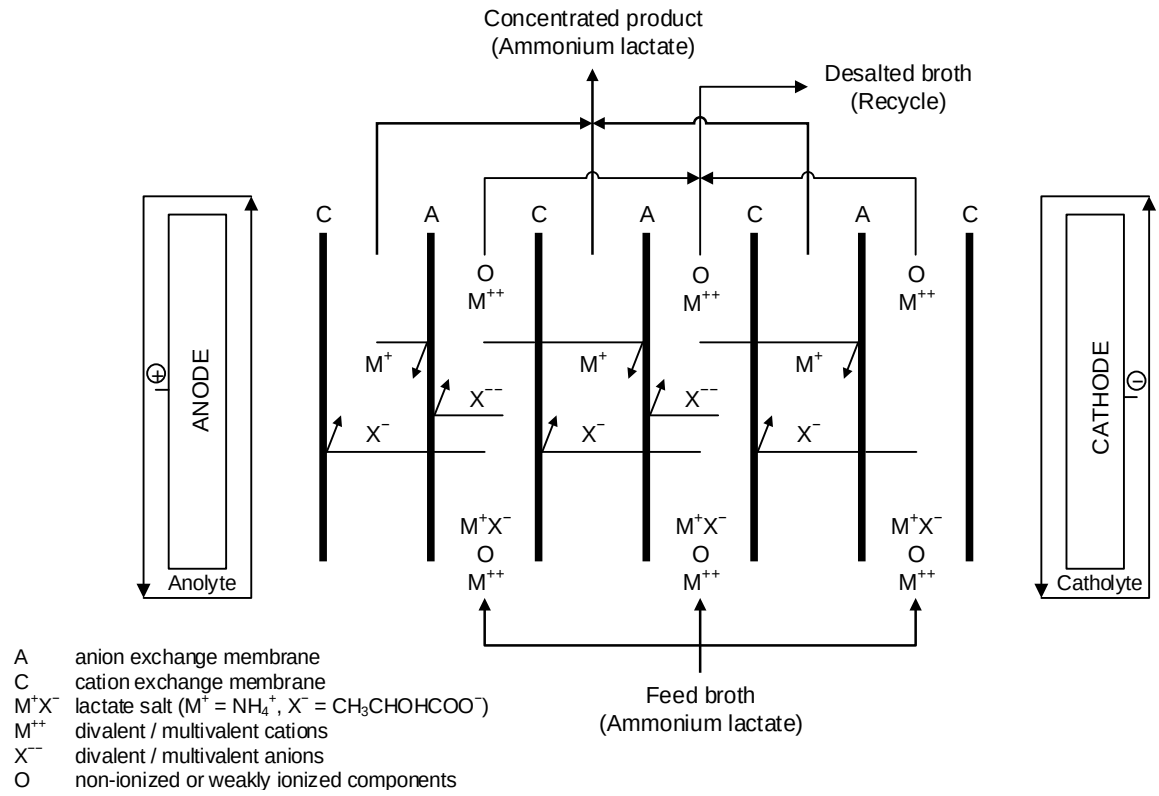

Figure 7. Principle of desalting CED configuration (adapted from Datta & Henry, 2006, p. 1126).

BED is a special type of electrodialysis applied for conversion of salts to corresponding acids. The process uses bipolar membranes which compose of cation and anion exchange membranes laminated together. They can split water molecules to hydrogen (H^+) and hydroxide (OH^-) ions. (Joglekar et al., 2006, p. 11.) In the BED step, the bipolar membranes

are arranged alternately with either anion or cation exchange membranes in a two-compartment configuration. The concentrated lactate salt is fed in the feed compartment, and the salt splits into ions because of the electric potential. The negative lactate ions permeate through the anion exchange membrane to the acid compartment, while the cations are retained in the feed compartment. These ions combine with the hydrogen and hydroxide ions split by the bipolar membranes, forming lactic acid and a corresponding base. (Jiang et al., 2016, p. 145.) The acidification degree of lactate salt in BED is as high as 99 % (Datta & Henry, 2006, p. 1125). Finally, lactic acid is purified by ion exchange, and the alkali stream is stripped and recycled, for instance, to the fermentation to be used as a pH regulator in the process (Joglekar et al., 2006, p. 11; López-Garzón & Straathof, 2014, p. 892).

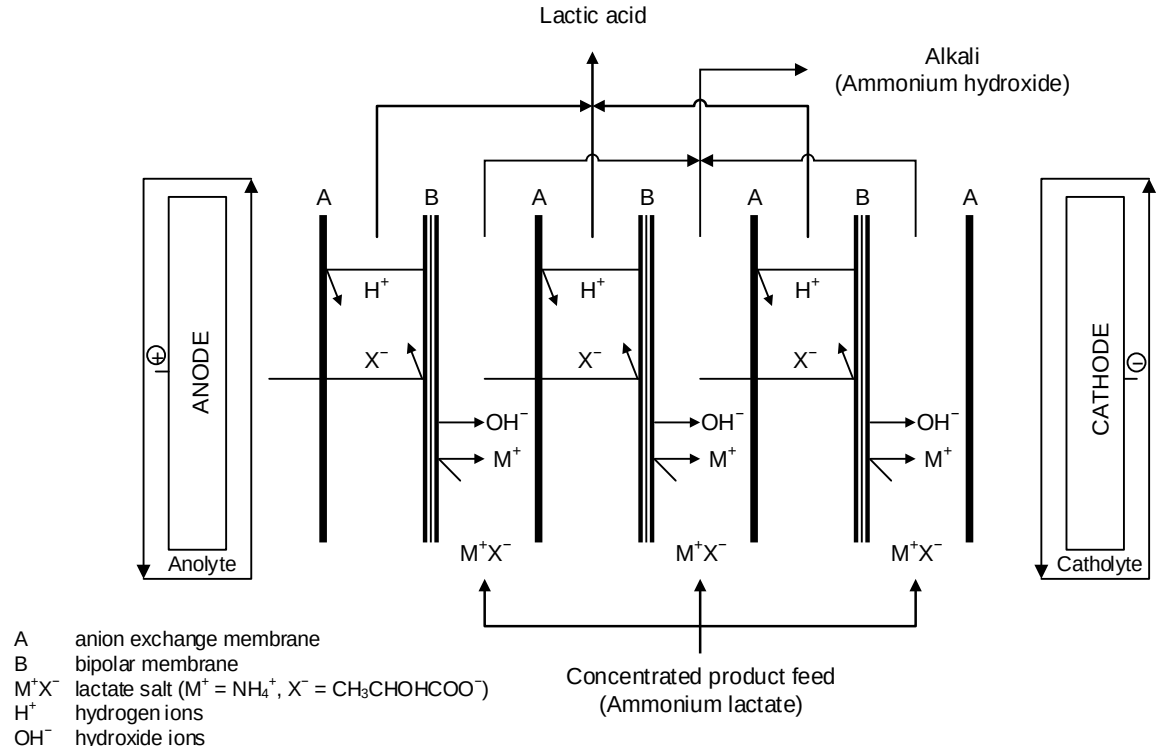

Figure 8. Principle of water-splitting BED configuration (adapted from Datta & Henry, 2006, p. 1126).

When combined with NF, CED-BED process can replace multiple downstream processing steps with only two steps, enabling simultaneous purification and concentration of lactic acid (Castillo Martinez et al., 2013, p. 73). Furthermore, the increase in the lactic acid concentration achieved by CED-BED cuts down the following concentration costs: for example, the requisite energy for evaporation is reduced by half. The removal of impurities also reduces subsequent purification costs. (Datta & Henry, 2006, p. 1125.)

The drawbacks of the CED-BED process include the propensity of the membranes for fouling, for which reason frequent cleaning is necessary (Wasewar, 2005, p. 169). Also, electrodialysis cannot separate charged components such as amino acids and other organic acids (Castillo Martinez et al., 2013, pp. 72–73). Even though the CED-BED process has been shown to be economically competent for recovery of lactic acid, the very high cost of commercial scale dialysis units and membranes and the high energy consumption still need to be optimized (López-Garzón & Straathof, 2014, pp. 892–893; Wasewar, 2005, p. 169).

4.3 Final stages of lactic acid recovery

The final stage in the downstream processing of lactic acid is its refining from a solution to obtain pure lactic acid. The most common methods include crystallization and sorption methods which are introduced in the following chapters.

4.3.1 Crystallization

Crystallization is used as a refining step to purify lactic acid. It has proven to be a successful method especially when refining lactic acid as calcium lactate from an aqueous solution. There are several techniques that can be applied for crystallization, including cooling crystallization, evaporation crystallization, and adiabatic crystallization. (Ren, 2010, pp. 10–11.)

The driving force in cooling and evaporation crystallization techniques is the supersaturation of the concentrated lactic acid solution, which is generated by lowering or increasing the temperature of the solution. The temperature should preferably be kept as low as possible to avoid formation of lactic acid oligomers and polymers. (Ren, 2010, p. 10.) Also, crystallization should be stopped when the solution becomes supersaturated with one or more of the impurities. The yield of the crystallization is determined on the basis of calcium lactate crystallized at that point. (López-Garzón & Straathof, 2014, p. 895.) The crystallized lactate can be separated from the mother liquor by any solid-liquid separation method, such as centrifugation, filtration, or a washing column (van Krieken, 2006, p. 5). To obtain a purer grade of lactic acid, the crystals can be dissolved in water and similarly recrystallized to remove impurities. Finally, the calcium lactate crystals can be dissolved in water and pH-adjusted with H_2SO_4 to release lactic acid and form gypsum. (Wasewar, 2005, p. 161.)

In adiabatic crystallization, the driving force is the supersaturation of the concentrated lactic acid solution, which is generated by heat neither being removed nor supplied. This is

achieved by a pressure drop that causes water to evaporate. As a result, temperature of the concentrated lactic acid solution drops and the concentration of lactic acid increases. Both effects lead to a decrease in the solubility of lactic acid and subsequent supersaturation. (van Krieken, 2006, p. 5.)

The main advantages of crystallization as a refining step are its selectivity and the high purity of the obtained product. Only some impurities may be incorporated in the crystal structure if they fit well therein. The impurities attached on the crystal surfaces can be washed off, but that will cause some product to be lost by dilution. (López-Garzón & Straathof, 2014, p. 895.)

4.3.2 Sorption methods

The advantage of sorption in the final purification of lactic acid lies in the fact that the surface chemistry of the resin can be designed to selectively recover the target molecules (López-Garzón & Straathof, 2014, p. 879). The resin should also possess high capacity, quick recovery, low regeneration consumption and stability, and be insoluble in acid, alkali, or organic solvents. Such materials include e.g. polymers with substituted acidic or basic groups. The resins used in the recovery of lactic acid can be classified into two categories: ion exchange resins and macroporous adsorption resins. (Li et al., 2016, pp. 2–3.) The adsorption resins adsorb lactic acid while the ion exchange resins adsorb the lactate ion (López-Garzón & Straathof, 2014, p. 879).

Adsorption is conducted in three main steps (Figure 9): 1) adsorption, 2) desorption, and 3) washing/regeneration. In the first step, lactic acid or lactate is adsorbed from the aqueous, clarified fermentation broth onto the resin while impurities flow through the column. Secondly, lactic acid or lactate is desorbed from the resin using a solution with counter ions or embedded solvent. Finally, the resin is regenerated and washed before using it in a new cycle. (López-Garzón & Straathof, 2014, pp. 880, 886.)

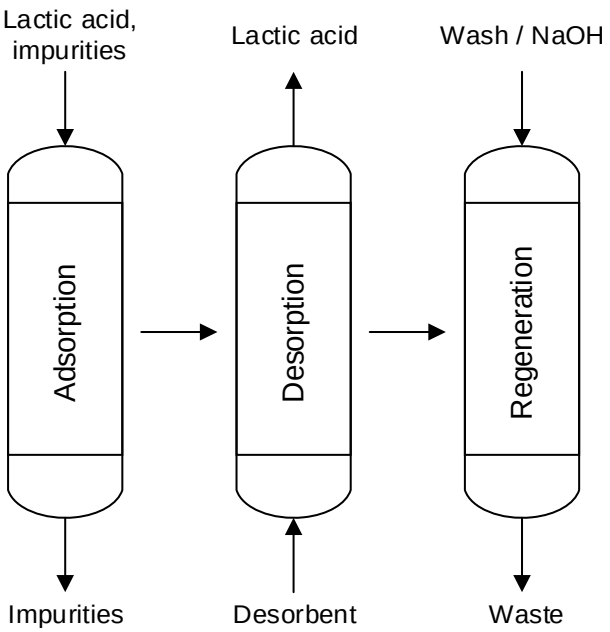

Figure 9. Purification of lactic acid by anion exchange (adapted from López-Garzón & Straathof, 2014, p. 882).

The advantages of sorption methods include their high selectivity, high yield, simple operation, and low cost (Ghaffar et al., 2014, p. 227). Compared with extraction, the solid adsorbents are easier to handle than liquid-liquid systems, and the auxiliary phase is easier to remove with less solvent losses (López-Garzón & Straathof, 2014, p. 879). On the contrary, adsorption or ion exchange resins require regeneration and feed pH adjustment to improve sorption efficiency, which requires large amounts of chemicals and produces also large amounts of waste liquor (Wasewar, 2005, p. 169). The resins are also prone to fouling and their exchange capacity weakens over time (Li et al., 2016, p. 3). The discontinuously operated process requires careful scheduling in each stage. To overcome some of the aforementioned problems, semi-continuous simulated moving beds have been applied also on an industrial scale to increase the production rate and decrease the solvent and energy requirements. (Li et al., 2016, p. 3; López-Garzón & Straathof, 2014, p. 880.)

4.4 In situ product removal

As lactic acid is formed in the fermentation, the pH of the fermentation broth starts to fall affecting the productivity of the microorganisms. To overcome this problem of inhibition, lactic acid can be removed in situ from the fermentation vessel. The in situ product removal can improve the productivity of the microorganisms and the product yield, and potentially

decrease the number of downstream processing steps and waste streams. Several methods can be used for recovery of lactic acid during fermentation including adsorption, ion exchange, reactive extraction, and membrane separation. (Boonmee, Cotano, & Amnuaypanich, 2016, pp. 2067–2068.)

Reactive extraction of lactic acid includes a water-immiscible phase in the fermentation vessel for continuous removal of lactic acid. Even though the technique can increase the productivity of microbial cells by two- to threefold, it is not preferred since the extractants can cause physical, chemical, and biochemical damage to the microorganisms. (Ataei & Vasheghani-Farahani, 2008, p. 1229.) New low-toxicity replacements to traditional organic solvents are being developed to improve the process (Litchfield, 2009, p. 371).

Membrane separation techniques such as MF, UF, NF, and electrodialysis are often coupled with fermentation. MF and UF membranes have pore sizes ranging from 0.01 to 0.2 µm, and they are used to selectively remove large molecules, such as proteins and microorganisms, from the fermentation broth for their subsequent recycling back to the fermenter. Lactic acid permeates through the MF or UF membrane and is further purified in the second stage by NF with an average pore size of 1 nm. The scheme of the process is illustrated in Figure 10. (Pal et al., 2009, pp. 1552, 1556.)

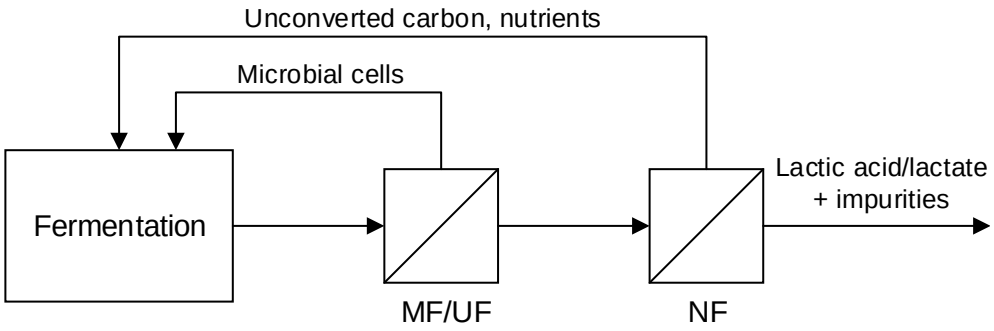

Figure 10. In-situ removal of lactic acid from fermenter by combination of MF/UF and NF (adapted from Jiang et al., 2016, p. 138).

MF or UF and activated carbon treatment coupled with CED have been used to recover a lactate product stream of a good quality with basically no waste stream and to increase the fermentation rate by up to 60 %. However, the high cost of the process due to power consumption and equipment costs remain a serious drawback. (Wasewar, 2005, p. 162.) The

membranes are also subject to fouling and concentration polarization which result in decreased performance. (Boonmee et al., 2016, p. 2068.)

Adsorption of the lactate ions on an anion exchange resin has been reported to increase product concentration and improve productivity of the microorganisms. The process has also been operated on an industrial scale. (Boonmee et al., 2016, p. 2068.) The main disadvantage of the method is that the fermentation broth contains also other anions, such as SO_4^{2-} and Cl^-, which compete with the lactate ions on the anion exchange resin. Some of these ions are necessary for the fermentation and have to be replenished to the process. Furthermore, additional chemicals (acids, bases, salt solutions) are needed for elution of lactic acid and for regeneration of the resin. (Aljundi, Belovich, & Talu, 2005, p. 5005; Boonmee et al., 2016, p. 2068.)

5 FORWARD OSMOSIS AS A PART OF LACTIC ACID PRODUCTION

Forward osmosis (FO) is an emerging membrane process that utilizes the phenomenon of osmosis to drive water across a semipermeable membrane. Because of the very low required hydraulic pressure, FO possesses many advantages such as lower energy input and lesser fouling. During the last decade, FO has attracted attention especially in the fields of power generation, seawater desalination, wastewater treatment, and food processing. (Cath, Childress, & Elimelech, 2006, p. 2; Zhao, Zou, Tang, & Mulcahy, 2012, p. 2.) New applications of FO in dewatering are being researched – one of them being concentration of carboxylic acids from aqueous solutions.

In this chapter, the principles and concept of FO are introduced in detail and the process is compared to the existing technologies used for concentration of lactic acid. The literature considering FO for concentration of carboxylic acids is also reviewed.

5.1 Forward osmosis

In this chapter, the principle and terminology of FO are first explained in detail. The most important problem associated with FO – concentration polarization – is then reviewed with its theoretical background, and different ways to prevent it are studied. The phenomena of fouling and reverse solute flux are also introduced. Finally, the specific kinds of membranes used in FO and different module configurations are presented.

5.1.1 Principle of forward osmosis

FO is a process that uses the concept of osmosis to separate water from dissolved solutes. Osmosis is defined as the natural movement of solvent molecules across a semipermeable membrane from higher solute concentration into lower solute concentration – striving to equalize the solute concentration on both sides of the membrane, as depicted in Figure 11. (Cath et al., 2006, p. 71.) In FO, a highly concentrated solution (draw solution) is used to draw water molecules from the more dilute feed solution. The semipermeable membrane allows the permeation of only water molecules while rejecting the solute molecules, thus resulting in concentration of the feed solution and dilution of the draw solution. (Qasim, Darwish, Sarp, & Hilal, 2015, p. 48.)

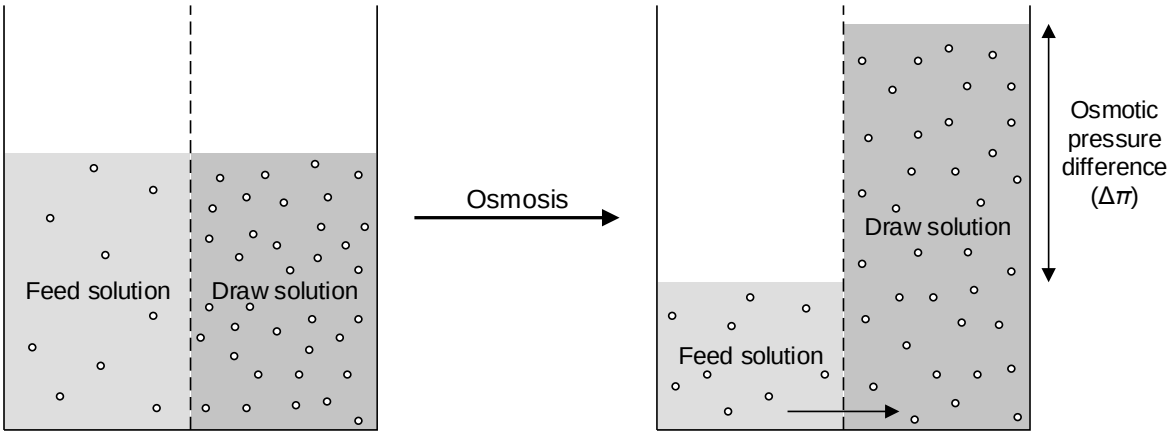

Figure 11. Principle of FO: water permeates to the more concentrated side of the membrane, equalizing the concentration difference. The osmotic pressure difference across the membrane, $\Delta\pi$, is the driving force of the process. The white dots represent the solutes. (Adapted from Qasim et al., 2015, p. 49.)

5.1.2 Osmotic pressure

Osmotic pressure describes the tendency of a solution to draw in water by osmosis. The osmotic pressure difference between the dilute feed solution with low osmotic pressure and concentrated feed solution with high osmotic pressure is the driving force of the FO process. (Cath et al., 2006, pp. 71–72.) Accordingly, water transport in osmotically driven processes is generally determined as

$$J_w = A(\sigma\Delta\pi - \Delta P), \tag{10}$$

where J_w is the water flux, A is the water permeability coefficient, σ is the reflection coefficient, $\Delta\pi$ is the osmotic pressure difference across the membrane, and ΔP is the hydraulic pressure difference across the membrane. Because no hydraulic pressure is applied in FO, $\Delta P = 0$. (Cath et al., 2006, p. 72.) The reflection coefficient σ describes a membrane's selective permeability towards a specific solute. It ranges from 0 to 1 being 0 when the membrane is freely permeable to the solute and 1 when the membrane is impermeable to the solute. (Darwish, Abdulrahim, Hassan, Mabrouk, & Sharif, 2016, p. 4273.) The water permeability coefficient, the so-called A-value, is mainly governed by a membrane's intrinsic properties, such as porosity and tortuosity. A high A-value is desirable as it indicates high water flux across the membrane. It is determined in RO mode by measuring the water flux under various hydraulic pressures (Phillip, Yong, & Elimelech, 2010, p. 5172):

$$A = \frac{J_W}{\Delta P}. \quad (11)$$

The osmotic pressure is strongly related to the solute concentration. For any dilute solution, the osmotic pressure (π) can be estimated from the extended van't Hoff equation

$$\pi = iMRT, \quad (12)$$

where i is the van't Hoff factor, M is the molar concentration of the solution, R is the gas constant, and T is the temperature. The osmotic pressure of a concentrated solution is estimated similarly from equation

$$\pi = \varphi MRT, \quad (13)$$

where φ is the osmotic pressure coefficient. (Ge, Ling, & Chung, 2013, p. 227.)

5.1.3 Draw solution

Draw solution is the highly concentrated solution on the permeate side of the membrane (Cath et al., 2006, p. 72). It is the source of the driving force of the FO process, and affects considerably the efficiency of the process (Akther et al., 2015, p. 511). The main criterion in the selection of the draw solute is its capability of generating a high osmotic pressure: the osmotic pressure of the draw solution must be higher than that of the feed solution to ensure a positive permeate flux (Ge et al., 2013, p. 227).

Draw solutions can be classified into three categories: organic-based, inorganic-based, and other compounds. These categories can be sub-classified into ionic and non-ionic compounds. (Akther et al., 2015, p. 511.) The main compounds used as draw solutes are inorganic salts, nutrient compounds (sugars), and volatile gases (Darwish et al., 2016, p. 4278). Magnetic nanoparticles are an example of a novel draw solute technology that has been a topic of several studies recently (Akther et al., 2015, p. 514). Osmotic pressures of various draw solutions are presented in Figure 12.

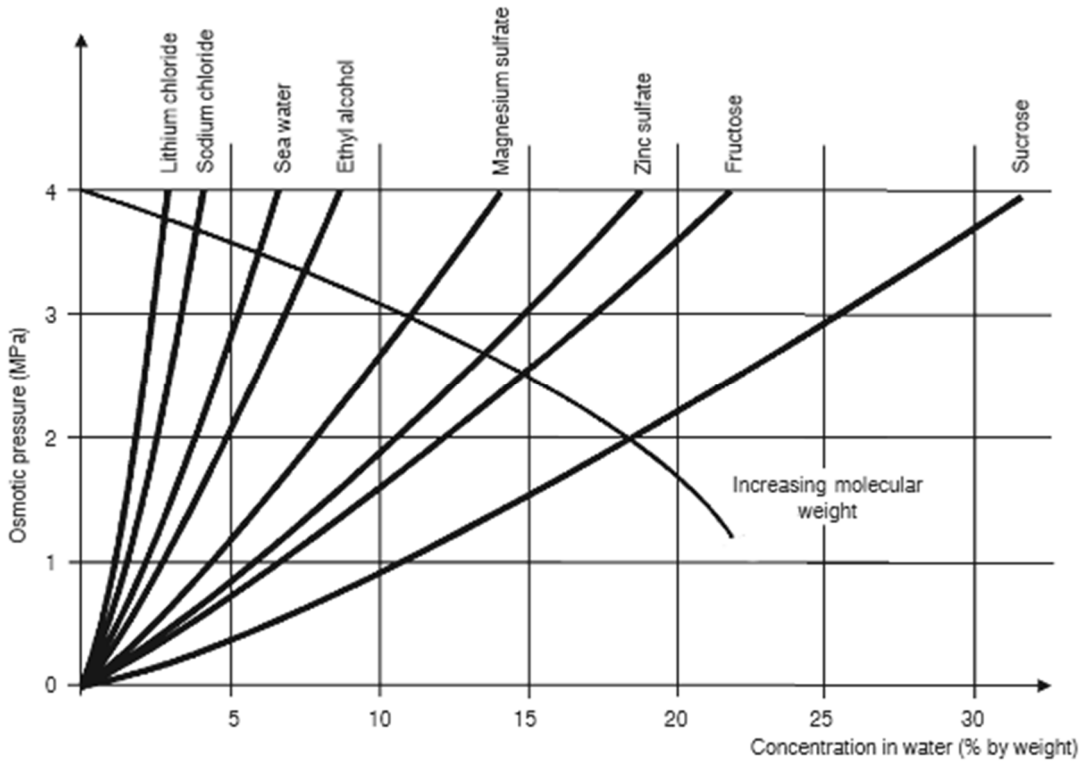

Figure 12. Osmotic pressures of various draw solutions (The Dow Chemical Company, 2015).

The draw solute should be highly soluble in water, non-toxic, inexpensive, easily recoverable, and chemically inert towards the membrane. Additionally, it should cause only low internal concentration polarization and reverse solute flux, generate high water flux across the membrane, and be unaffected by changes in pH. (Akther et al., 2015, p. 511; Qasim et al., 2015, p. 61.)

The need for regeneration of draw solutes from the diluted draw solution after FO process is the main factor limiting wider use of FO. Regeneration removes water from the diluted draw solution by magnetic, thermal, or mechanical means. The regeneration step is often so energy-intensive that it makes the FO process unattractive compared to pressure-driven membrane processes such as NF or RO. Easy recovery and regeneration of the draw solutes is, therefore, crucial. In an ideal case, the diluted draw solution can be utilized within the process without regeneration making FO preeminent in terms of energy consumption. (Ge et al., 2013, pp. 227–228.)

5.1.4 Concentration polarization

The phenomenon of concentration polarization is one of the most challenging problems within all membrane processes, whether they are driven by osmotic or external pressure. Concentration polarization denotes the concentration gradients taking place at the membrane-solution interface because of selective transfer of species through the semi-permeable membrane. (Akther et al., 2015, p. 507.) Due to these gradients, the osmotic pressure difference between feed and draw solutions is much smaller at the membrane active layer than in the bulk (Cath et al., 2006, p. 73). Therefore, the actual water flux across the membrane falls, being significantly lower than the theoretical values (Qasim et al., 2015, p. 51).

The membranes used in osmotically driven membrane processes are typically asymmetric: they consist of a porous support layer and a dense active layer. The concentration polarization phenomenon occurring within the support layer is referred to as internal concentration polarization (ICP) and on the surface of the membrane active layer as external concentration polarization (ECP). It has been shown that the effect of ECP on decreased water flux is negligible compared to that of ICP. (Cath et al., 2006, p. 73.)

In FO applications, the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution. In this orientation, concentrative ECP occurs as the retained solutes of the feed build up on the active layer. Because FO operates under no or low hydraulic pressure, the solutes do not tend to build up on the active layer, and ECP is very low. It can still be further reduced by increasing the flow velocity and turbulence at the membrane surface or by optimizing the water permeation rate. (Qasim et al., 2015, p. 51.)

Dilutive ICP takes place within the porous support layer as the draw solution is diluted by the permeating water (Cath et al., 2006, p. 73). As illustrated in Figure 13, ICP can significantly decrease the effective osmotic pressure difference across the membrane and result in up to 80 % decline in water permeation rate compared to the theoretical values (Akther et al., 2015, p. 508). Unlike ECP, ICP is more difficult to mitigate because it occurs within the support layer, and alteration of hydrodynamic conditions, such as flowrate of the draw solution, does not influence it (Zhao et al., 2012, p. 9).

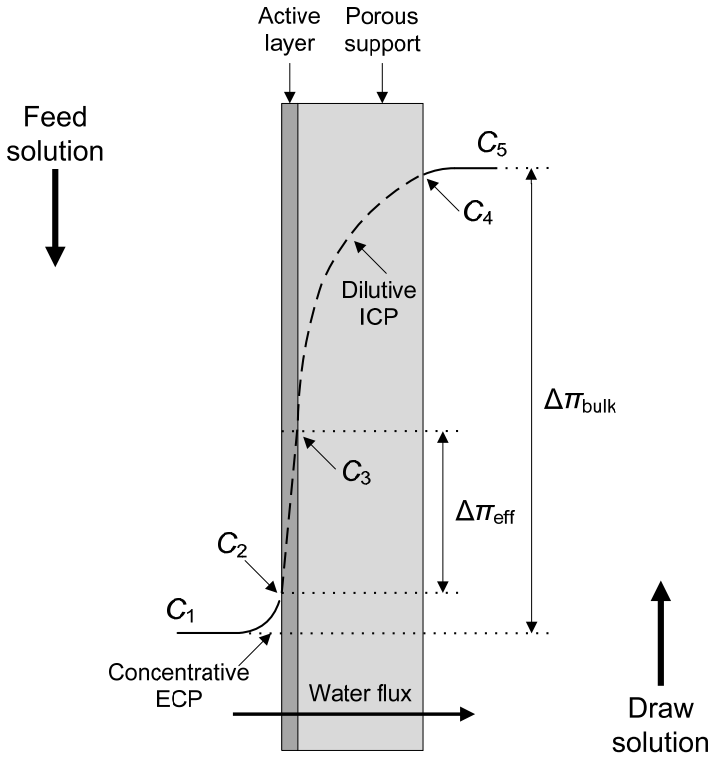

Figure 13. Concentration profile across an asymmetric membrane with the active layer facing the feed solution in FO. C_1 and C_5 are the concentrations of the bulk feed and bulk draw solutions, respectively. C_2 and C_4 are the concentrations of the feed–active layer and draw solution–support layer interfaces, respectively. C_3 is the concentration at the active layer–support layer interface. Due to ICP, the effective osmotic pressure across the membrane ($\Delta\pi_{eff}$) is much lower than the osmotic pressure difference between bulk feed and bulk draw solutions ($\Delta\pi_{bulk}$). (Adapted from Cath et al., 2006, p. 74.)

Loeb, Titelman, Korngold, and Freiman (1997, p. 249) have estimated the water flux behavior (J_W) in the presence of dilutive ICP:

$$J_W = \frac{1}{K}\ln\left(\frac{A\pi_D + B}{A\pi_F + B + J_W}\right), \tag{14}$$

where K is the solute resistivity to diffusion, A and B are the water and solute permeability coefficients, respectively, and π_D and π_F are the osmotic pressures of the draw and feed solutions, respectively. The solute permeability coefficient, the so-called B-value, is a measure of a membrane's active layer. A low B-value is desirable as it indicates low solute flux across the membrane. It is determined by measuring the water flux and salt rejection (R) under various hydraulic pressures in RO mode and calculated as follows:

$$B = J_W\left(\frac{1-R}{R}\right) \tag{15}$$

and

$$R = 1-\frac{C_P}{C_F}\times 100\ \%, \tag{16}$$

where C_P is the salt concentration in the permeate and C_F is the mean salt concentration in the feed. (Cath et al., 2006, p. 75; Phillip et al., 2010, p. 5172.)

The solute resistivity to diffusion K in Eq. (14) is related to the support layer properties and solute diffusivity by equation

$$K = \frac{S}{D}, \tag{17}$$

where S is the structural parameter of the support layer and D is the solute diffusion coefficient (McCutcheon & Elimelech, 2006, p. 240). The so-called S-value describes the structural characteristics of a membrane and is expressed as

$$S = \frac{t_s\tau}{\varepsilon}, \tag{18}$$

where t_s is the thickness, τ is the tortuosity, and ε is the porosity of the membrane support layer (McCutcheon & Elimelech, 2006, p. 240). The S-value is a widely used measure for evaluation of a membrane's propensity to cause ICP (Manickam & McCutcheon, 2015, p. 70).

Equation (14) indicates that a smaller value of K leads to enhancement in water flux and reduced ICP. To attain that, the solute diffusivity D in Eq. (17) should be as high as possible, which can be achieved by increasing the filtration temperature or changing the draw solute (McCutcheon & Elimelech, 2006, p. 246). A small S-value is also preferred as it leads to reduced ICP effects. According to Eq. (18), the support layer should, therefore, be as thin and porous as possible to allow the draw solutes to diffuse more easily inside it. (Akther et al., 2015, pp. 509, 516.)

5.1.5 Fouling

Fouling means the accumulation of material on the surface or in the pores of a membrane weakening the performance of the membrane. It can occur by several mechanisms: pore blockage, deposition of particles on the membrane surface, and adsorption caused by interactions between the membrane and solutes or particles. For some molecules, a high level of concentration polarization may also result in gel formation on the membrane surface. (Field, 2010, pp. 1–2.) Fouling is a problem that concerns all membrane processes, but is less significant in osmotically driven processes, like FO, that operate under no or low hydraulic pressure. Membranes in such processes require less cleaning and maintenance, have a longer lifetime, and can be more productive over time. Additionally, fouling in FO membranes can be easily removed by backwashing, so there is no or less need for chemical cleaning. (Akther et al., 2015, p. 509.)

5.1.6 Reverse solute flux

In the reverse solute flux phenomenon, the solute molecules permeate from the draw solution to the feed solution due to the concentration gradient across the membrane. It is inevitable in FO, and may harm the process by worsening fouling and decreasing efficiency. (Akther et al., 2015, p. 509.) The reverse flux of an individual solute (J_S) can be described by Fick's law

$$J_S = B\Delta C, \tag{19}$$

where B is the solute permeability coefficient and ΔC is the concentration difference across the membrane (Hancock & Cath, 2009, p. 6769).

Phillip et al. (2010, p. 5174) proved that the reverse solute flux is strongly dependent on the selectivity of the membrane active layer and is not influenced by the concentration of the draw solution or the structure of the support layer. Therefore, a membrane with a highly selective active layer could effectively minimize the reverse solute flux. Hancock and Cath (2009, p. 6772) also showed that a draw solution consisting of multivalent ions can significantly reduce the reverse solute flux. However, more severe ICP is likely to occur because of the larger ion sizes and lower diffusion coefficients of multivalent cations.

5.1.7 Membranes

The membranes used in FO are asymmetric: they consist of a porous support layer and a dense active layer. The membrane should ideally possess the following characteristics: high chemical resistance, high mechanical strength, a dense and selective active layer for reduced reverse solute flux, as thin and porous support layer as possible for reduced ICP, and hydrophilicity for higher water flux and lower fouling. (Cath et al., 2006, pp. 75–76.) The development of membranes with such properties has been of growing interest since the 2000s and is yet in progress. The recently developed FO membranes can be categorized by their fabrication method into thin film composite, phase inversion, and chemically modified membranes. (Akther et al., 2015, p. 515.) Despite of the new advances, the selection of commercial FO membranes is still very limited – as compiled in Table VI.

Table VI. Commercially available FO membranes and their manufacturers (Terefe et al., 2016, p. 183).

Company	Membrane type	Configuration
Aquaporin A/S	Aquaporin thin film composite	Flat sheet
Fluid Technology Solutions (formerly Hydration Technology Innovations)	Cellulose triacetate	Spiral wound
	Thin film composite	Spiral wound
Oasys Water	Thin film composite	Spiral wound
Porifera	Thin film composite	Plate and frame
Toray Chemical Korea	Thin film composite	Spiral wound
Toyobo	Thin film composite	Hollow fiber

Phase inversion membranes

Phase inversion membranes are prepared by precipitating a liquid polymer solution into a porous, solid membrane. They are provided in flat sheet and hollow fiber configurations. Phase inversion membranes are typically made of cellulose acetate – a material that is widely available, highly hydrophilic, mechanically robust, resistant to chloride degradation and other oxidants, and has a low fouling propensity. On the other hand, it is prone to biological damage and hydrolysis, which is why the operation temperature should be kept below 35 °C or pH in the range of 4–6. (Akther, et al., 2015, pp. 515–516.) Besides cellulose acetate, polybenzimidazole is another widely used material for phase inversion membranes. Polybenzimidazole shows excellent thermal and chemical stability, mechanical strength,

and self-charged properties, but its high price and fragility remain serious concerns. (Qasim et al., 2015, p. 56.)

Thin film composite membranes

Thin film composite (TFC) membranes are constructed of multiple layers and are provided both in flat sheet and hollow fiber configurations. The conventional technique is to first prepare the porous support layer by phase inversion, after which the dense active layer is fabricated onto the support layer by interfacial polymerization. The active layer consists most often of polyamide and the support layer of polysulfone or polyethersulfone. TFC membranes have gained popularity due to their higher water flux and salt rejection compared to cellulosic membranes. They can also be used in a wider pH range and are more resistant towards hydrolysis and biodegradation. However, the polyamide active layer makes TFC membranes subject to fouling. The support layer should be highly hydrophilic to mitigate ICP, whereas hydrophobic polysulfone is used in most membranes. (Qasim et al., 2015, pp. 57–60.) Hydrobhobicity of the material prevents proper wetting of the support layer. Because mass transport can occur only in the wetted porosity of the support layer, the transport is inhibited, thus resulting in increased ICP. (McCutcheon & Bui, 2014, p. 269.)

Aquaporin biomimetic membranes are a novel modification of TFC membranes. Aquaporins are hour-glass-shaped membrane proteins that are naturally present in all living cells. They form channels that selectively transport water molecules across the membrane while rejecting other ions and solutes. (Tang, Zhao, Wang, Hélix-Nielsen, & Fane, 2013, p. 35.) Aquaporin biomimetic membranes are constructed of three different components: aquaporins, a thin film layer of lipids or polymers in which aquaporins are embedded, and a polymer support structure. The composition can be applied to both flat sheet and hollow fiber membranes. (Habel et al., 2015, p. 308.) The aquaporin biomimetic membranes are still in the development stage, but they have shown promising water permeability and selectivity characteristics (Tang, Wang, Petrinić, Fane, Hélix-Nielsen, 2015, pp. 100–102).

Chemically modified membranes

Chemical modification is used to optimize the membrane performance; to adjust the support or active layer characteristics, for instance. The structural parameters of support layer have been modified by including materials such as titanium dioxide nanoparticles, carbon nanotubes, or zeolites in the membrane. Chemical modification and coating has also been used

to improve hydrophilicity of the support layer. A positively charged active layer has been created by chemical post-treatment of a hollow fiber membrane to reduce salt transport across the membrane. (Akther et al., 2015, p. 516.) A novel layer-by-layer assembly has given a high rejection against divalent ions and high thermal stability and has been applied to produce thin-film inorganic membranes (Qasim et al., 2015, p. 60).

5.1.8 Modules

Unlike other membrane processes, FO has four flow connections (feed in, feed out, draw in, draw out), which has to be considered in the module design. The FO membranes can be assembled in similar configurations as RO and UF membranes; they can be packed in plate and frame, spiral wound, tubular, and hollow fiber modules. (Cath et al., 2006, p. 76.) Of these four configurations, most of the research has been directed towards the spiral wound and hollow fiber modules.

Most of the commercially available FO modules are assembled in a special spiral-wound configuration. The flow pattern in such a module differs from that in an RO spiral-wound module (Figure 14). The draw solution flows through the spacers between the rolled membranes while the feed solution is fed in the central collecting tube, which is blocked halfway through. There is also a glue line at the center of the membrane envelope directing the feed solution to flow inside the entire envelope. The major drawback of the spiral-wound FO modules is the difficulty of cleaning and backwashing. (Cath et al., 2006, p. 77.)

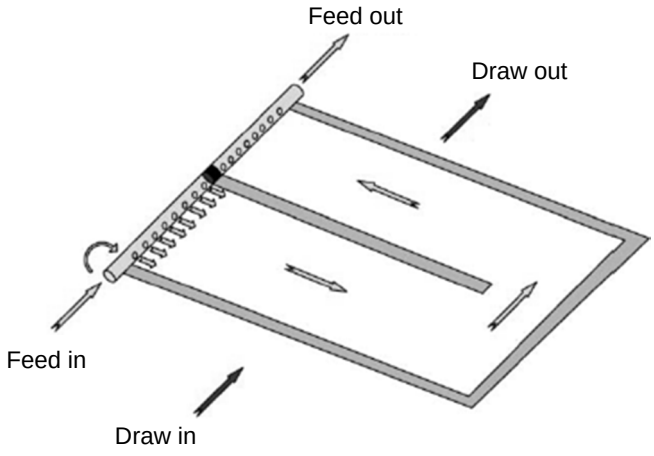

Figure 14. Flow patterns in a spiral-wound module designed for FO (adapted from Cath et al., 2006, p. 77).

Plate and frame modules are assembled in different sizes and scales. However, their packing density is low, which increases the costs. The module also lacks adequate membrane support, and the range of possible operating conditions is limited. (Cath et al., 2006, p. 77.) The structure of a plate and frame module is presented in Figure 15.

Hollow fiber and tubular modules are very similar in their assembly, as illustrated in Figure 15. The surface area in the hollow fiber module is much larger, because the diameter of the hollow fiber membranes is < 1 mm while that of the tubular membranes is > 2 mm. The main difference of the modules is in their flow pattern: it is laminar in the hollow fiber module and turbulent in the tubular module. The turbulent flow can enhance mixing at the membrane surface reducing ECP, fouling, and scaling. In the tubular and hollow fiber FO modules, feed and draw solutions can easily flow on both sides of the membrane. The modules are easy to fabricate and have a high packing density. The membranes are also self-supported, so there is no need for a support layer, which may reduce ICP. (Cath et al., 2006, pp. 77–78.)

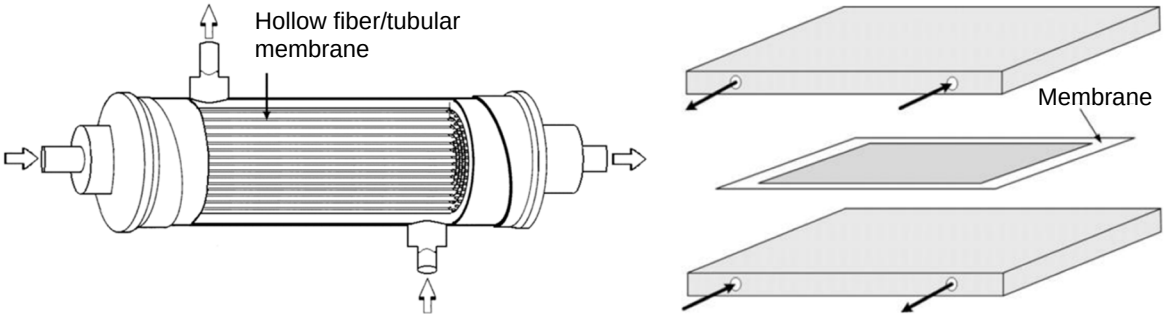

Figure 15. Structures of (a) tubular or hollow fiber module, and (b) plate and frame module (adapted from Camacho et al., 2013, p. 100).

5.2 Comparison of forward osmosis to other separation methods

The advantages of FO include low energy consumption because of operation under no or low hydraulic pressure, simple operation, flexibility in scaling, reduced chemical consumption, high rejection for contaminants, high water recovery, low fouling tendency, and easy fouling removal (Abousnina & Nghiem, 2013, p. 571). Despite all the advantages, the need for energy-intensive regeneration of the diluted draw solution is the major drawback limiting

the use of FO by making the process uncompetitive compared to other membrane processes such as NF and RO. For this reason, the potential of FO lies in the applications where no regeneration of the draw solution is required. It is important to consider possible utilization of the diluted draw solution when designing an application. (Shaffer, Werber, Jaramillo, Lin, & Elimelech, 2015, pp. 276, 282.) Otherwise, a traditional pressure-driven membrane process (NF or RO) would be reasonable to replace with FO only if 1) fouling is high, 2) the osmotic pressure of the feed solution is high, or 3) the osmotic pressure of the feed solution is low.

FO has potential to be applied as a concentration step in the recovery of lactic acid to enhance energy-effectiveness of the processing scheme. Table VII summarizes advantages and disadvantages of technologies used in the recovery of lactic acid.

Table VII. Summary of separation technologies used in the recovery of lactic acid.

	Advantages	Disadvantages
Precipitation	High selectivity High product purity	Feed concentration of 20–30 % Consumption of $Ca(OH)_2$ or $CaCO_3$ and H_2SO_4 Formation of gypsum as by-product
Reactive extraction	High product purity High product yield Simple operation Dilute feed solution	Extractant cost pH dependency Chemical consumption Dilute product Difficult handling of the liquid phases Complexity of the process
Esterification-hydrolysis / reactive distillation	High product purity Easy scale-up Separation of lactic acid from other organic acids	Feed concentration of 20–30 % Phase transition High utility and energy costs Chemical consumption Dilute product Formation of esters and dimers
NF / RO	High water flux Simple operation Easy scale-up No chemicals Dilute feed solution	Fouling Lactic acid rejection Dilute product Product purity Product yield
CED-BED	Simultaneous concentration and purification Dilute feed solution	Fouling Charged components such as amino acids and other organic acids can not be separated High energy consumption High installation cost
FO	Simple operation No chemicals Easy scale-up No hydraulic pressure Dilute feed solution Low energy consumption	Low water flux Regeneration of the draw solution Lactic acid rejection

5.3 Forward osmosis for separation of carboxylic acids

Even though other membrane processes, such as NF, RO, and CED-BED, have been recognized and successfully applied for concentration of lactic acid or other carboxylic acids, only few studies considering FO as an alternative have been reported. The research considering FO for concentration of carboxylic acids will be reviewed below.

Chang et al. (2012) have patented the method of using FO for concentration of dilute fermentation broths. In the method, a fermentation broth containing e.g. microorganisms, proteins, plant cells, and primary metabolites (ethanol, butanol, acetic acid, citric acid, lactic acid, etc.) is used as the feed solution. The draw solution is a waste solution with high osmotic pressure or a solution consisting of sodium chloride, magnesium chloride, or ammonium carbamate. The FO filtration is carried out as a batch process, a continuous process, or a pressure assisted process by applying pressure to the feed chamber or a vacuum to the draw chamber. The process may also be carried out in multiple stages. After the FO filtration, the diluted draw solution can be transferred to a solute regeneration system. Chang et al. also provided an example of using FO to concentrate succinic acid. In their experiment, they used an actual fermentation broth containing 67 g/L succinic acid as feed solution, and adjusted the pH of the solution to 8–9. They used 30 wt% NaCl as draw solution. The membrane was a CTA FO membrane. They succeeded to concentrate succinic acid by more than twofold to a concentration of 153 g/L in the filtration that lasted 88 hours.

Cho, Lee, and Park (2012) successfully utilized FO to concentrate butyric acid with magnesium chloride as draw solution. They first compared the performances of RO and FO membranes in FO mode using deionized water as feed and 1, 3, and 5 M $MgCl_2$ as draw solution. They found out that an FO membrane made of CTA with embedded polyester support and larger pore size minimized ICP resulting in the highest water flux in the range of 11–19 L/(m^2 h). That particular membrane also possessed the lowest reverse salt flux of ~0.3 g/(m^2 h). They then compared the performances of the RO and FO membranes in concentration of 2 000 ppm butyric acid with 5 M $MgCl_2$ as draw solution. Again, the highest water flux of approximately 17 L/(m^2 h) was obtained with the FO membrane, while that with the RO membrane was less than 4 L/(m^2 h). They also determined periodically the concentration factor of butyric acid during both filtrations and noticed that the forward flux of butyric acid with the FO membrane became higher and higher as the butyric acid concentration in the feed rose during filtration. The actual concentration factor in the end of the filtration was 1.65, while the ideal concentration factor based on the water recovery rate would have been 1.95.

Abousnina and Nghiem (2013) studied water removal from a solution containing 300 mg/L acetate with 0.5 M NaCl as draw solution. They compared the performance of two different NF and two different FO membranes in FO mode under varying values of feed solution pH.

No permeate flux was obtained with the NF membranes, but the two FO membranes produced water fluxes of 3.5 and 6.5 L/(m^2 h) and reverse salt fluxes of 1.4 and 4.7 g/(m^2 h), respectively. They noticed that the water flux and reverse salt flux are independent of the pH of the feed solution. However, they discovered that pH is the key parameter to govern the rejection and solute flux of acetate, as the rejection of acetate gradually decreased with decreasing pH. For example, by decreasing the pH of the acetate solution from 7 to 4, the rejection dropped from 100 % to 60 %. That is because of the combination of the solution pH, membrane surface charge, and dissociation of acetate. Increased feed solution pH can increase the negative surface charges of the membrane. Furthermore, acetate is present either as neutral acetic acid or as negatively charged, dissociated acetate depending on the pH of the solution (pK_a = 4.7). Under a low pH, neutral acetic acid can more easily permeate across the less negatively charged membrane. That suggests that, instead of size exclusion, charge repulsion is the dominant rejection mechanism. Finally, because the highest water flux of 6.5 L/(m^2 h) in FO mode was obtained using a CTA FO membrane with embedded polyester support, that particular membrane was also used in a pressure retarded osmosis (PRO) experiment to compare the two operating modes. Because of ICP effects, a higher water flux of 9.0 L/(m^2 h) was obtained in the PRO mode. However, the reverse salt flux in PRO mode was significantly higher, 25 g/(m^2 h), while that in FO was only 4.7 g/(m^2 h).

Ruprakobkit, Ruprakobkit, and Ratanatamskul (2016) modeled and validated experimentally carboxylic acid concentration with ammonium chloride as draw solution. They determined the acid permeability coefficients of the TFC FO membrane for acetic, butyric, lactic, and valeric acids. The permeability coefficient of lactic acid was the lowest, 0.15 L/(m^2 h), while those of acetic, butyric, and valeric acids were 2.10, 0.64, and 0.49 L/(m^2 h), respectively. In their simulations of FO filtrations with 10 mM carboxylic acid as feed and 1 M NH_4Cl as draw solution, lactic acid had the lowest drop in rejection from 100 % to 97.2 % under 30 h system operation. That is because the pKa value of lactic acid is 3.86, which is significantly lower than those of the other acids, and the amount of dissociated fraction of lactic acid in the feed solution is higher. Therefore, the membrane repels the negatively charged lactate ions more efficiently. Ruprakobkit et al. simulated the FO concentration performance for lactic acid as a function of draw solution concentration and volume. They discovered that the performance is enhanced when both the draw solution volume and concentration are increased.

6 MATERIALS AND METHODS

Concentration of lactic acid using FO was explored in the experimental part of this study. Purification of lactic acid, although being very essential, was not included in this study. In the experiments, dilute lactic acid was used as feed solution and concentrated glucose as draw solution. By using glucose, the diluted draw solution after FO filtration could be recycled to the fermentation vessel and utilized as the carbohydrate source of the fermentation, as proposed in Figure 16. The requirement for regeneration of the draw solution would thereby be eliminated, thus enhancing the effectiveness of the FO process.

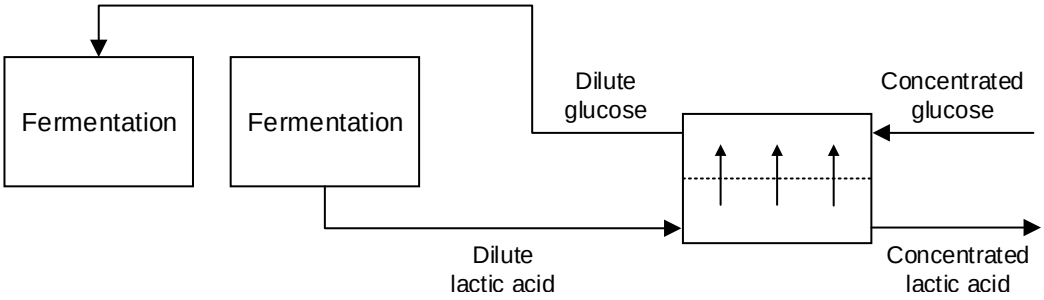

Figure 16. Proposed scheme for incorporation of FO into the downstream processing of lactic acid.

Firstly, the effect of feed and draw solution temperatures on FO performance was determined to find the optimum operating conditions. The experiments were conducted with two different membranes on a laboratory-scale FO module. Secondly, after identifying the most suitable membrane and temperature combination, a longer concentration run was carried out on a bench-scale FO module. The materials and methods used in these experiments are described in detail in the following chapters.

6.1 Filtration equipment

The FO filtration equipment used in this study consisted of individual tanks, pumps (Liquiport NF 1.100), and heat exchangers for feed and draw solutions, and a membrane module. The volume of each tank was 10 L. The feed and draw solutions were circulated through heat exchangers to the membrane module and then back to the tanks. The membrane module was operated in a co-current mode. The pipelines were adjusted with flow meters, and online temperature, mass, conductivity, and pressure data was collected on the computer. The actual setup and its schematic diagram are presented in Figures 17 and 18.

Figure 17. FO filtration equipment.

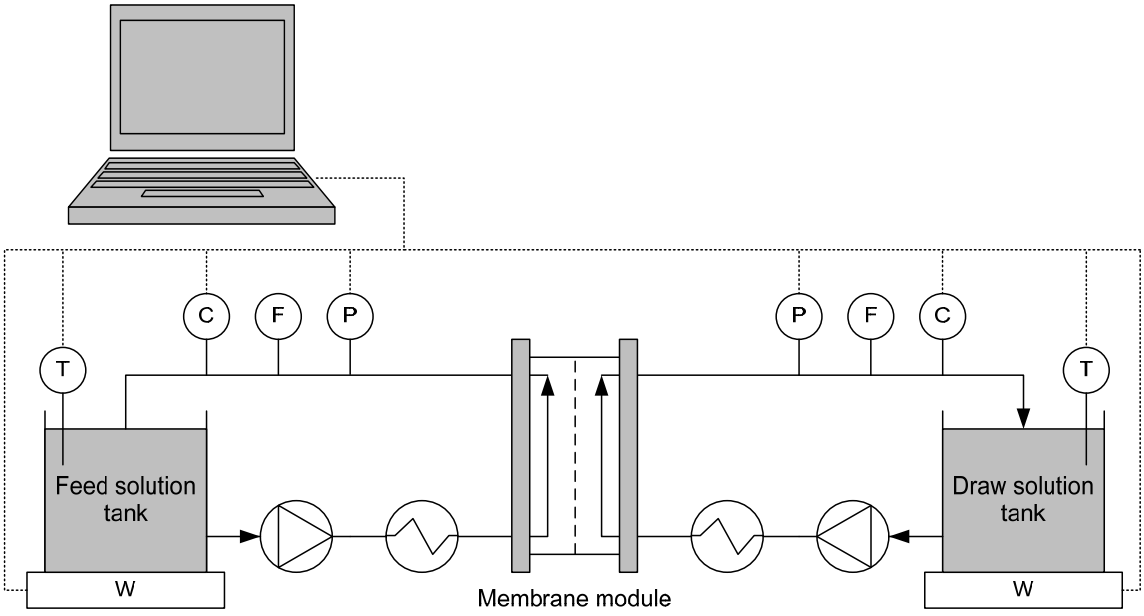

Figure 18. Schematic diagram of the FO filtration setup. Inline and online measurements: C = conductivity, F = flow, P = pressure, T = temperature, and W = mass.

Two different membrane modules were used in the experiments: a laboratory-scale CF042P-FO and a bench-scale SEPA CF-FO. Their specifications are given in Table VIII.

Table VIII. Specifications of the CF042P-FO and SEPA CF-FO modules (Sterlitech Corporation, 2015a, 2015b).

	CF042P-FO	SEPA CF-FO
Manufacturer	Sterlitech Corporation	Sterlitech Corporation
Membrane active area	42 cm^2	140 cm^2
Maximum pressure	27 bar	69 bar
Maximum temperature	260 °C	177 °C
pH range	Membrane dependent	Membrane dependent
Cell body	PTFE	316 stainless steel

Conductivity, pH, and degrees Brix measurements were used to analyze samples in the experimental part. An Atago Master-10α refractometer was used to determine the degrees Brix. The determination range of the refractometer was 0–10 °Bx. A VWR CO 3000 H meter with a CO11 electrode was used for the conductivity measurements. The pH was measured by a VWR pH110 meter or a VWR pHenomenal® pH 1000 H meter with a pHenomenal® 111 electrode. The osmotic pressures were measured by Wescor Vapro® vapor pressure osmometer model 5600. The determination range of the osmometer was approximately 0–25 bar.

6.2 Membranes and their characterization

Two different FO membranes were used in the experiments: Aquaporin Inside™ and Toray. Their specifications are given in Table IX.

Table IX. Specifications of the Aquaporin and Toray membranes (Sterlitech Corporation, 2016; Toray Chemical Korea, Inc., 2015).

	Aquaporin	Toray
Manufacturer	Aquaporin A/S	Toray Chemical Korea, Inc.
Membrane type	Flat sheet Thin-film composite with Aquaporin Inside™ coating	Flat sheet Thin-film composite with polyamide coating
Base membrane material	Polyethersulfone	Polysulfone
Membrane thickness	110 ± 15 µm	100 µm
Water flux	> 7 L/(m^2 h)	35 ± 3 L/(m^2 h)
NaCl reverse flux	< 2 g/(m^2 h)	< 0.5 g/(L)
Temperature range	5–50 °C 65 °C short term exposure	< 45 °C
pH range	2–11	2–11

When a new membrane was taken into use, it was first cut into the correct size to fit either the CF042P-FO or SEPA CF-FO module and soaked in deionized water at +5 °C overnight. The membrane was then placed into the module with the active layer facing the feed solution, and it was characterized.

Membrane characterization was always performed before and after an FO run to measure the water flux and evaluate the performance of the membrane. In the characterization, 3 kg of deionized water was used as feed and 2 kg of 1 M NaCl as draw solution. The flow rates of the feed and draw solutions were adjusted to 1.0–1.2 L/min, and their temperatures were maintained at 25±1 °C. The duration of the filtration was approximately 1 hour.

The conductivities of the feed and draw solutions were monitored during characterization to make sure that the membrane was operating steadily. The membrane was characterized in terms of water flux (J_W) which was calculated by using equation

$$J_W = \frac{\Delta V}{A_m \Delta t}, \tag{20}$$

where ΔV is the permeate volume, A_m is the membrane active area, and Δt is the time interval. A 20-minute time interval was used in the calculations. The same membrane was used in several sequential experiments and was replaced when its performance started to decline.

6.3 Properties of lactic acid and glucose solutions

The osmotic pressures and degrees Brix of lactic acid and glucose solutions of varying concentrations were determined to construct calibration curves. The effect of dissociation of lactic acid on degrees Brix, osmotic pressure, and conductivity was determined by analyzing lactic acid without pH adjustment and with its pH adjusted to 3.5 with 15 M NaOH.

6.4 Effect of feed and draw solution temperatures on water flux

The effect of feed and draw solution temperatures on water flux in concentration of lactic acid was studied by carrying out FO filtrations with different feed and draw solution temperature combinations. A three-level full factorial design was constructed for temperatures of 20, 40, and 60 °C, as illustrated in Figure 19. The set of 9 experiments was performed with both Aquaporin and Toray membranes using 8 % lactic acid (pH = 3.5) as feed and 60 % glucose as draw solution. Additionally, the water flux with deionized water as feed and 60 % glucose as draw solution at the central point 40–40 °C was measured for both membranes. All experiments were performed using the laboratory-scale CF042P-FO module.

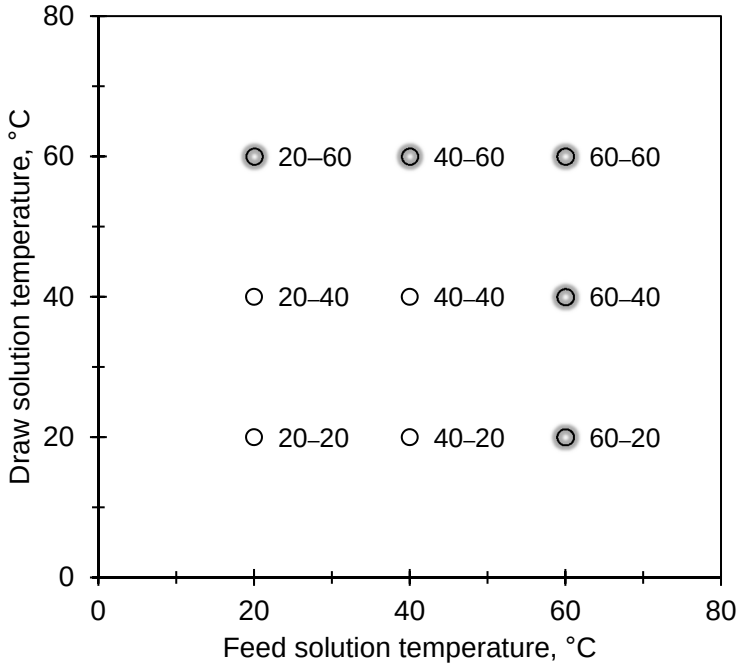

Figure 19. The 3^2 design of the temperature-change experiments. The experiments were performed using two different membranes: Aquaporin and Toray. The data points highlighted with grey go beyond the recommended temperature range of the Toray membrane.

Approximately 2 kg (2.0 L) of feed solution and 1 kg (0.7 L) of draw solution was used in each filtration. The feed solution was prepared by diluting 90 wt% aqueous lactic acid (VWR BDH Prolabo) to 8 wt% with deionized water. The pH of the solution was then adjusted to 3.5 by adding 15 M NaOH with mixing. The draw solution was prepared by heating deionized water and adding anhydrous D-(+)-glucose (VWR BDH Prolabo) to it. The samples before filtrations were taken of both solutions.

Before starting a run, a pH meter was mounted in the draw tank to monitor the pH change of the draw solution during filtration. Feed and draw solutions were then weighed and added to the tanks, and the run was started. The volumetric flow rates of the feed and draw solutions were set to 1.0–1.2 L/min (0.2 m/s), and their temperatures were adjusted to the desired values. The duration of the filtration was approximately 2 hours. Finally, the samples after filtration were collected from the feed and draw solutions. Conductivity, pH and degrees Brix were measured from the feed and draw solution samples taken before and after filtration. The water flux across the membrane was calculated from the filtration data using Eq. (20).

Additionally, the flux behavior with deionized water as feed and 60 % glucose as draw solution at 40 °C was determined for both Aquaporin and Toray membranes. The amount of feed solution was 2 kg and the amount of draw solution 1 kg. The filtrations were conducted similarly as described above. The water flux was calculated from Eq. (20).

6.5 Concentration of lactic acid

In the concentration experiment, the most favorable temperature combination (60–40 °C) was used to determine the extent of concentration of lactic acid by FO. The experiment was conducted with the bench-scale SEPA CF-FO module using Toray membrane. Approximately 3 kg (3.0 L) of 8 wt% lactic acid with its pH adjusted to 3.5 was used as feed and 4 kg (2.8 L) of 60 wt% glucose as draw solution. The solutions were prepared similarly as described in the previous chapter.

Feed and draw solutions were weighed and added to the tanks, and the run was started. The volumetric flow rates of the feed and draw solutions were set to 1.0–1.2 L/min (0.2 m/s), and their temperatures were adjusted to the desired values. The filtration was let to run until the flux reached the value of 0 L/(m^2 h). Finally, the samples after filtration were collected from the feed and draw solutions. Conductivity, pH, degrees Brix, and osmotic pressure were measured from the feed and draw solution samples taken before and after filtration. The lactic acid and glucose concentrations were also determined by high-performance liquid chromatography (HPLC) performed by VTT´s team of Bioprocess engineering.

The on-line filtration data was used to determine the water flux across the membrane from Eq. (20). Water recovery rate (*WR*) – a measure of the amount of water being removed from the feed – and concentration factor (*CF*) were also calculated according to equations

$$WR = \frac{\Delta V}{V_{\mathrm{F,i}}} \times 100\ \% \tag{21}$$

and

$$CF = \frac{1}{1 - \frac{WR}{100\ \%}}, \tag{22}$$

where ΔV is the permeate volume and $V_{F,i}$ is the initial volume of the feed solution.

The concentration data obtained by HPLC was used to calculate the forward solute flux of lactic acid (J_{LA}) and reverse solute flux of glucose (J_{Glc}) as

$$J_{LA} = \frac{\left(V_{D,i} + \Delta V\right) \times C_{LA(D),f}}{A_m \Delta t} \tag{23}$$

and

$$J_{Glc} = \frac{\left(V_{F,i} - \Delta V\right) \times C_{Glc(F),f}}{A_m \Delta t}, \tag{24}$$

where $V_{D,i}$ is the initial volume of the draw solution, $C_{LA(D),f}$ is the final lactic acid concentration in the draw solution, $C_{Glc(F),f}$ is the final glucose concentration in the feed solution, A_m is the membrane active area, and Δt is the time interval. Furthermore, the forward rejection of lactic acid (R_{LA}) and reverse rejection of glucose (R_{Glc}) were calculated from equations

$$R_{LA} = \frac{C_{LA(F),i} - \left(\frac{C_{LA(D),f}\left(V_{D,i} + \Delta V\right)}{\Delta V}\right)}{C_{LA(F),i}} \times 100\ \% \tag{25}$$

and

$$R_{Glc} = \frac{C_{Glc(D),i} - \left(\frac{C_{Glc(F),f}\left(V_{F,i} - \Delta V\right)}{\Delta V}\right)}{C_{Glc(D),i}} \times 100\ \%, \tag{26}$$

where $C_{LA(F),i}$ is the initial lactic acid concentration in the feed solution and $C_{Glc(D),i}$ is the initial glucose concentration in the draw solution. The forward rejection is defined as the percentage of feed solutes being retained in the feed solution and the reverse rejection as the percentage of draw solutes being retained in the draw solution.

The final yields of lactic acid in the feed solution ($Y_{LA,F}$) and the draw solution ($Y_{LA,D}$) were determined from equations

$$Y_{LA,F} = \frac{C_{LA(F),f} \times \left(V_{F,i} - \Delta V\right)}{C_{LA(F),i} \times V_{F,i}} \times 100\ \% \tag{27}$$

and

$$Y_{LA,D} = \frac{C_{LA(D),f} \times \left(V_{D,i} + \Delta V\right)}{C_{LA(F),i} \times V_{F,i}} \times 100\ \%, \tag{28}$$

where $C_{LA(F),f}$ is the final lactic acid concentration in the feed solution. The calculation examples of Eqs. (20)–(28) are provided in Appendix II.

7 RESULTS AND DISCUSSION

Concentration of lactic acid by FO with glucose as draw solution was studied in the experimental part of this study. The effect of filtration conditions on FO water flux was determined by conducting short filtrations with two different membranes (Aquaporin and Toray) under varying feed and draw solution temperature combinations. After identifying the most favorable conditions, a longer concentration run was carried out to evaluate the performance of the process and to find out the extent of water recovery that can be obtained by FO. Properties of glucose and lactic acid solutions, such as osmotic pressure, were also measured. The results are presented and discussed in this chapter.

7.1 Properties of lactic acid and glucose solutions

The osmotic pressures of aqueous glucose and lactic acid solutions were measured. The effect of dissociation of lactic acid on osmotic pressure was determined by measuring osmotic pressures of lactic acid solutions with and without pH adjustment. Figure 20 shows the obtained calibration curves relating the lactic acid or glucose concentration to the osmotic pressure. Calibration curves for degrees Brix were also determined and are illustrated in Figure 21.

All of the calibration curves for osmotic pressure in Figure 20 fit well to the experimental data. Because of the determination range of the osmometer (0–25 bar), only rather low solution concentrations could be measured. If higher concentrations could have been measured, the calibration curves would be more accurate. Because the osmotic pressure behaves rather linearly with low solute concentrations, the calibration curves are now assumed to be linear. However, that is often not the case for any compound, which can be observed also from Figure 12. Extrapolation of osmotic pressures of concentrations beyond the calibration range using the calibration curves can, therefore, be very inaccurate.

In the FO filtrations, 8 % lactic acid (pH = 3.5) was used as feed solution and 60 % glucose as draw solution. It can be seen that the pH adjustment affects the osmotic pressure of the lactic acid solution: the osmotic pressure of 8 % lactic acid without pH adjustment is 18 bar, while that of lactic acid with its pH adjusted to 3.5 is 25 bar. In the pH adjustment of lactic acid, NaOH was added to the solution. This addition of ions increases the chemical potential

of the solution and thereby increases the osmotic pressure. Furthermore, the osmotic pressure of 60 % glucose obtained by extrapolation is about 105 bar, which makes the osmotic pressure difference between feed and draw solutions 80 bar.

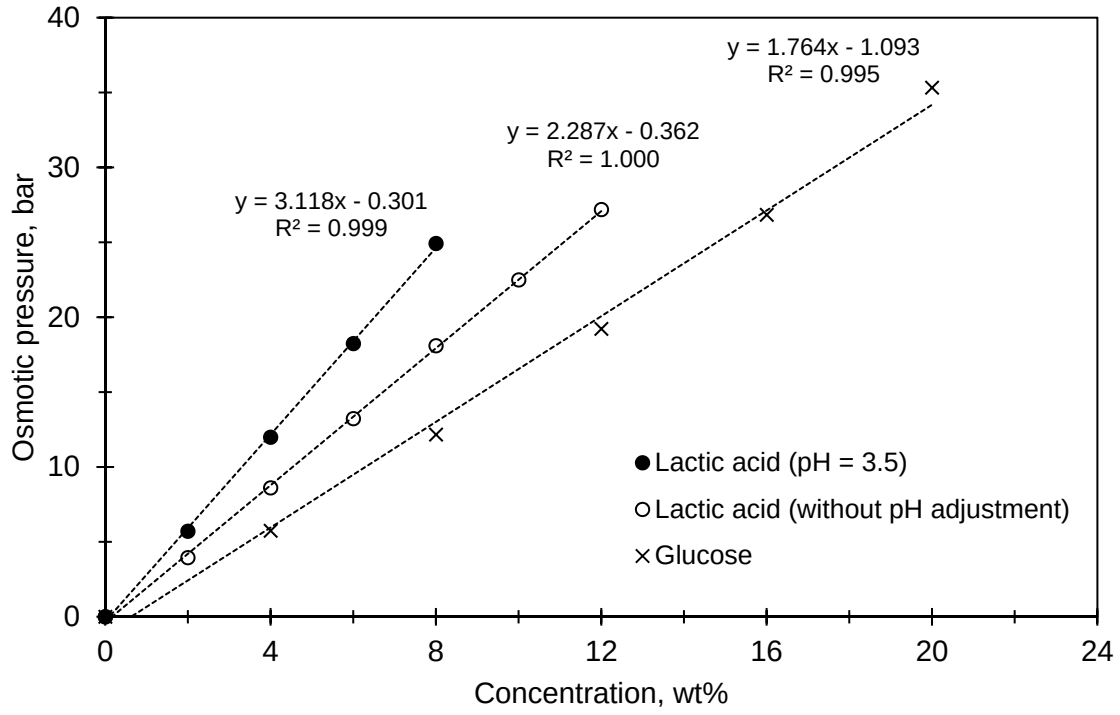

Figure 20. Osmotic pressure of aqueous glucose, aqueous lactic acid without pH adjustment, and aqueous lactic acid with its pH adjusted to 3.5.

All of the calibration curves for degrees Brix in Figure 21 fit well to the experimental data. Degrees Brix is a very straightforward measure of the sugar content of an aqueous solution and can be used to estimate the concentration of the solution. The measurement is based on refractive index, which describes how light propagates through the medium. Refractive index is affected by density of the solution and atomic interactions of the solutes, and – unlike osmotic pressure – behaves linearly with increasing concentration, making extrapolation from the calibration curves accurate. Lactic acid has a lower refractive index than glucose, which is why it measures lower on degrees Brix. Again, the dissociation of lactic acid under elevated pH increases atomic interactions in the solution and affects degrees Brix: for 8 % lactic acid without pH adjustment it is 5.4 °Bx while for lactic acid with its pH adjusted to 3.5 it is 6.7 °Bx. Degrees Brix of the 60 % glucose is obtained by extrapolation, being exactly 60 °Bx.

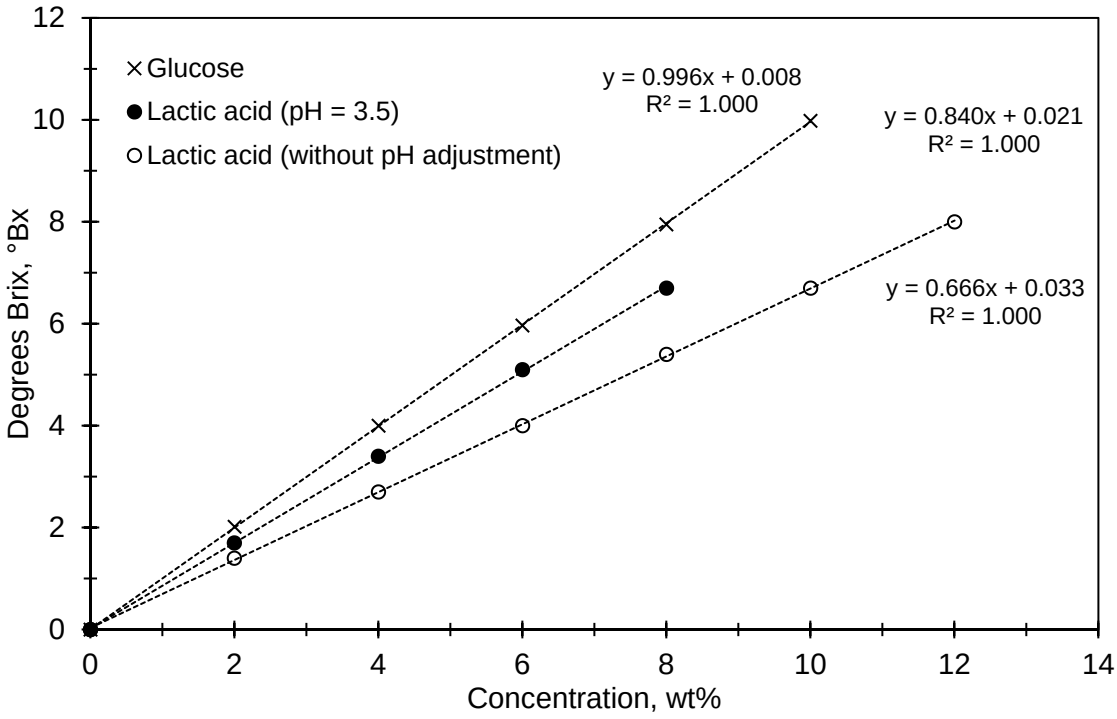

Figure 21. Degrees Brix of aqueous glucose, aqueous lactic acid without pH adjustment, and aqueous lactic acid with its pH adjusted to 3.5.

7.2 Effect of feed and draw solution temperatures on water flux

The effect of filtration conditions on FO water flux was determined by conducting short filtrations with two different membranes under varying feed and draw solution temperature combinations. The membranes were characterized in terms of water flux before and after each filtration. The results from the membrane characterizations and FO filtrations are presented below.

The experiments with varying feed and draw solution temperatures followed the experimental design depicted in Figure 19. However, at data points 40–20 °C and 60–20 °C, the draw solution could not be cooled to the desired temperature of 20 °C, and the matrix got its final shape illustrated in Figure 22.

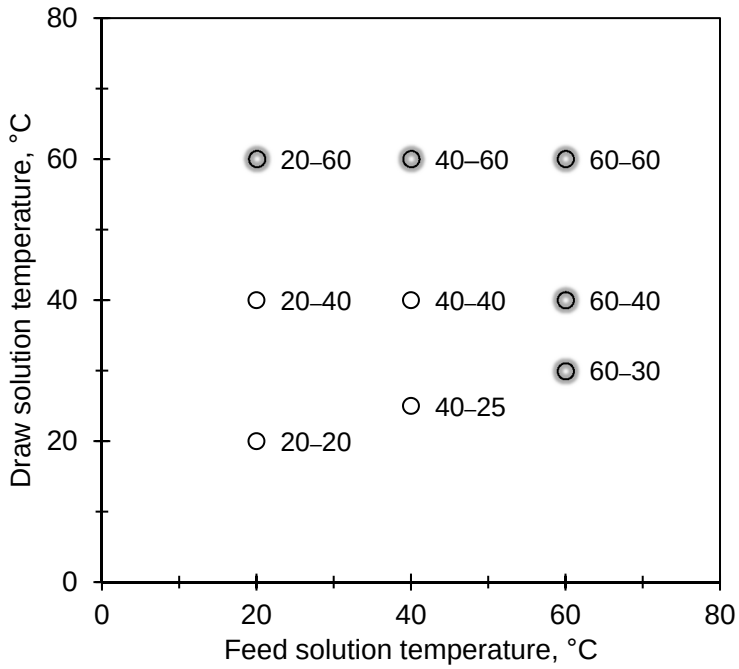

Figure 22. The final design of the temperature-change experiments. The experiments were performed using two different membranes: Aquaporin and Toray. The data points highlighted with grey go beyond the recommended temperature range of the Toray membrane.

7.2.1 Membrane characterizations

The membrane was characterized in terms of water flux before and after each filtration experiment by using deionized water as feed and 1 M NaCl as draw solution. The osmotic pressure of 1 M NaCl is approximately 50 bar, which is also the osmotic pressure difference across the membrane (Tang, She, Lay, Wang, & Fane, 2010, p. 132). Overviews of the water fluxes obtained using Aquaporin and Toray membranes on the CF042P-FO module are presented in Figures 23 and 24, respectively. The water fluxes remained very stable during characterizations, because the filtration time was only 1 hour. On average, the water flux before filtration with the Aquaporin membrane was 8.3 ± 1.0 L/(m^2 h) and after filtration 7.1 ± 1.0 L/(m^2 h). Similarly, the water flux before filtration with the Toray membrane was 27.1 ± 3.6 L/(m^2 h) and after filtration 26.9 ± 3.3 L/(m^2 h).

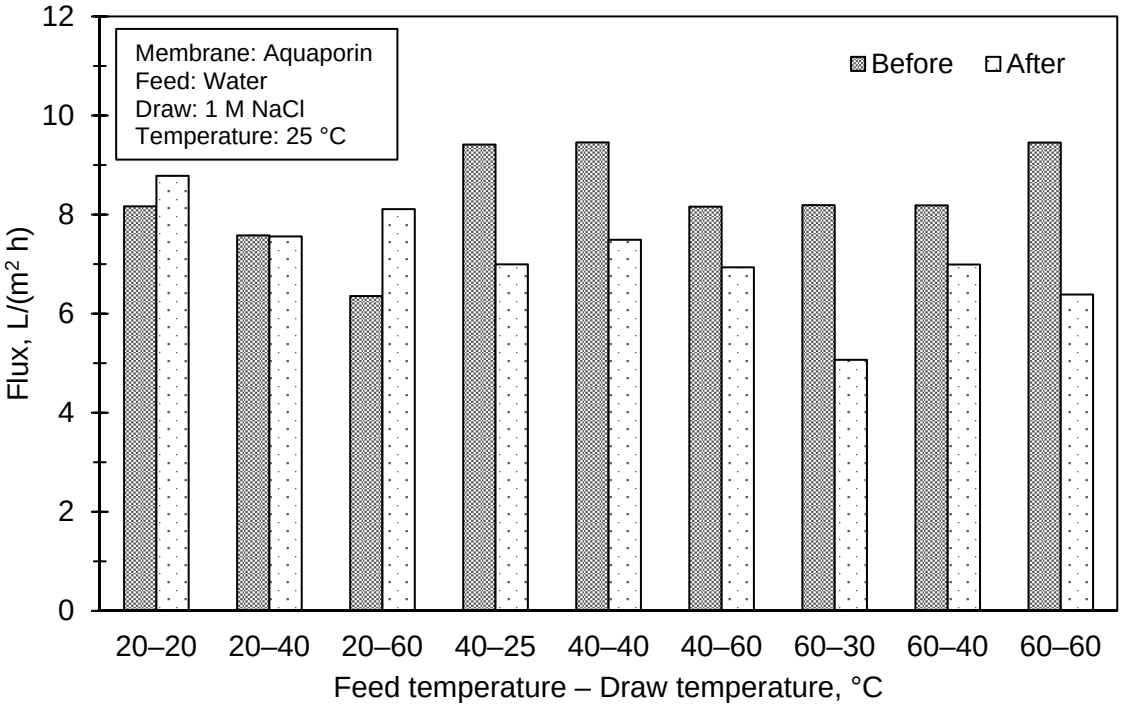

Figure 23. Water flux variation in the characterization of the Aquaporin membrane in FO mode. Deionized water was used as feed and 1 M NaCl as draw solution. The filtration temperature was 25 °C.

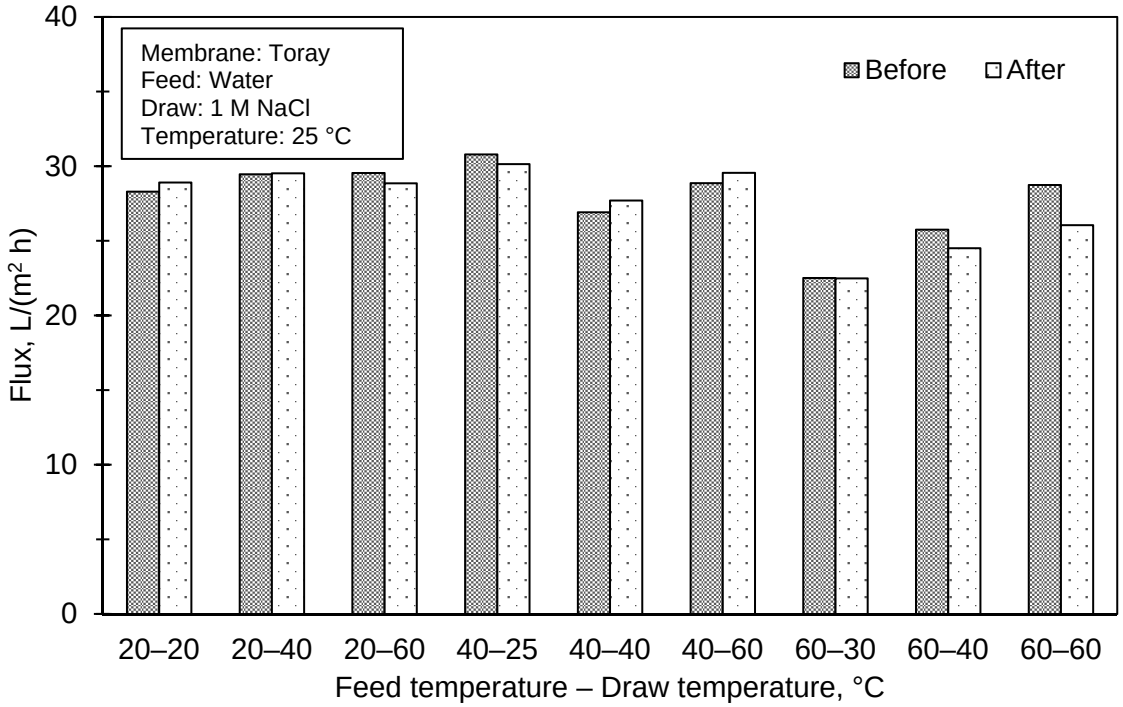

Figure 24. Water flux variation in the characterization of the Toray membrane in FO mode before and after FO experiments. Deionized water was used as feed and 1 M NaCl as draw solution. The filtration temperature was 25 °C.

When comparing Figures 23 and 24, it can be seen that the characterizations of Toray gave approximately a three times higher water flux than those of Aquaporin. Difference in the membrane structures can explain the difference. Aquaporin has an aquaporin-based active layer with polyethersulfone support layer, while Toray has a polyamide active layer with polysulfone support layer. Presumably, the polyamide active layer is more easily permeable to water molecules than the aquaporin channels are. The water fluxes obtained with Aquaporin also had a considerable amount of variation between pre- and post-filtration characterizations compared to those obtained with the Toray membrane.

Additionally, as demonstrated in Figure 22, some of the experimental points were carried out beyond the recommended temperature range of the Toray membrane, above 45 °C. When comparing the characterizations conducted before and after those experimental points, there cannot be seen any significant collapse or increase in water flux that would indicate severe membrane damage caused by the high temperature. It is possible that the membrane has been somewhat affected by the highest temperature combination, 60–60 °C, since the highest drop in water flux from 28.7 to 26.1 L/(m^2 h) can be observed between the characterizations of that particular filtration. However, because the water flux is still of a reasonable magnitude, the effect of temperature should not be exaggerated.

7.2.2 Forward osmosis filtrations

The water flux across the membrane was measured using deionized water as feed and 60 % glucose as draw solution, so that there would be no ECP effects present. The fluxes obtained using Aquaporin and Toray membranes are compared in Figure 25. The average water flux with Aquaporin was 11.5 L/(m^2 h) while that with Toray was 1.5 times higher being 17.6 L/(m^2 h). Comparing the values to the water fluxes obtained in the membrane characterizations with 1 M NaCl as draw solution (Figures 23 and 24), it can be seen that the flux with Toray dropped from 27.1 to 17.6 L/(m^2 h) while with Aquaporin it increased from 8.3 to 11.5 L/(m^2 h) when the draw solution was changed to 60 % glucose. The 1 M NaCl and 60 % glucose solutions have osmotic pressures of approximately 50 bar and 100 bar, respectively, for which reason the flux was expected to increase with 60 % glucose as draw solution. That suggests that the support layer of Toray possesses a higher tendency for ICP when glucose is used as draw solution, thus significantly decreasing the water flux across the membrane. Glucose has a larger molecular size and higher viscosity than NaCl, for

which reason it does not diffuse as easily inside the porous support layer, resulting in worsened ICP.

The very different ICP properties can be explained by the different support layer materials and structures of the membranes: Toray has a polysulfone support layer and Aquaporin a polyethersulfone support layer. Polysulfone is composed of sequential aromatic and aliphatic units, and it has a hydrophobic nature. Polyethersulfone has a similar structure, but with more sulfur dioxide molecules, which increase the hydrophilicity of the material. (Galanakis, Castro-Muñoz, Cassano, & Conidi, 2016, p. 191.) Hydrobhobicity of the polysulfone prevents proper wetting of the support layer. Because mass transport can occur only in the wetted porosity of the support layer, the transport is inhibited and the ICP phenomenon is increased.

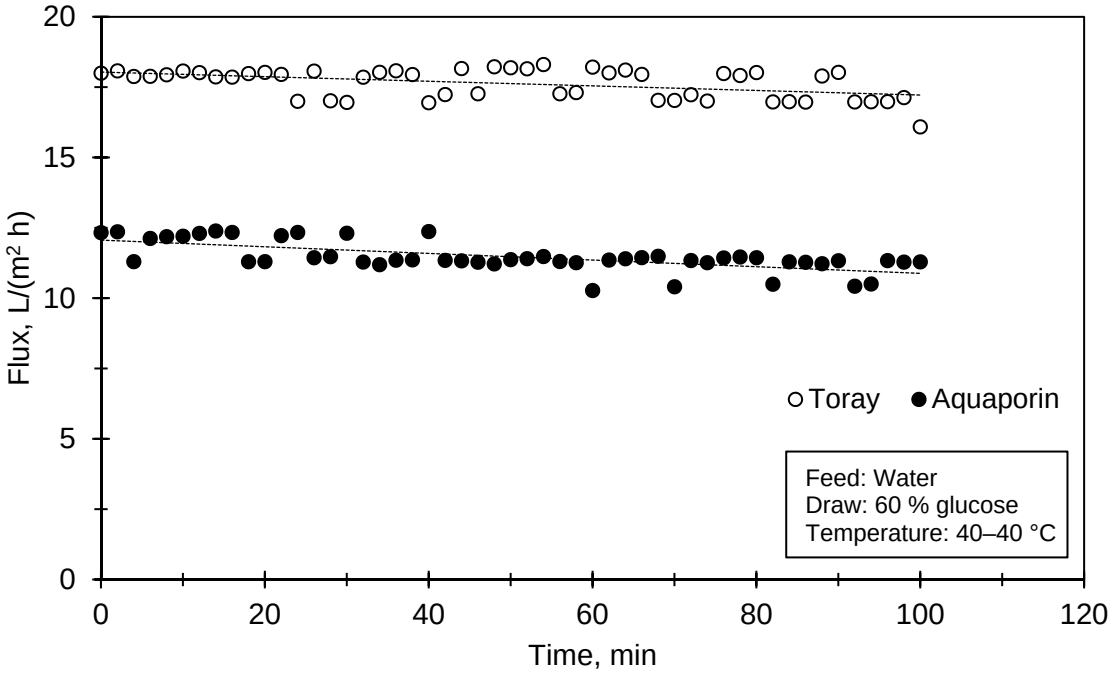

Figure 25. Water flux across the Aquaporin and Toray membranes in FO mode with deionized water as feed and 60 % glucose as draw solution. The filtration temperature was 40 °C.

The water fluxes obtained using different feed–draw solution temperature combinations with the Aquaporin membrane are presented in Figure 26. A clear correlation between the feed and draw solution temperatures and water flux can be seen. The feed solution temperature is the dominating parameter: the higher is its temperature, the higher is the water flux. For instance, when the draw solution temperature was kept constant at 40 °C and the feed

solution temperature was increased from 20 to 40 and finally to 60 °C, the flux increased from 2.5 to 5.4 and to 8.8 L/(m^2 h), respectively. This is because a higher feed solution temperature reduces the viscosity of the permeate, which increases significantly the water flux across the membrane. However, the elevated temperature enhances also diffusivity of lactic acid and leads to increased forward solute flux.

According to Figure 26, the draw solution temperature is not as significant when using the Aquaporin membrane, but it also possesses the same trend as the feed solution temperature: the higher is its temperature, the higher is the water flux. In the same manner, when the feed solution temperature was kept constant at 40 °C and the draw solution temperature was raised from 20 to 40 and finally to 60 °C, the flux increased from 4.6 to 5.4 and to 5.9 L/(m^2 h), respectively. With increasing the draw solution temperature, a similar phenomenon happens as described above with the feed solution: a higher temperature lowers viscosity of the concentrated glucose solution and enhances diffusivity of the glucose molecules. As a result, ICP is mitigated as the glucose molecules can diffuse more easily inside the porous support layer, and the water flux across the membrane increases. The enhanced diffusion of glucose can, again, cause increased reverse solute flux across the membrane.

The filtration temperature affects the osmotic pressures of the feed and draw solutions and that way influences the filtration performance. According to Eqs. (12) and (13), the osmotic pressure of a solution becomes higher with increasing temperature. For example, when raising the temperature from 20 to 60 °C, the osmotic pressure of 60 % glucose increases by 14 bar, and the osmotic pressure of 8 % lactic acid (pH = 3.5) similarly by 3 bar. It can be concluded that the feed solution temperature has an insignificant effect on the osmotic pressure while the draw solution temperature can increase the osmotic pressure difference across the membrane and enhance water flux when operating under high temperatures.

To sum up, the highest water flux of 10.0 L/(m^2 h) with the Aquaporin membrane was obtained when both feed and draw solution were kept at the highest temperature of 60 °C. Under that temperature, the osmotic pressure difference across the membrane was the highest, and the diffusivities of glucose and water molecules were enhanced.

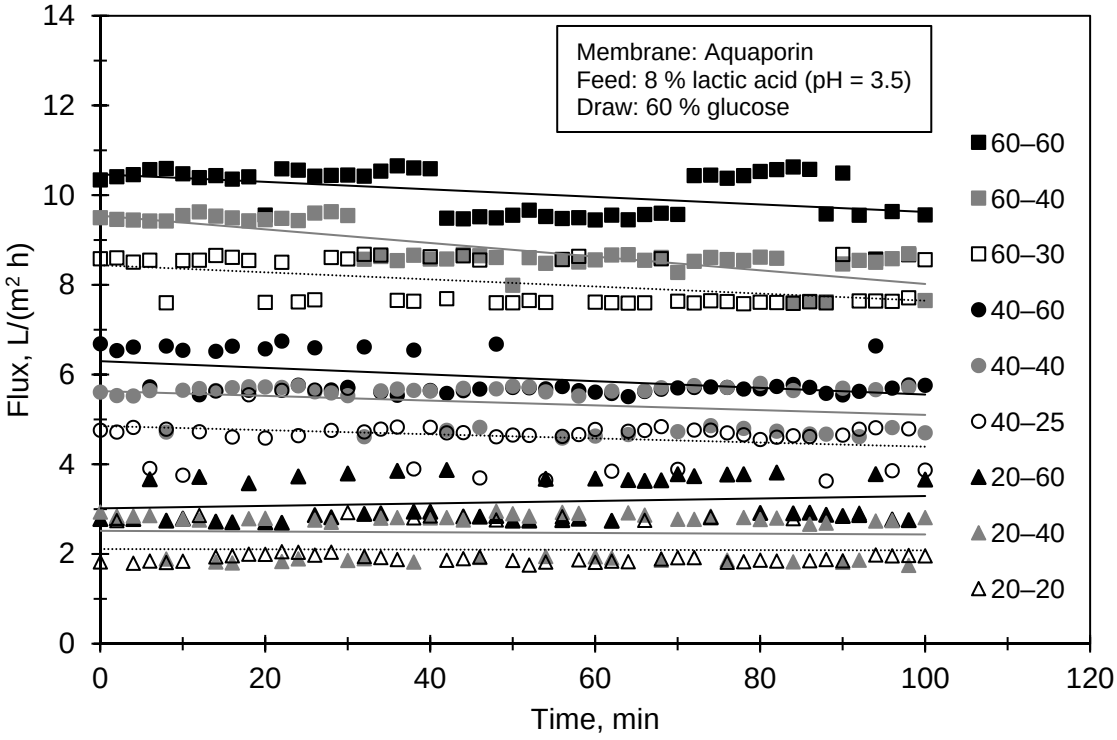

Figure 26. Effect of feed and draw solution temperatures on water flux. The filtrations were conducted on Aquaporin membrane in FO mode using 8 % lactic acid (pH = 3.5) as feed and 60 % glucose as draw solution. The temperature combinations are indicated as “Feed temperature – Draw temperature”.

The water fluxes obtained using different feed–draw solution temperature combinations with the Toray membrane are presented in Figure 27. It can be seen that the correlation between feed and draw solution temperatures and water flux is not as clear with Toray as it is with Aquaporin. The feed solution temperature is again the dominating parameter as the water flux clearly increases with an increase in temperature because of the enhanced diffusivity of water molecules. When the feed solution temperature was raised from 20 to 40 and further to 60 °C with a constant draw solution temperature of 40 °C, the water flux increased from 3.9 to 7.3 and to 14.3 L/(m^2 h), respectively.

According to Figure 27, the water flux with Toray is increased with a transmembrane temperature difference by keeping the draw solution under a lower temperature than the feed solution. For example, the water flux reached its highest value of 19.2 L/(m^2 h) under the temperature combination of 60–30 °C, while with elevated draw solution temperatures under 60–40 °C and 60–60 °C the flux remained at ~14 L/(m^2 h). A similar observation can be done with the feed solution temperature of 40 °C with varying draw solution temperatures. Furthermore, the lowest feed solution temperature of 20 °C combined with any of the draw

solution temperatures gave the lowest flux, 3.7–3.9 L/(m^2 h), because the transmembrane temperature difference was of non-favorable direction.

A remaining concern is the recommended maximum operating temperature of the Toray membrane (45 °C). The highest water fluxes were obtained under the feed solution temperature of 60 °C when that limit was exceeded. However, no signs of membrane damage can be distinguished in any of the 2-hour filtrations: the flux is stable, and there is no prominent change in the feed or draw solution conductivity or pH. Also, the membrane characterizations conducted after filtrations show no implication of sudden decline in the membrane performance (Figure 24).

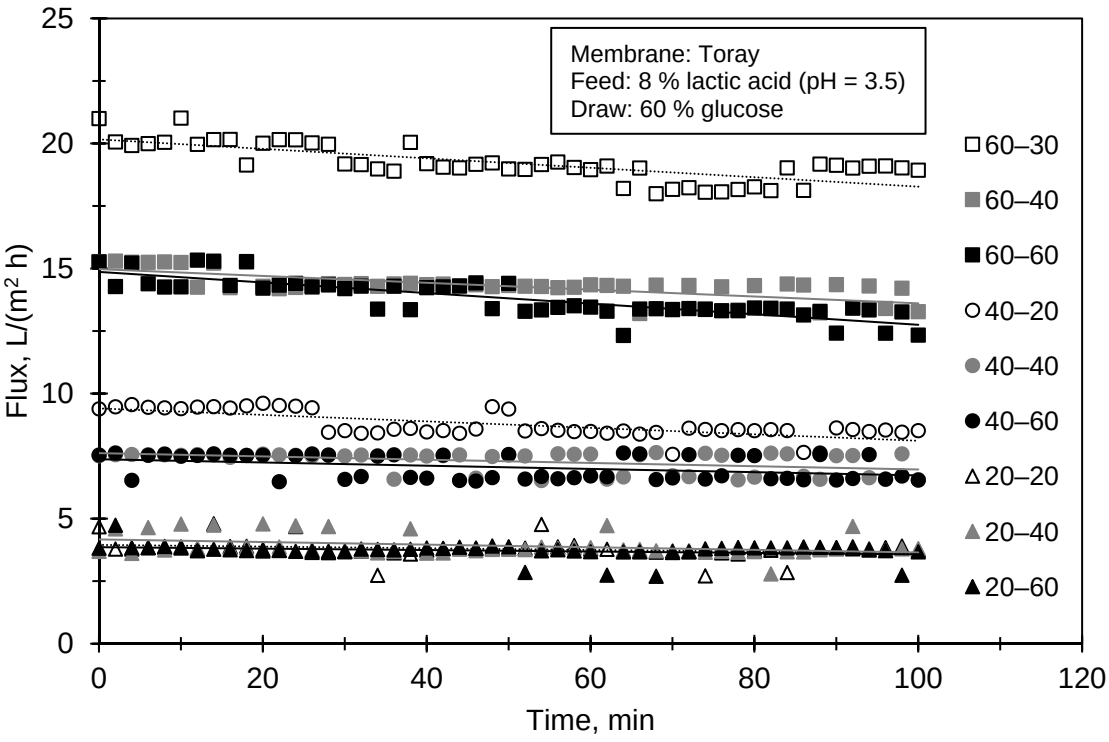

Figure 27. Effect of feed and draw solution temperatures on water flux. The filtrations were conducted on Toray membrane in FO mode using 8 % lactic acid (pH = 3.5) as feed and 60 % glucose as draw solution. The temperature combinations are indicated as “Feed temperature – Draw temperature”.

Comparing Figures 26 and 27, it can be seen that Toray operates more efficiently under the studied conditions, possessing overall a higher water flux than Aquaporin. The fluxes obtained with Toray range from 3.7 to 19.2 L/(m^2 h) while with Aquaporin from 2.1 to 10.0 L/(m^2 h), which makes the difference between maximum fluxes nearly twofold. Overall,

all of the water fluxes seem to drop slightly towards the end of the filtration, and the drop is sharper with a higher water fluxes. That is because the draw solution is diluted by the permeating water and the osmotic pressure difference between feed and draw solutions is decreased, thus decreasing the water flux. The amount of collected permeate in the 2-hour filtrations varied from 18 g to 115 g depending on the water flux, and since the initial mass of the draw solution was 2 kg, the dilution was rather low.

The measured degrees Brix, pH, and conductivity values of the feed and draw solutions in all of the FO filtrations are listed in Appendix I. On average, the 8 % lactic acid solution had an initial pH of 3.49 ± 0.03 and a conductivity of 15.6 ± 0.5 mS/cm. The pH of the solution dropped only marginally and the conductivity rose slightly in most of the filtrations due to the increasing concentration of the solution. However, the conductivity decreased in the experiments that were conducted under the feed solution temperature of 20 °C and had the lowest water fluxes.

Correspondingly, the 60 % glucose solution had an initial pH of 4.07 ± 0.08 and a conductivity of 3.2 ± 0.2 µS/cm. The pH dropped slightly in all of the filtrations, while the conductivity increased consistently with increasing water flux. With the Toray membrane, however, the increase was significantly higher, which indicates somewhat larger forward solute flux of lactic acid. Under the filtration temperature of 40–40 °C, for example, the draw solution conductivity with Aquaporin increased from 3.2 to 12.2 µS/cm while with Toray from 3.3 to 90.7 µS/cm.

7.3 Concentration of lactic acid

When determining the effect of feed and draw solution temperatures on FO performance, the highest water flux of all the measurements was obtained with the Toray membrane under the freed-draw solution temperature combination of 60–30 °C (Figure 27), for which reason the particular membrane and temperature combination were used in the concentration experiment. However, the draw solution temperature could not be maintained at 30 °C during the filtration, so the final temperature combination was 60–40 °C. The filtration was let to run until the flux ceased, which took approximately 16 hours. The obtained flux is presented in Figure 28. The obtained flux was high, having its maximum of 18.9 L/(m^2 h) at 1 hour of operation, after which it started to fall smoothly until reaching the value of 4.6 L/(m^2 h) after 15 hours of operation. The feed tank ran then empty and the flux declined sharply until it finally stopped. The flux decreases because the driving force of the process,

osmotic pressure difference across the membrane, becomes gradually smaller and smaller as water permeates through the membrane, resulting in concentration of the feed solution and dilution of the draw solution. Figure 29 shows that the water recovery rate in the end of the filtration was as high as 84.7 %, because there was evidently no fouling limiting the water transport. That water recovery rate corresponds the concentration factor of 6.5.

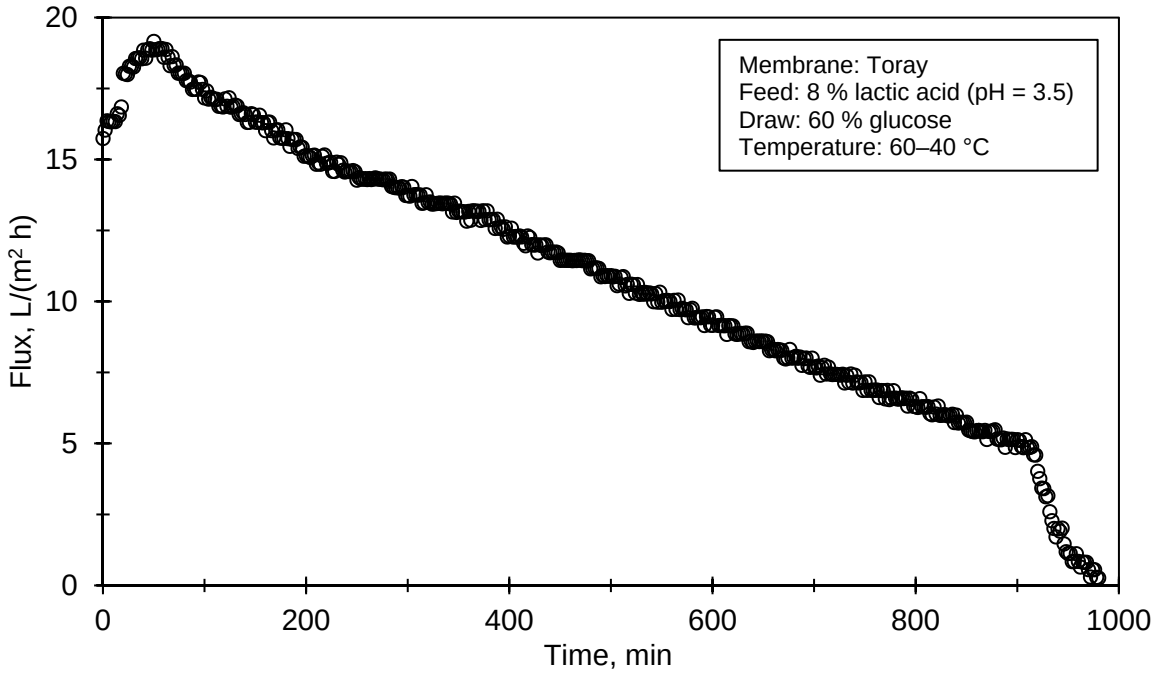

Figure 28. Flux in concentration of lactic acid with 8 % lactic acid (pH = 3.5) as feed and 60 % glucose as draw solution. The feed and draw solution temperatures were 60 °C and 40 °C, respectively. The filtration was conducted using the Toray membrane in FO mode.

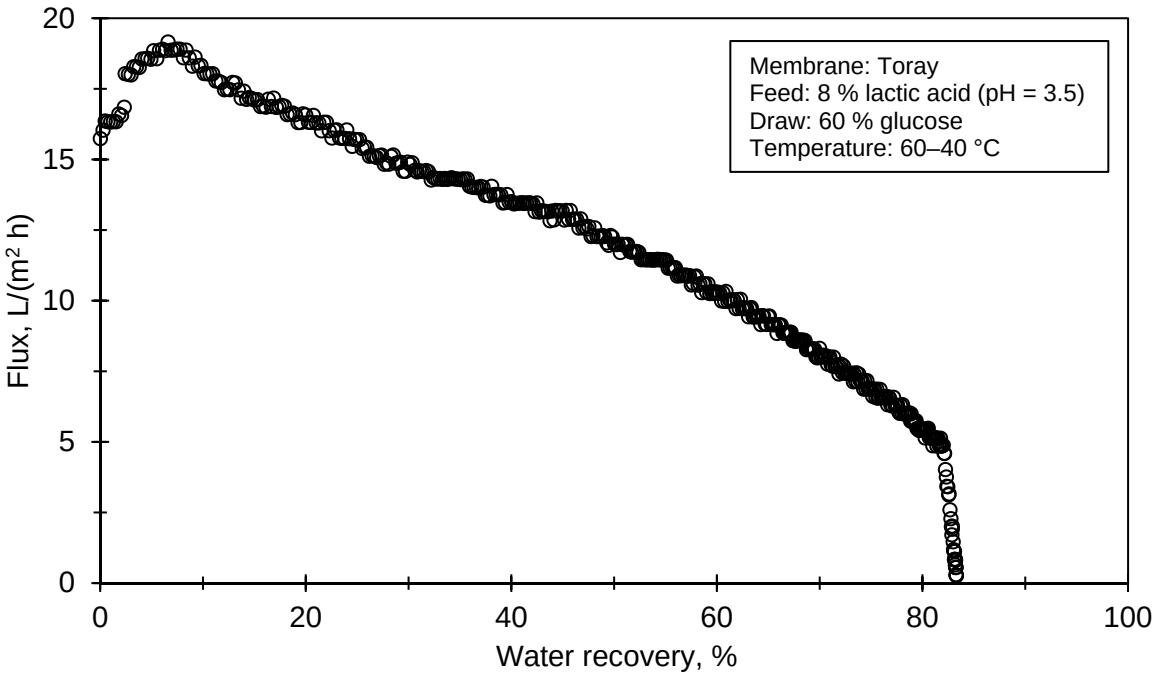

Figure 29. Water recovery in concentration of lactic acid with 8 % lactic acid (pH = 3.5) as feed and 60 % glucose as draw solution. The feed and draw solution temperatures were 60 °C and 40 °C, respectively. The filtration was conducted using the Toray membrane in FO mode.

According to the results of the HPLC analysis presented in Table X, lactic acid was concentrated from 8 % to nearly 32 % and glucose diluted from 60 % to 35 %. The real concentration factor of lactic acid was, therefore, 4.0 instead of 6.5. That is because the membrane did not reject lactic acid completely. The analysis results show that there had been solute fluxes of both compounds: the final glucose concentration in the feed solution was 0.26 % and the final lactic acid concentration in the draw solution 1.19 %.

Table X. Initial and final lactic acid and glucose concentrations of the feed and draw solutions.

Sample		Concentration, wt%	
		Lactic acid	Glucose
Feed solution	Initial	6.78	
	Final	31.77	0.26
Draw solution	Initial		58.37
	Final	1.19	35.05

The rejections and solute fluxes of glucose and lactic acid as well as the final yield of lactic acid are presented in Table XI. The Toray membrane's rejection towards lactic acid was

very low, only 56.0 %, while towards glucose it was as high as 99.9 %. Furthermore, the solute flux of lactic acid was 336.0 g/(m^2 h), which is 60 times higher than that of glucose, 5.6 g/(m^2 h). The solute flux could also be observed in the draw solution conductivity in Figure 30. The draw solution conductivity increased from 0 to 1.75 mS/cm, which was due to the high solute flux of lactic acid. During filtration, the feed solution conductivity was doubled from 17 mS/cm to 35 mS/cm because of the gradually increasing concentration of lactic acid. Finally, the yields of lactic acid in the feed and draw solutions in the end of the filtration were 75.4 % and 37.3 %, respectively. The values don't add up to 100 % because they were calculated based on the initial lactic acid concentration of the feed solution, 6.78 %, analyzed by HPLC. The analysis result is likely slightly too low, as it should be closer to 8 %, and that causes error to the calculation. Nevertheless, the final product yield of 75.4 % shows that a substantial amount of lactic acid was retained in the feed solution.

The factors affecting a membrane's rejection towards a compound include the molar mass of the compound, filtration temperature, solution pH, membrane characteristics, etc. In this case, the difference in the molar masses of lactic acid and glucose can explain their very different solute fluxes. The molar masses of lactic acid and glucose are 90.0 g/mol and 180 g/mol, respectively. The lower molar mass and molecular size enhance diffusivity of lactic acid, thus resulting in an increased solute flux.

The filtration temperature is another key parameter determining the solute flux: the higher is the temperature, the higher is the diffusivity of the solutes. The considerably high feed solution temperature of 60 °C, therefore, explains the high solute flux and low rejection of lactic acid. In this case, the feed solution temperature also exceeded the recommended maximum operating temperature of the membrane, which may have influenced the rejection. The rejection can be enhanced by conducting the filtration at a lower temperature, but at the expense of water flux.

As listed in Appendix I, the feed solution pH remained nearly constant being 3.47 in the beginning and 3.50 after filtration, while the pH of the draw solution decreased slightly from 4.06 to 3.46. The pH of the feed solution affects considerably the rejection of a carboxylic acid, because the active layer of the Toray membrane is made of polyamide which possesses a surface charge. At a high pH, the low proton concentration leads to deprotonation of the hydrophilic sites of the membrane, making the charge of the membrane negative. Furthermore, at a high pH lactic acid is dissociated into anionic lactate, which is more efficiently rejected by the negatively charged membrane. At a low pH, conversely, the high

proton concentration leads to protonation of the hydrophilic sites, making the charge of the membrane positive. At a low pH, lactic acid is present in its neutral form and permeates more easily across the less negatively charged membrane.

At a pH of 3.5, the relative abundancy of lactic acid is 70 % and of lactate 30 % (Figure 2). The fraction of neutral lactic acid is high and can explain the low rejection. By adjusting the feed solution pH to 4.5, for example, the relative abundancy of lactic acid would be only 20 % and of lactate 80 %. Consequently, the membrane charge would become more negative and reject the negative lactate ions more efficiently. It should be noted that a higher dissociation degree of lactic would also increase the ionic activity of the solution and cause an increase in the osmotic pressure. The osmotic pressure difference across the membrane would become smaller, which could affect the FO water flux.

Table XI. Solute fluxes and rejections of lactic acid and glucose, and final yield of lactic acid in the feed and draw solutions.

	Solute flux, $g/(m^2\ h)$	Rejection, %	Yield, %	
			Feed solution	Draw solution
Lactic acid	336.0	56.0	75.4	37.3
Glucose	5.6	99.9		

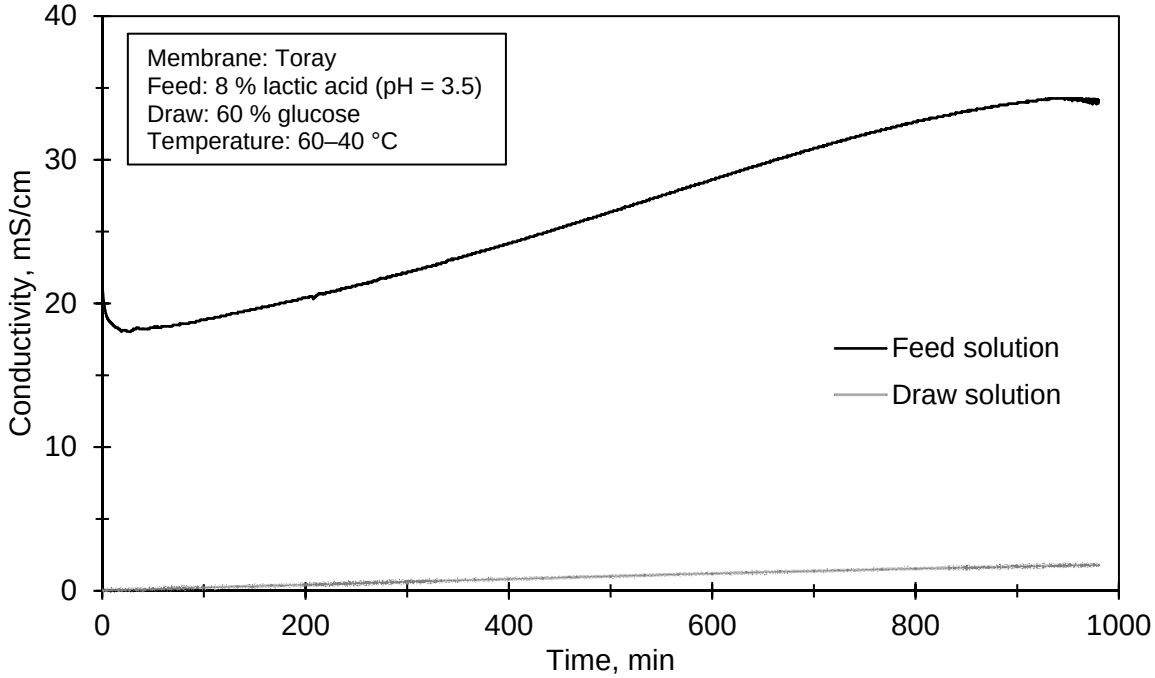

Figure 30. Feed and draw solution conductivities during concentration of lactic acid. Feed solution was 8 % lactic acid (pH = 3.5) and draw solution 60 % glucose. The feed and draw solution temperatures were 60 °C and 40 °C, respectively. The filtration was conducted using the Toray membrane in FO mode.

The HPLC analysis results were used to determine the initial and final osmotic pressures of the feed and draw solutions by extrapolation from the calibration curves (Figure 20). The solute fluxes of both lactic acid and glucose were taken into account in the determination. The estimated osmotic pressures are presented in Table XII. The initial osmotic pressures of the feed and draw solutions were 20.8 and 101.9 bar, respectively, which makes their osmotic pressure difference approximately 80 bar. The final osmotic pressures of the feed and draw solutions were 98.7 and 64.1 bar, respectively. However, the osmotic pressure difference would then be of wrong direction and the feed solution would draw water from the draw solution. Figure 28 also shows that the process was working properly during the entire filtration time. Therefore, it can be concluded that the final osmotic pressure of the feed solution is unreasonably high which indicates that the calibration curve of lactic acid (pH = 3.5) in Figure 20 would rather curve down with higher concentrations instead of being linear.

Table XII. Estimated initial and final osmotic pressures of the feed and draw solutions.

Sample		Osmotic pressure, bar		
		Lactic acid	Glucose	Total
Feed solution	Initial	20.8		20.8
	Final	98.7	0.0	98.7
Draw solution	Initial		101.9	101.9
	Final	3.4	60.7	64.1

With the SEPA CF-FO module, the characterization of the Toray membrane before filtration gave a water flux of 37.4 L/(m^2 h) and the characterization after filtration 29.5 L/(m^2 h). The decrease in the water flux may be because the membrane was exposed to a temperature higher than its maximum operating temperature limit (45 °C) for a long time, which may have caused damage to the membrane.

8 TECHNO-ECONOMIC FEASIBILITY

The conventional production sequence of lactic acid by fermentation involves a complicated downstream processing scheme that can account for up to 50 % of the total production costs (Wasewar, 2005, p. 159). Therefore, the price of lactic acid is relatively high, which has hindered its usage in potential, large-volume markets. It is important to reduce the downstream processing costs by developing more economical and ecological solutions. FO has potential to serve as a low-cost concentration step in the recovery of lactic acid.

This feasibility study gives an idea for the integration of FO concentration into the downstream processing of lactic acid. In this suggested concept, glucose is used as draw solution and the need for regeneration of the diluted draw solution is eliminated by using it directly in the fermentation process. Also, the heat coming from the sterilization of the nutrients, glucose in this case, is utilized within the process. The purification and final concentration methods of lactic acid are not considered in detail in this study. The techno-economic feasibility of FO as a part of lactic acid production will be evaluated on the basis of this concept and the results obtained in the experimental section.

8.1 Incorporation of forward osmosis into the recovery of lactic acid

A preliminary concept for incorporation of FO concentration into the downstream processing of lactic acid is presented in Figure 31. The mass flow rates, concentrations, and temperatures of the streams were calculated to demonstrate the performance of the process. The results obtained in the concentration of lactic acid in the experimental part of this study were utilized in the calculations. The concept and the calculations are explained in more detail below.

In the concept, fermentation is carried out in batch mode. The lactic acid concentration of the broth after fermentation is assumed to be 8 %. The broth is heated by a series of heat exchangers to the temperature of 60 °C before entering the FO module. The heat available within the process is utilized, but it is necessary to heat the feed solution to the desired temperature by external energy.

The draw solution (60 % glucose) is first sterilized by autoclavation and is then cooled from the temperature of 100 °C to 30 °C before entering the FO module. The temperatures of the feed and draw solutions after heat exchangers were calculated from equations

$$T_{F,f} = T_{F,i} - \frac{\left(\dot{m}_{W(D)} C_{P,W} + \dot{m}_{Glc(D)} C_{P,Glc}\right) \times \left(T_{D,f} - T_{D,i}\right)}{\dot{m}_{W(F)} C_{P,W} + \dot{m}_{LA(F)} C_{P,LA}} \quad (29)$$

and

$$T_{D,f} = T_{D,i} - \frac{\left(\dot{m}_{W(F)} C_{P,W} + \dot{m}_{LA(F)} C_{P,LA}\right) \times \left(T_{F,f} - T_{F,i}\right)}{\dot{m}_{W(D)} C_{P,W} + \dot{m}_{Glc(D)} C_{P,Glc}}, \quad (30)$$

where $T_{D,i}$ and $T_{F,i}$ are the temperatures of draw (glucose) and feed (lactic acid) solutions before heat exchanger, respectively, $T_{D,f}$ and $T_{F,f}$ are the temperatures of draw and feed solutions after heat exchanger, respectively, $\dot{m}_{W(F)}$ and $\dot{m}_{LA(F)}$ are the mass flow rates of water and lactic acid in the feed solution, respectively, $\dot{m}_{W(D)}$ and $\dot{m}_{Glc(D)}$ are the mass flow rates of water and glucose in the draw solution, respectively, and $C_{P,W}$, $C_{P,LA}$, and $C_{P,Glc}$ are the specific heat capacities of water, lactic acid, and glucose, respectively.

The FO module is operated counter-currently. The average water flux across the membrane is assumed to be 12 L/(m^2 h) and the membrane area 4.0 m^2. The lactic acid and glucose concentrations in the feed and draw solutions after the module were calculated from equations

$$w_{LA,f} = \frac{w_{LA,i} \times \dot{m}_{F,i}}{\dot{m}_{F,i} - \dot{m}_W} \quad (31)$$

and

$$w_{Glc,f} = \frac{w_{Glc,i} \times \dot{m}_{D,i}}{\dot{m}_{D,i} + \dot{m}_W}, \quad (32)$$

where $w_{LA,f}$ and $w_{LA,i}$ are the final and initial lactic acid concentrations in the feed solution, $\dot{m}_{F,i}$ is the initial mass flow rate of the feed solution, $w_{Glc,f}$ and $w_{Glc,i}$ are the final and initial glucose concentrations in the draw solution, $\dot{m}_{D,i}$ is the initial mass flow rate of the draw solution, and $\dot{m}_W$ is the mass flow rate of water across the membrane. The rejection of lactic acid was assumed to be 100 % in the calculations.

The membrane module is assumed to be adiabatic. The feed solution temperature is assumed to remain constant throughout the module, while the draw solution is heated by the water permeating across the membrane. The draw solution temperature after the FO module was calculated from

$$T_{\mathrm{D,f}} = T_{\mathrm{D,i}} + \frac{\dot{m}_{\mathrm{W}} C_{\mathrm{P,W}} \times \left(T_{\mathrm{F,i}} - T_{\mathrm{D,i}}\right) + \left(\dot{m}_{\mathrm{W(D),i}} C_{\mathrm{P,W}} + \dot{m}_{\mathrm{Glc(D),i}} C_{\mathrm{P,Glc}}\right) \times \left(T_{\mathrm{D,i}} - T_{\mathrm{D,i}}\right)}{\left(\dot{m}_{\mathrm{W}} + \dot{m}_{\mathrm{W(D),i}}\right) \times C_{\mathrm{P,W}} + \dot{m}_{\mathrm{Glc(D),i}} C_{\mathrm{P,Glc}}}, \qquad (33)$$

where $\dot{m}_{\mathrm{W(D),i}}$ and $\dot{m}_{\mathrm{Glc(D),i}}$ are the initial mass flow rates of water and glucose in the draw solution, respectively.

The feed solution is concentrated from 8 % to 38 % in the FO module, and it continues to further concentration and purification. The draw solution, on its half, is diluted from 60 % to 15 % and heated from 30 °C to 55 °C in the module. The diluted draw solution is then cooled down to 30 °C and recycled to the fermenter.

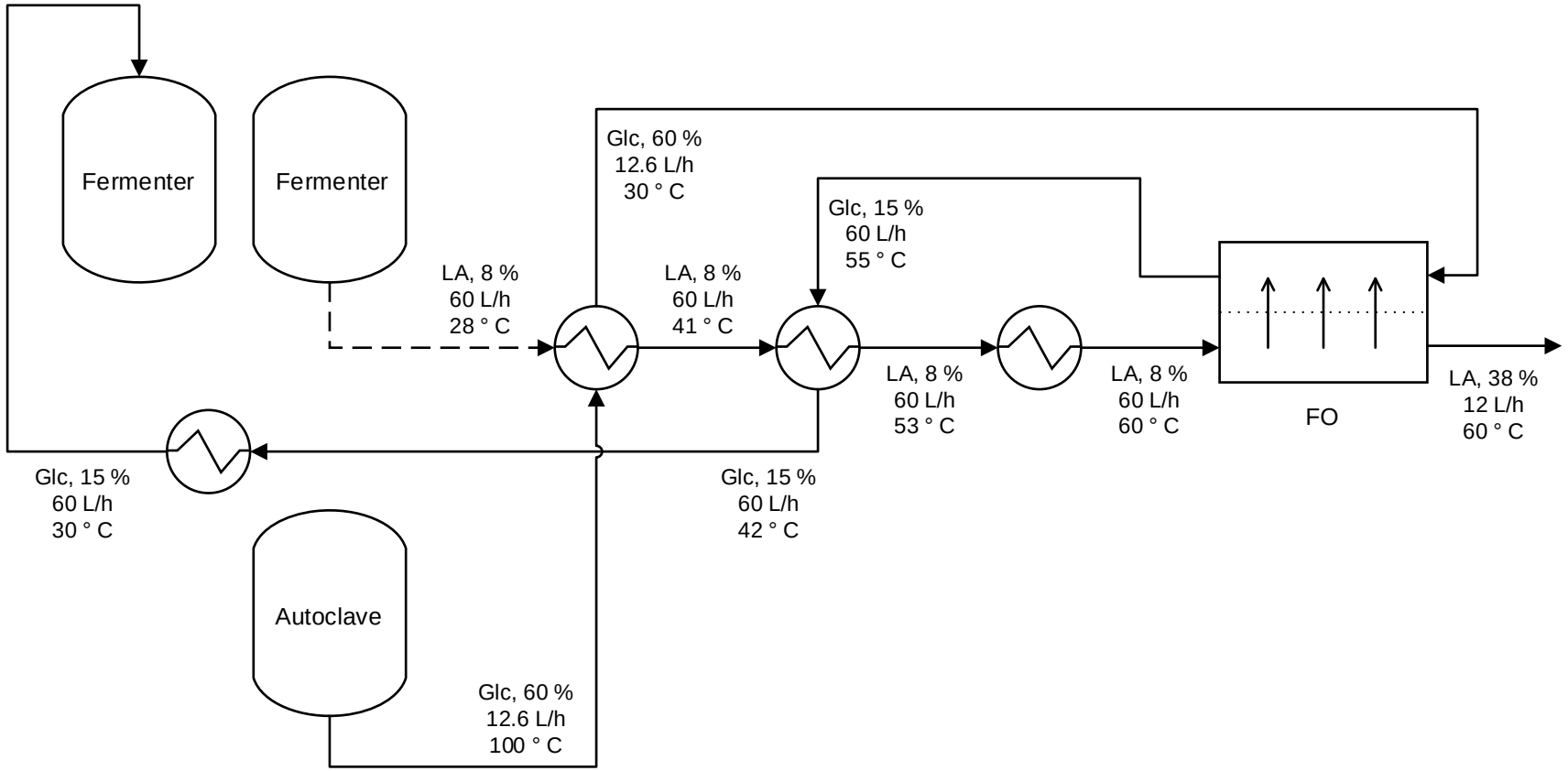

Figure 31. Incorporation of FO into downstream processing of lactic acid.

8.2 Feasibility of forward osmosis

The obtained water flux was 18.9 L/(m^2 h) at its maximum and declined to 4.6 L/(m^2 h) – being 12 L/(m^2 h) on average. The flux is of a reasonable magnitude considering the fact that the osmotic pressure of 8 % lactic acid (pH = 3.5) is high, nearly 25 bar. However, the water flux is related to the required membrane area and because the FO membranes are still expensive, the water flux should be higher to minimize the capital costs related to the membranes. When comparing FO to RO, higher water fluxes can be obtained by RO but with an extremely high operational pressure. For example, Li, Shahbazi, Williams, & Wan (2008) studied the concentration of lactic acid by a combination of NF and RO membranes. They used a fermentation broth with a lactic acid concentration of 5 % and pH of 5.5. In the first step, they separated lactic acid from the broth by NF and then concentrated the obtained lactic acid solution by RO in the second step. They used operational pressures of 4.1 and 5.5 MPa in the RO filtration and obtained permeate fluxes of ~28 L/(m^2 h) and ~38 L/(m^2 h), respectively.

A high water recovery of 84 %, corresponding to concentration by sixfold, was achieved in the concentration of lactic acid. However, the membrane did not reject all of lactic acid, and in reality, it was concentrated only by fourfold from 8 % to nearly 32 %. Because FO can be used to concentrate lactic acid only to a certain degree, further processing is needed to reach the final product concentration and purity.

The membrane presented a rejection of only 56.0 % for lactic acid and 99.9 % for glucose. A lot of product was lost in the permeate, and the final yield of lactic acid in the feed solution was 75 %. Therefore, the lactic acid rejection has to be significantly improved to enhance the feasibility of the process. It should also be noted that FO only concentrates the feed and does not remove any impurities. Instead, the low solute flux of glucose can even worsen the product purity. Further purification after FO is needed so that the final lactic acid product meets the prescribed quality specifications, an example of which is presented in Table IV.

The glucose solution is sterilized by autoclavation prior to its use in the process. The glucose solution exits the autoclave at a temperature of approximately 100 °C, the heat energy of which could be utilized within the process to heat up the feed solution. A higher feed solution temperature increases the water flux across the membrane, but at the expense of possibly lower lactic acid rejection. Apart from that, a lot of savings in energy costs can be

achieved if water used in the fermentation can be sufficiently sterilized by FO instead of being sterilized by autoclavation.

To sum up, FO is a low-energy process that could serve as a concentration step in the downstream processing of lactic acid. By utilizing the heat energy of the autoclaved, concentrated glucose solution within the process and recycling the diluted glucose to the fermentation, the energy requirements of the process can be reduced and FO becomes competitive compared to RO. Because FO operates under no hydraulic pressure, it has reduced operational costs. Research has also showed that FO possesses lower fouling and easier fouling removal than other pressure-driven membrane processes, which reduces the cleaning costs (Akther et al., 2015, p. 509). However, the lactic acid rejection should be significantly increased and the water flux somewhat enhanced to make the process attractive. Additional concentration and purification of lactic acid after FO is also needed to obtain the final product.

9 CONCLUSIONS

Recovery of lactic acid from a fermentation broth with the conventional techniques is very complicated and economically and ecologically unattractive. Therefore, alternative techniques are being developed and researched to enhance the downstream processing scheme. In this study, the use of FO for concentration of lactic acid was explored. The results will serve as a base for future studies.

The effect of feed and draw solution temperatures on FO water flux was studied with two different membranes (Aquaporin and Toray), when dilute lactic acid (pH = 3.5) was used as feed solution and concentrated glucose as draw solution. It was discovered that the feed solution temperature is the dominating factor affecting the water flux across the membrane: the higher its temperature, the higher the water flux. The finding is in agreement with theory and previous research. The effect of draw solution temperature, however, was membrane dependent. With Aquaporin an increase in draw solution temperature increased the water flux. With Toray, conversely, a decrease in draw solution temperature enhanced the water flux, thus making the transmembrane temperature difference favorable. Altogether, higher water fluxes were obtained using the Toray membrane, but the increasing water flux also indicated higher solute flux of lactic acid. The difference in the membrane performances can be explained by the different membrane structures.

The Toray membrane under the feed solution temperature of 60 °C and draw solution temperature of 40 °C was used to evaluate the performance of FO in concentration of lactic acid. A moderate water flux of 12 L/(m^2 h) and a water recovery of up to 84 % were obtained. However, the membrane presented a rejection of only 56 % for lactic acid under the studied conditions. Thus, the final yield of lactic acid in the feed solution was only 75 %, which would make the process infeasible on a larger scale. It is worth remarking that the membrane's recommended maximum operating temperature was exceeded in the filtration, which may have influenced the rejection.

In this study, a scheme for integration of FO into the downstream processing of lactic acid with aqueous glucose as the draw solution was proposed and its feasibility was evaluated. FO has potential to serve as an energy-efficient concentration step in the downstream processing of lactic acid. Because concentration is an essential part of the downstream processing, it is possible to integrate FO to nearly any of the existing schemes of lactic acid recovery; it can be used instead of evaporation, for example, to concentrate the lactic acid

solution prior to calcium hydroxide precipitation or esterification-hydrolysis methods. Because FO can concentrate lactic acid only to a certain degree and does not remove any impurities, further purification and concentration is needed to meet the quality requirements of the final product.

By recycling the diluted glucose solution to the fermentation vessel and utilizing it as the carbohydrate source of the fermentation, the energy-efficiency of the FO process can be enhanced by eliminating the requirement for the energy-intensive regeneration of the draw solution. As the glucose solution has to be sterilized by autoclavation, the energy requirements can be further reduced by utilizing the heat energy of the hot glucose solution in the heating of the feed solution. However, the crucial factor determining the feasibility of FO for concentration of lactic acid is the membrane's rejection towards lactic acid: it has to be significantly improved to make the process competitive compared to other techniques.

Future studies with a similar setup are suggested. In the few previous studies dealing with concentration of carboxylic acids by FO, the feed solution pH has been determined to affect the rejection of the acid. In this study, the membrane structure and increasing water flux also seemed to affect the acid rejection. Therefore, the effect of feed solution pH, filtration temperature, and membrane structure on the FO performance when concentrating lactic acid are worth studying in more detail to find more optimum operating conditions. It is also recommended to study the concentration of a real, pretreated fermentation broth in addition to a single-component model solution. Furthermore, because the selection of commercial FO membranes is currently very limited, development and research of new membranes with more optimized structures is needed to improve the trade-off between high water flux and selectivity.

10 SUMMARY

The objective of this study was to evaluate feasibility of FO for concentration of lactic acid from a fermentation broth. The literature review described briefly the properties, applications, and traditional production processes of lactic acid. A focus was set on reviewing the most commonly used recovery and purification techniques in the downstream processing of lactic acid and introducing the process of FO. The literature considering FO for concentration of carboxylic acids was reviewed, and the process was compared to the existing technologies used for concentration of lactic acid.

The use of FO can offer lower energy consumption because of operation under no or low hydraulic pressure. For the same reason, FO also possesses significantly lower fouling than pressure-driven membrane operations. Furthermore, FO modules are flexible in scaling, easy to operate and incorporate into the downstream processing. The two main issues of the process, however, are the energy-intensive regeneration of the draw solution and ICP that can significantly decrease the filtration performance by lowering the water flux across the membrane.

A concept for utilizing FO in the concentration of lactic acid was proposed in this study. It included using concentrated glucose as the draw solution and utilizing it as the carbohydrate source of the fermentation after FO filtration. That way, the energy-intensive regeneration of the diluted draw solution could be eliminated, thus enhancing the energy-efficiency of the process. As the glucose solution has to be sterilized by autoclavation, the energy requirements could be further reduced by utilizing the heat energy of the hot glucose stream within the process.

In the experimental part, concentration of lactic acid by FO with glucose as draw solution was studied. First, experiments with varying feed and draw solution temperatures were carried out on two different membranes to minimize the ICP effects and find the maximum water flux. The feed solution temperature was identified as the dominating factor affecting the water flux across the membrane: the higher its temperature, the higher the water flux. There was a significant difference in the performance of the two membranes.

The most favorable feed–draw solution temperature combination and membrane were used to concentrate lactic acid from an aqueous solution. In this filtration, lactic acid was concentrated by fourfold from an initial concentration of 8 % to 32 %. A moderate water flux of

12 L/(m^2 h) on average and a water recovery rate of up to 84 % were obtained. However, the solute flux of lactic acid during filtration was very high because the membrane presented a poor rejection of 56 % for lactic acid, for which reason a process with such conditions would be infeasible on a larger scale. FO has still potential to be a viable treatment option for concentration of lactic acid but further research is needed to optimize the filtration conditions in terms of feed solution pH, filtration temperature, and membrane selection.

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APPENDIX I. EXPERIMENTAL DATA

Properties of lactic acid and glucose solutions

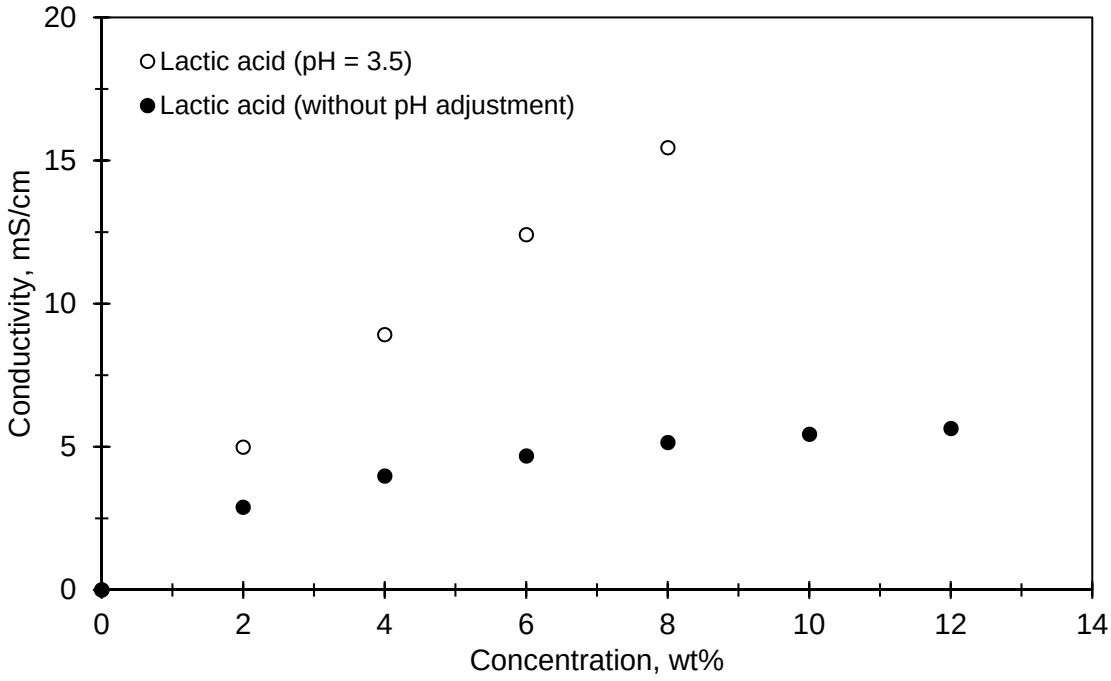

Figure A-1. Conductivity of lactic acid without pH adjustment and with its pH adjusted to 3.5.

Effect of feed and draw solution temperatures on water flux

Temperature:	40–40 °C
Feed solution:	8 % lactic acid (pH = 3.5)
Draw solution:	60 % glucose

Table A-I. Properties of the initial and final feed and draw solution samples.

Membrane		Degrees Brix, °Bx		pH, –		Conductivity, µS/cm	
		W	Glc	W	Glc	W	Glc
Aquaporin	Initial	0.0	59.9	5.36	3.98	0.7	3.4
	Final	0.0	52.0	4.02	3.88	30.8	11.6
Toray	Initial	0.0	59.9	5.87	4.15	0.5	3.5
	Final	0.0	48.0	5.43	4.34	2.4	11.4

Table A-II. Average water flux in the FO filtrations.

Membrane	Average water flux, $L/(m^2\ h)$
Aquaporin	11.5
Toray	17.6

Membrane:	Aquaporin
Feed solution:	8 % lactic acid (pH = 3.5)
Draw solution:	60 % glucose

Table A-III. Properties of the initial and final feed and draw solution samples.

Temperature, °C		Degrees Brix, °Bx		pH, –		Conductivity, µS/cm	
		LA	Glc	LA	Glc	LA	Glc
20–20	Initial	6.7	60.0	3.47	4.01	14860	3.0
	Final	6.6	56.4	3.42	3.84	14750	7.3
20–40	Initial	6.7	60.0	3.47	4.14	16140	3.4
	Final	6.7	57.0	3.22	3.76	15680	5.7
20–60	Initial	6.7	60.0	3.50	4.14	16150	3.2
	Final	6.7	54.9	3.45	3.86	15960	9.4
40–25	Initial	6.8	60.0	3.49	4.06	15700	2.8
	Final	6.9	55.9	3.45	3.60	15760	10.7
40–40	Initial	6.8	59.9	3.51	4.14	16300	3.2
	Final	7.0	55.0	3.46	3.59	16440	12.2
40–60	Initial	6.7	59.9	3.58	3.96	15820	3.4
	Final	6.8	54.9	3.41	3.62	16030	10.9
60–30	Initial	6.8	60.0	3.52	4.10	15980	3.0
	Final	7.0	53.0	3.53	3.39	16240	21.2
60–40	Initial	6.7	59.9	3.50	3.87	15580	3.7
	Final	6.9	54.0	3.48	3.40	15850	20.8
60–60	Initial	6.7	59.9	3.52	4.21	15290	3.0
	Final	7.1	52.8	3.49	3.38	15750	23.5

Table A-IV. Average water flux in the FO filtrations.

Temperature, °C	Average water flux, L/(m^2 h)
20–20	2.1
20–40	2.5
20–60	3.2
40–20	4.6
40–40	5.4
40–60	5.9
60–30	8.0
60–40	8.8
60–60	10.0

Membrane:	Toray
Feed solution:	8 % lactic acid (pH = 3.5)
Draw solution:	60 % glucose

Table A-V. Properties of the initial and final feed and draw solution samples.

Temperature, °C		Degrees Brix, °Bx		pH, –		Conductivity, µS/cm	
		LA	Glc	LA	Glc	LA	Glc
20–20	Initial	6.7	59.9	3.46	4.06	15110	3.6
	Final	6.7	55.0	3.39	3.63	14680	36.7
20–40	Initial	6.7	60.0	3.47	4.03	14910	3.0
	Final	6.7	55.4	3.30	3.45	14690	43.4
20–60	Initial	6.7	59.9	3.49	3.98	15500	3.0
	Final	6.7	56.4	3.39	3.53	15220	47.1
40–25	Initial	6.6	60.0	3.49	4.06	14740	3.3
	Final	6.8	52.9	3.40	3.57	14550	94.5
40–40	Initial	6.7	59.9	3.50	4.22	15880	3.3
	Final	6.8	53.9	3.40	3.52	15910	90.7
40–60	Initial	6.7	59.9	3.47	3.98	14690	2.9
	Final	6.8	54.9	3.48	3.53	14640	91.0
60–30	Initial	6.8	59.9	3.47	4.04	16390	3.4
	Final	7.4	48.0	3.43	3.35	17410	159.8
60–40	Initial	6.7	60.0	3.46	4.07	15740	3.1
	Final	7.1	51.0	3.39	3.43	16120	129.4
60–60	Initial	6.7	60.0	3.49	4.03	15130	2.9
	Final	6.9	52.0	3.43	3.40	15250	180.9

Table A-VI. Average water flux in the FO filtrations.

Temperature, °C	Average water flux, L/(m^2 h)
20–20	3.8
20–40	3.9
20–60	3.7
40–20	8.8
40–40	7.3
40–60	7.1
60–30	19.2
60–40	14.3
60–60	13.8

Concentration of lactic acid

Membrane:	Toray
Feed solution:	8 % lactic acid (pH = 3.5)
Draw solution:	60 % glucose

Initial mass of feed solution: 3040 g
Initial mass of draw solution: 3839 g
Mass of permeate: 2489 g

Table A-VII. Initial and final lactic acid and glucose concentrations of the feed and draw solutions.

Sample		Concentration, g/L	
		Lactic acid	Glucose
Feed solution	Initial	68.95	
	Final	339.6	2.8
Draw solution	Initial		772.37
	Final	14.14	416.28

Table A-VIII. Properties of the initial and final feed and draw solution samples.

Temperature, °C		Degrees Brix, °Bx		pH, –		Conductivity, µS/cm	
		LA	Glc	LA	Glc	LA	Glc
60–40	Initial	6.7	59.9	3.47	4.06	15530	3.4
	Final	32.3	36.3	3.50	3.46	24100	1575.0

APPENDIX II. CALCULATION EXAMPLES

Equation (20): Water flux in concentration of lactic acid at t_1 = 0 min

$$J_W = \frac{\Delta V}{A_m \Delta t} = \frac{\left[m_F(t_1) - m_F(t_2) \right] / \rho_W}{A_m (t_2 - t_1)}$$

$$= \frac{(2.532 - 2.460)\ \text{kg} / 0.983\ \text{kg/L}}{0.014\ \text{m}^2 \times \frac{(20 - 0)\ \text{min}}{60\ \text{min/h}}} = 15.7\ \text{L}/(\text{m}^2\ \text{h}),$$

where $m_F(t)$ is the mass of the feed solution at time t, t is the time, and ρ_W is the density of water.

Equation (21): Water recovery rate

$$WR = \frac{\Delta V}{V_{F,i}} \times 100\ \% = \frac{\Delta m_F / \rho_W}{m_{F,i} / \rho_F}$$

$$= \frac{(2.533 - 0.044)\ \text{kg} / 0.983\ \text{kg/L}}{3.040\ \text{kg} / 1.017\ \text{kg/L}} \times 100\ \% = 84.7\ \%,$$

where Δm_F is the change in the mass of the feed solution, $m_{F,i}$ is the initial mass of the feed solution, and ρ_F is the density of the feed solution.

Equation (22): Concentration factor

$$CF = \frac{1}{1 - \frac{WR}{100\ \%}} = \frac{1}{1 - \frac{84.7\ \%}{100\ \%}} = 6.5$$

Equation (23): Forward solute flux of lactic acid

$$J_{LA} = \frac{\left(V_{D,i} + \Delta V\right) \times C_{LA(D),f}}{A_m \Delta t} = \frac{\left(\frac{m_{D,i}}{\rho_D} + \frac{\Delta m_F}{\rho_W}\right) \times C_{LA(D),f}}{A_m \Delta t}$$

$$= \frac{\left(\frac{3.839\ \text{kg}}{1.323\ \text{kg/L}} + \frac{(2.533 - 0.044)\ \text{kg}}{0.983\ \text{kg/L}}\right) \times 14.14\ \text{g/L}}{0.014\ \text{m}^2 \times 16.33\ \text{h}}$$

$$= \frac{\left(2.902\ \text{L} + 2.532\ \text{L}\right) \times 14.14\ \text{g/L}}{0.014\ \text{m}^2 \times 16.33\ \text{h}} = 336.0\ \text{g/(m}^2\ \text{h)},$$

where $m_{D,i}$ is the initial mass of the draw solution and ρ_D is the density of the draw solution.

Equation (24): Reverse solute flux of glucose

$$J_{Glc} = \frac{\left(V_{F,i} - \Delta V\right) \times C_{Glc(F),f}}{A_m \Delta t} = \frac{\left(\frac{m_{F,i}}{\rho_F} - \frac{\Delta m_F}{\rho_W}\right) \times C_{Glc(F),f}}{A_m \Delta t}$$

$$= \frac{\left(\frac{3.040\ \text{kg}}{1.017\ \text{kg/L}} - \frac{(2.533 - 0.044)\ \text{kg}}{0.983\ \text{kg/L}}\right) \times 2.80\ \text{g/L}}{0.014\ \text{m}^2 \times 16.33\ \text{h}}$$

$$= \frac{\left(2.989\ \text{L} - 2.532\ \text{L}\right) \times 2.80\ \text{g/L}}{0.014\ \text{m}^2 \times 16.33\ \text{h}} = 5.6\ \text{g/(m}^2\ \text{h)}$$

Equation (25): Rejection of lactic acid

$$R_{LA} = \frac{C_{LA(F),i} - \left(\frac{C_{LA(D),f} \left(V_{D,i} + \Delta V \right)}{\Delta V} \right)}{C_{LA(F),i}} \times 100\ \%$$

$$= \frac{68.95\ \text{g/L} - \left(\frac{14.14\ \text{g/L} \times \left(2.902\ \text{L} + 2.532\ \text{L} \right)}{2.532\ \text{L}} \right)}{68.95\ \text{g/L}} \times 100\ \% = 56.0\ \%$$

Equation (26): Rejection of glucose

$$R_{Glc} = \frac{C_{Glc(D),i} - \left(\frac{C_{Glc(F),f} \left(V_{F,i} - \Delta V \right)}{\Delta V} \right)}{C_{Glc(D),i}} \times 100\ \%$$

$$= \frac{772.37\ \text{g/L} - \left(\frac{2.8\ \text{g/L} \times \left(2.989\ \text{L} - 2.532\ \text{L} \right)}{2.532\ \text{L}} \right)}{772.37\ \text{g/L}} \times 100\ \% = 99.9\ \%$$

Equation (27): Yield of lactic acid in the feed solution

$$Y_{LA,F} = \frac{C_{LA(F),f} \times \left(V_{F,i} - \Delta V \right)}{C_{LA(F),i} \times V_{F,i}} \times 100\ \%$$

$$= \frac{339.6\ \text{g/L} \times \left(2.989\ \text{L} - 2.532\ \text{L} \right)}{68.95\ \text{g/L} \times 2.989\ \text{L}} \times 100\ \% = 75.4\ \%$$

Equation (28): Yield of lactic acid in the draw solution

$$Y_{LA,D} = \frac{C_{LA(D),f} \times \left(V_{D,i} + \Delta V\right)}{C_{LA(F),i} \times V_{F,i}} \times 100\ \%$$

$$= \frac{14.14\ \ g/L \times \left(2.902\ L + 2.532\ L\right)}{68.95\ \ g/L \times 2.902\ L} \times 100\ \% = 37.3\ \%$$