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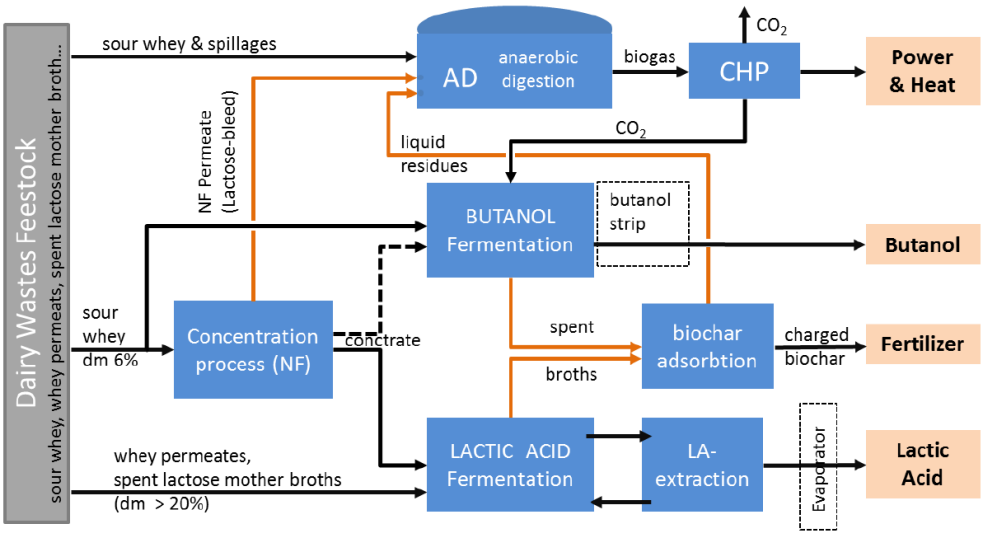
“UP-WHEY”: Combined biomass valorisation to bioenergy, industrial feedstocks and bio-based products



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Zusammenfassung

Um Produkte, die bisher aus fossilen Rohstoffen gewonnen worden sind, zu subtituieren, rückt auch die Valorisierung von Abfall- und Seitenströmen in den Fokus. Insbesondere den mit organischen Inhaltsstoffen und interessaten Vorprodukten versehenen Seitenströmen aus Molkereien kommt hier besondere Bedeutung zu und wurde im Rahmen eines Gemeinschaftprojektes mit österreichischen Partner näher untersucht.

Im von der Hochschule für Life Sciences (HLS) der Fachhochschule Nordwestschweiz in Muttenz (BL) untersuchten Projektteil wurde eine Methodik zur Identifizierung, Bewertung und Optimierung eines geeigneten Membranextraktionssystems (ME) für die Extraktion von Milchsäure (LA) aus LA-haltigen Strömen aufgezeigt, die von einer Modelllösung bis hin zu Fermentationsbrühen reicht. Es wurde festgestellt, dass ein Lösungsmittel bestehend aus 20 Gew.-% Trioctylamin (TOA) in Decanol für die ME-Extraktion von LA geeignet war und eine ausreichende LA-Extraktionsrate und eine geringe toxische Wirkung auf die spezifischen Milchsäurebakterien Lactobacillus Plantarum DSMZ 264 zeigte (die entsprechenden Experimente wurden am Leibniz-Institut für Agrartechnik und Bioökonomie - ATB in D-Potsdam durchgeführt, während alle anderen Experimente und Simulationen an der HLS, durchgeführt wurden.

Durch die Kenntnis eines geeigneten ME-Systems und die Optimierung seiner Betriebsbedingungen wie Lösungsmittelzusammensetzung, Durchflussrate und Extraktionstemperatur wurde die Leistung der In-situ-LA-Membranextraktion experimentell erfasst.

Durch in-situ Entfernung der während der Fermentation gebildeten Milchsäure ist neben dem Wegfall der für die pH-Stabilisierung und Milchsäuregewinnung notwendigen Chemikalien sowie dank der emulsionsfreien Extraktion nicht mehr notwendigen, energieintensiven Zentrifugation auch ein kontinuierlicher Fermentationsbetrieb denkbar. So ist es beispielsweise für einen 20 m^3 Fermenter mit einer LA-Produktion von 0.3 g/L^*h^{-1} mit rund 320 m^2 Membranfläche möglich, die LA-Konzentration über einen längeren Zeitraum bei konstant 30 g/L zu halten – was bei einem Betrieb von 18 Tagen zu rund 2.9 Tonnen LA führt.

Selbst in Batch-Fahrweise konnte durch die in-situ Extraktion von Milchsäure aus Fermentationsbrühen die LA-Produktion während der Fermentation um das etwa 3,75-fache im Vergleich zur konventionellen LA-Batch-Fermentation erhöht werden.

Die hier vorgeschlagene und entwickelte Technologie wurde für die Implementierung in zwei spezifischen Seitenströmen der beteiligten österreichischen Industrien evaluiert. Die Ergebnisse dieser Bewertung zeigten, dass die LA-Membranextraktion sehr wohl in der Lage ist, Milchsäure, die fermentativ mit Seitenströme von Molkereien betrieben wird, erfolgreich zu extrahieren und damit die organische Belastung dieser Abwässer zu reduzieren. Dieser Ansatz ist somit im gleichen Masse auch interessant für die in diesem Sektor tätigen Schweizer Unternehmen.

Neben Milchsäure wurde auch die Membranextraktion anderer Carbonsäuren wie der Mandel-, Itacon- und Bernsteinsäure aus Testlösungen untersucht. Auch hier zeigte sich die prinzipielle Machbarkeit des Verfahrens auf – mit teilweise auch höheren Gesamtstoffdurchgangskoeffizienten als bei der Milchsäure, womit sich weitere Anwendungsgebiete für dieses Verfahren aufzeigten.

Summary

In order to substitute products that have previously been obtained from fossil raw materials, the focus is also on the valorization of waste and side streams. In particular, the side streams from dairies containing organic ingredients and interesting preliminary products are of particular importance and were examined in more detail as part of a joint project with Austrian partners.

As part of the current general drive to substitute products previously obtained from fossil raw materials, there is a growing focus on the valorization of waste and side streams. Side streams from dairies, containing organic ingredients and interesting preliminary products, are of particular

importance, and were examined in detail as part of a joint project with Austrian partners and the University of Applied Sciences and Arts Northwestern Switzerland (FHNW).
The project investigation by the FHNW School of Life Sciences (HLS) in Muttenz (BL) demonstrated a methodology to identify, evaluate and optimize a membrane extraction (ME) system suitable for extracting lactic acid (LA) from streams ranging from a model solution to fermentation broths. It was found that a solvent consisting of 20 wt% trioctylamine (TOA) in decanol was suitable for the ME of LA and showed a sufficient LA extraction rate, as well as a low toxic effect on the specific lactic acid bacterium Lactobacillus Plantarum DSMZ 264. The latter experiments were performed at the Leibniz Institute for Agricultural Engineering and Bioeconomy - ATB in D-Potsdam, while all other experiments and simulations were performed at the HLS.

By knowing a suitable ME system and optimizing its operating conditions such as solvent composition, flow rate and extraction temperature (20 wt% of TOA in decanol, 20 kg/h flow rate for each phase, and at an extraction temperature of 25°C), the performance of in situ LA membrane extraction was experimentally recorded.

By in-situ removal of the lactic acid formed during fermentation, continuous fermentation operation is also conceivable, in addition to eliminating the chemicals necessary for pH stabilization and lactic acid production and, thanks to the emulsion-free extraction, the energy-intensive centrifugation that is no longer necessary. For example, for a 20 m^3 fermenter with an LA production of 0.3 g/L^*h^{-1} with around 320 m^2 of membrane surface, it is possible to keep the LA concentration at a constant 30 g/L over a longer period of time - which is the case with an operation of 18 days around 2.9 tons of LA.

Even in batch mode, the in-situ extraction of lactic acid from fermentation broths increased LA production during fermentation by approximately 3.75 times compared to conventional LA batch fermentation.

The technology proposed and developed here was evaluated for implementation in two specific side streams of the Austrian industries involved. The results of this evaluation showed that LA membrane extraction is very capable of successfully extracting lactic acid, which is fermented with side streams from dairies, and thus reducing the organic contamination of these wastewaters. This approach is therefore equally interesting for Swiss companies operating in this sector.

The final step was to evaluate the performance of ME on fermentable carboxylic acids such as mandelic, itaconic and succinic acids, where the in situ ME approach could potentially be applied. This leaves the window open for further applications of the technology.

Résumé

Afin de substituer les produits obtenus jusqu'à présent à partir de matières premières fossiles, la valorisation des déchets et des flux secondaires est également au centre de l'attention. Les flux secondaires des laiteries qui contiennent des substances organiques et des produits intermédiaires intéressants revêtent une importance particulière et ont été étudiés de plus près dans le cadre d'un projet commun avec des partenaires autrichiens.
Dans la partie du projet étudiée par la Hochschule für Life Sciences (HLS) de la Fachhochschule Nordwestschweiz à Muttenz (BL), une méthode d'identification, d'évaluation et d'optimisation d'un système d'extraction à membrane (ME) approprié pour l'extraction d'acide lactique (LA) à partir de flux contenant du LA a été mise en évidence, allant d'une solution modèle à des bouillons de fermentation. Il a été constaté qu'un solvant composé de 20 % en poids de trioctylamine (TOA) dans du décanol convenait pour l'extraction ME de LA et présentait un taux d'extraction de LA suffisant et un faible effet toxique sur les bactéries spécifiques de l'acide lactique Lactobacillus Plantarum DSMZ 264 (les expériences correspondantes ont été réalisées à l'Institut Leibniz pour la technique agricole et la bioéconomie - ATB à D-Potsdam, tandis que toutes les autres expériences et simulations ont été réalisées à l'HLS,.

La connaissance d'un système ME approprié et l'optimisation de ses conditions de fonctionnement, telles que la composition du solvant, le débit et la température d'extraction, ont permis de mesurer expérimentalement les performances de l'extraction par membrane LA in situ.
L'élimination in situ de l'acide lactique formé pendant la fermentation permet non seulement de supprimer les produits chimiques nécessaires à la stabilisation du pH et à l'extraction de l'acide lactique, mais aussi d'envisager un fonctionnement continu de la fermentation grâce à l'extraction sans émulsion, qui ne nécessite plus de centrifugation à forte consommation d'énergie. Par exemple, pour un fermenteur de 20 m3 avec une production de LA de 0,3 g/L*h-1 et une surface de membrane d'environ 320 m2, il est possible de maintenir la concentration de LA à un niveau constant de 30 g/L pendant une période prolongée - ce qui permet d'obtenir environ 2,9 tonnes de LA pour un fonctionnement de 18 jours.
Même en mode batch, l'extraction in situ de l'acide lactique des bouillons de fermentation a permis d'augmenter la production de LA pendant la fermentation d'environ 3,75 fois par rapport à la fermentation batch conventionnelle de LA.

La technologie proposée et développée ici a été évaluée pour être mise en œuvre dans deux flux secondaires spécifiques des industries autrichiennes impliquées. Les résultats de cette évaluation ont montré que l'extraction par membrane LA est tout à fait capable d'extraire avec succès l'acide lactique qui est fermenté avec des flux secondaires de laiteries et de réduire ainsi la charge organique de ces effluents. Cette approche est donc tout aussi intéressante pour les entreprises suisses actives dans ce secteur.
Outre l'acide lactique, l'extraction par membrane d'autres acides carboxyliques tels que les acides amylique, itaconique et succinique a également été étudiée à partir de solutions tests. Là aussi, la faisabilité de principe du procédé a été démontrée, avec parfois des coefficients de transfert de masse totale plus élevés que pour l'acide lactique, ce qui a permis d'identifier d'autres domaines d'application pour ce procédé.

Main findings

Attached are brief findings of this project as an executive summary of the intended deliverables:

- It could be shown, that with the use of membrane contactors, a direct capturing of lactic acid from fermentation broth is possible and feasible from a technology point of view. For this process, the fermentation broth does not need to be mixed with the solvents and thus not separated after the extraction, e.g. with energy consuming centrifugation and no formation takes place
- In both 2 and 5 l scale it could be shown that with sweet whey as a feedstock, lactic acid could be produced in a fermentation process and the lactic acid could be extracted with membrane contactors in-situ. The membranes did not suffer from any clogging nor fouling and could be cleaned after the extraction without any residual. It was however observed that the production rate of lactic acid from sweet dairy whey is with 0.3 $g/l^{*}h^{-1}$ below expectations (3-5 $g/l^{*}h^{-1}$), because the conditions (such as nutrient and substrate composition, ash content, pH, etc.) provided by the whey medium differ from those of commercial media (such as MRS), which are perfectly prepared for optimal LA bacteria growth..
- A sound parameter study was carried out in order to further optimize the extraction process with respect to the reduction of required membrane area to a minimum. It could be shown that with optimized process parameters the required membrane area could be reduced from up to 2500 m^2/m^3 Fermentation volume to just 9.2 m^2/m^3.
- Other carboxylic acids than lactic acids were investigated with membrane contactors, too. It could be shown that for higher value carboxylic acids mandelic acid, the mass transfer per m^2 membrane area is 3-5x higher than for lactic acid. Thus, direct capturing of these carboxylic acids from fermentation broth are an interesting process technology, also from an economic point of view.

Contents

Abbreviations

DES	Deep Eutectic Solvent	
DoE	Design of experiment	
LA	Lactic acid	
ME	Membrane extraction	
PTFE	Polytetrafluorethylene	
TOA	Tri-n-octylamine	
Symbols		
A	Membrane area	[m^2]
C	Concentration	[g/m^3]
ΔC	Difference of LA concentration	[g/m^3]
D	Lactic acid distribution coefficient	[-]
Kov	Overall mass transfer coefficient	[m/s]
m	Mass of solute	[g]
$\dot{m}$	Mass transfer rate	[g/s]
S:F	Solvent-to-feed ratio	[-]

1 Introduction

1.1 Background information and current situation

The demand for bio-based chemicals has increased tremendously in the last couple of years [1]. Beside fermentation, the valorisation of side-streams becomes a more and more interesting source for (platform) chemicals. The “up-whey” project focuses on dairy waste feedstocks (=whey) for the production of Butanol, Fertilizer and Lactic Acid as a representative of a wider group of other carboxylic acids [2–5].

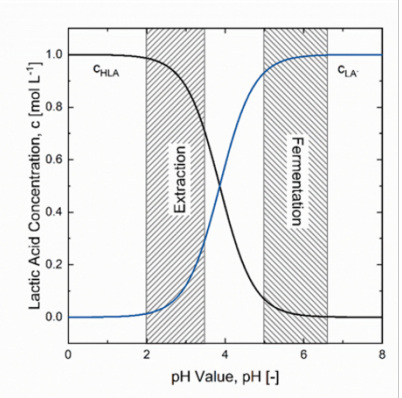
The dairy sector is an essential financial sector in Europe. According to the European Dairy Association report in 2016, more than 12000 dairy companies in the EU27 regions are processing $160 \cdot 10^6$ tons (Megatons=Mt) milk for products. Cheese production was at 10 Mt, delivering approximately 4 Mt whey as a co-product. Exports of whey outside EU were at 30-55 Mt. More detailed, a distinction is made between sweet and sour whey, containing different amounts and concentration of e.g. lactic acid (see below). However, no statistical data on sour whey is available. Assuming a reasonable share of 35%, a total 1.3Mt of sour whey result, which contains approx. 0.9 Mt lactose and 0.2 Mt lactic acid, representing a volume of approximately $21*10^6$ m^3.

Both dairy and cheese production are an important sector of the Swiss economy, too. Thus, research and development for the valorisation of dairy waste streams is of greater importance for the economy in the Alpine region.

It is described in literature [1–7] that Lactic acid can be extracted and further purified by liquid-liquid extraction (LLE). LLE is a technology, where a dissolved component (or more) will be extracted from one liquid phase into another liquid phase. The two liquid phases, however, may not mix into each other. These requirements are fulfilled e.g. with water and solvent as liquid phases.

During LLE however, formation of stable emulsions may occur, which needs to be broken by further treatment like centrifugation. Thus, additional equipment as well as energy is required for this purpose. Additionally, most of the solvents used for the liquid-liquid extraction are harmful to the microorganisms in the fermentation broth. Thus, the extraction process cannot be carried out during the fermentation and further effort is required to maintain the fermentation process at a certain productivity level: In order to avoid a pH-decrease in the fermentation broth due to the formation of Lactic *acid*, Calcium hydroxide $Ca(OH)_2$ has to be added to the process which leads in parallel to a precipitation of lactate. At the end of the fermentation, Sulfuric acid (H_2SO_4) is required to release the lactic acid from the lactate. The remaining Calcium hydroxide and Sulfuric acid then reacts to gypsum. Thus, beside the requirement for process chemicals (~450 kg $Ca(OH)_2$ and 500 kg H_2SO_4 per ton lactic acid, for broth neutralization) the co-”production” of gypsum is a draw-back of the fermentative production of lactic acid.

For LLE of lactic acid from fermentation broth, a pH-shift would be beneficial, since the microorganisms normally operate well in a pH range from 5-7, whereas the extraction of lactic acids is preferably carried out at a pH < 4 (see Figure 1). However, this pH-shift would require extra chemicals and effort. Thus, the lactic acid LLE is carried out at the same pH as the fermentation.



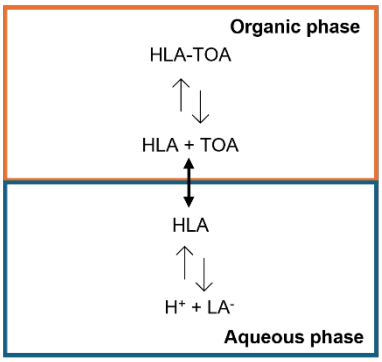


Figure 1. Optimum pH concentration for both Lactic acid extraction and fermentation and LA mass transport mechanism during membrane (reactive-)extraction.

Using so-called membrane contactors, lactic acid can be extracted “in-situ” from the fermentation broth via a by-pass installation (see Figure 2). This approach avoids the requirement for the chemicals ($Ca(OH)_2$ and H_2SO_4) for the process stability, reduces the contact time of the fermentation broth with the (partially toxic to microorganisms) solvents and do not require any phase mixing nor phase separation before and after the extraction.

In addition, this approach principally allows a continuous fermentation rather than a batch operation.

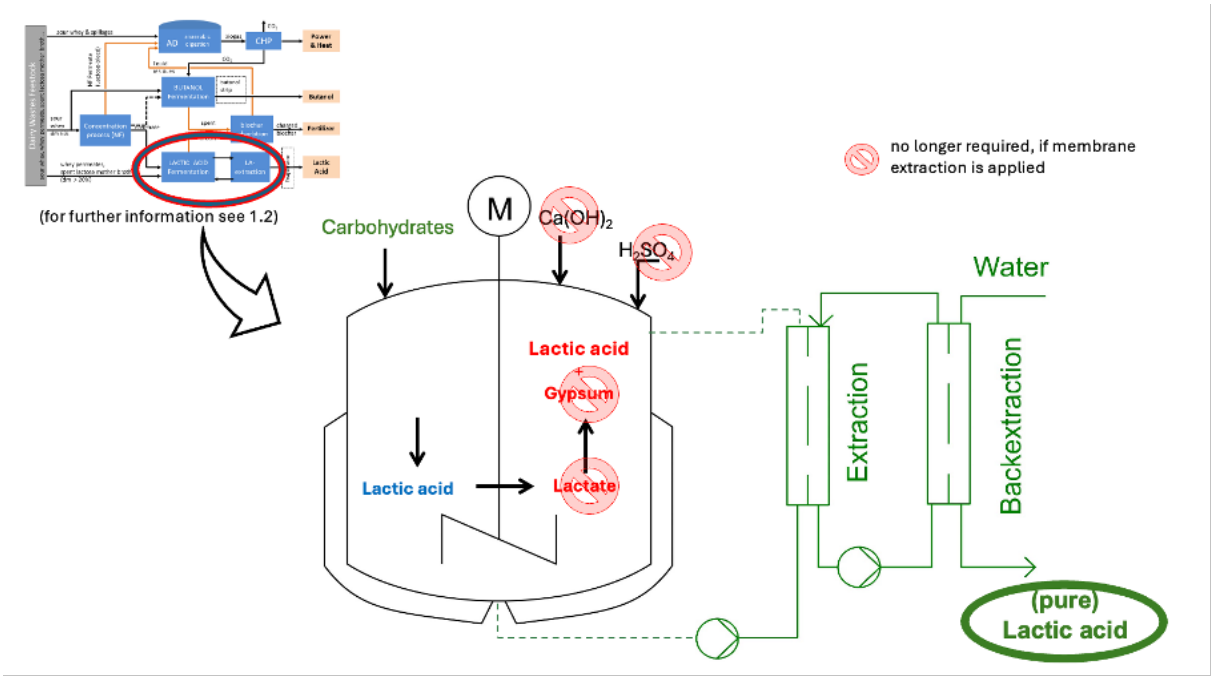


Figure 2. Principle of capturing (=direct extraction) and polishing of Lactic acid from fermentation with Membrane contactors (Extraction & Back extraction step).

Additionally, lactic acid is already available in sour whey streams at lower concentrations. Thus, this side streams needs to be pre-concentrated (e.g. by nanofiltration), before any reasonable liquid-liquid extraction process are economical feasible.

Membrane contactors are an interesting alternative to conventional liquid-liquid extraction. This technology was first described in depth in 1984 by Kiani et al. (Lit) and is a major research area of the Group of Prof. Riedl at HLS in Muttenz (BL).
Membrane contactors support the contact between to fluid phases by immobilizing the phase interface at the membrane pore`s exit. Thus, the phases do not need to be mixed and thus no separated after the extraction. In many cases, this approach thus avoids the formation of stable emulsions, which is disadvantageous for the mass transfer, the process stability and finally for the energy required for the phase separation afterwards, which in turn can only be carried out by centrifugation. The principle of membrane extraction is shown in Figure 3.

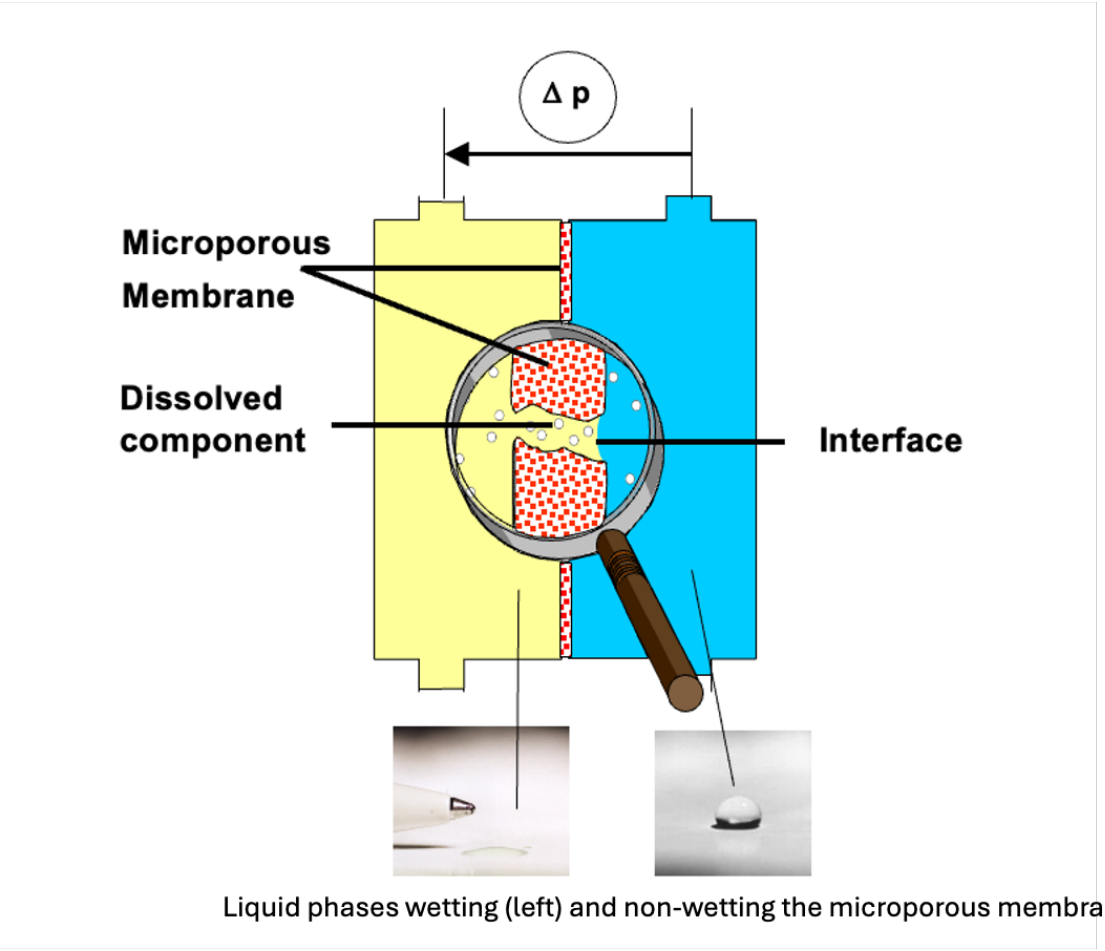


Figure 3. Principle of membrane extraction with membrane contactors.

So far, (industrial) references of membrane extraction are rare, mainly due to the unavailability of membrane modules which fit to challenging requirements like processing fermentation broth with suspended solids and a higher tendency to block porous structure. In recent past, $MemO_3$ GmbH (Möhlin, AG) however succeeded to supply these kinds of robust membranes in industrial size and standards. Therefore, further investigation in the use of these membrane contactors for the direct extraction of lactic acid is a promising approach to overcome stronger limitations during the state-of-the-art valorisation of biomass.

1.2 Purpose of the project

As part of the ERA-Net Project “Up whey” - Upstream processing of lactose whey for bulk chemicals and energy production together with Austrian Partners from Industry and Academia (TU Graz, TU Wien), the work packages for HLS were to investigate an innovative downstream process for a direct capturing of Lactic Acid from fermentation broth by means of membrane contactors (see Figure 3).
The Era-Net project is shown in Figure 4 as a glance in with the research area for which HLS is responsible is marked in red.

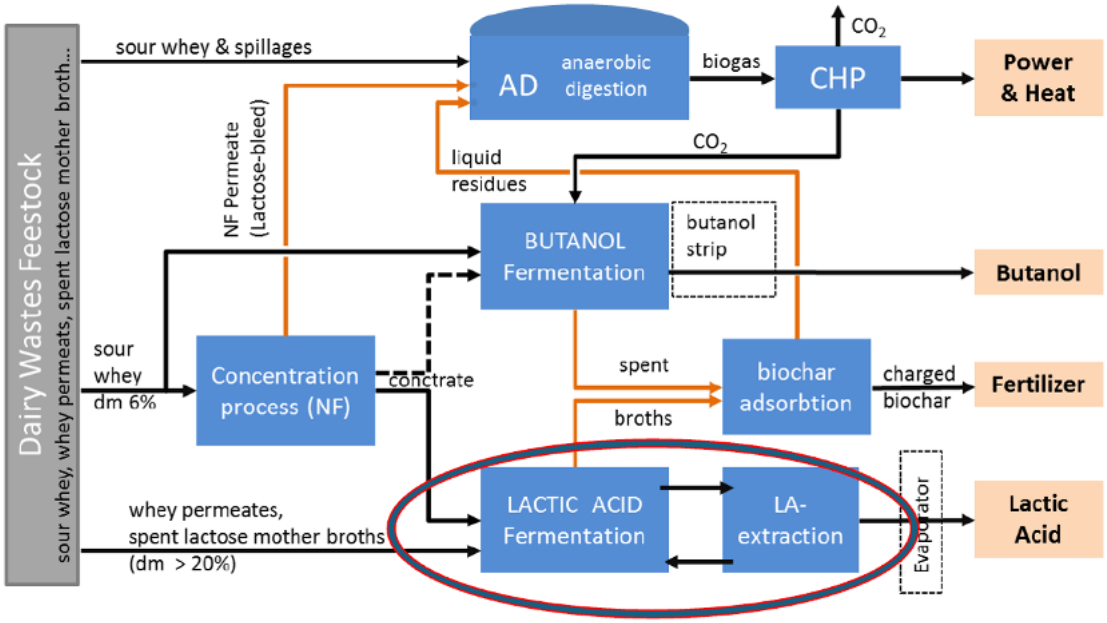


Figure 4. Overview of the whole Up-Whey project. Marked in red is the Milestone 2, in which we HLS is responsible

Within UP-Whey HLS will develop a separation and downstream process for lactic acid for complex fermentation broths. This will be achieved by applying a membrane-supported liquid-liquid extraction process to recover LA without impurities.

The approach is to extract lactic acid in-situ directly from the fermentation broth using membrane extraction. Even though the membrane-extraction process can be described (and partially predicted) with a rigorous mass transfer model (Lit), the key parameter for the applied type of membranes, the process parameters (flow rate, temperature, concentration) and the target component needs to be evaluated by experiments in order to feed the mass transfer model with sound data. In order to reduce the level of complexity for the initial trails, a test system containing lactic acid in aqueous solution was used. In a later stage, a fermentation broth, feed with spent dairy whey, was used for the membrane extraction trails, too.
The experiments are supported and reduced to a minimum while maintaining the required statistical certainty by using a tool for statistical planning of experiments (“Stavex” from Aicos, Allschil, BL).

1.3 Objectives

In accordance to the Up-Whey project purposes (see above), the objectives of the HLS work were as following:

1. (successful) membrane extraction of lactic acid from model solutions with extraction rates which are in a typical range for LA membrane extraction processes ($4*10^{-6}$ m/s to $3*10^{-7}$ m/s [8–10]), measured by the overall mass transfer coefficient K_{ov} - “proof of concept”.
2. (in case of successful step 1): Apply this membrane extraction set-up to an industrial feedstock (=fermentation broth) and show (again) the proof of concept for this setting. Additionally, the stability of the membrane process with regard to potentially clogging, fouling and cleanability is also part of this objective.
3. (in case of successful step 1 and/or step 2): Further improvements of the membrane extraction process with a special regard to increase the overall mass transfer and thus reducing the required membrane area for a given fermentation volume / feed stream. With this information it should be then assessed whether further investigations or even a piloting appear to make sense from an economic perspective.

2 Description of facility

2.1 Membrane extraction set up

The main equipment used was the membrane extraction (ME) setup is shown in Figure 5. The ME setup is comprised of the following units:

- Two jacketed vessels (1 and 2 in Figure 5).
- Two gear pumps (3 and 4 in Figure 5).
- One membrane-assisted extraction module (5 in Figure 5).
- Two Coriolis flowmeters (6 in Figure 5).
- Four pressure sensors (7 in Figure 5).
- Two temperature sensors (8 in Figure 5).

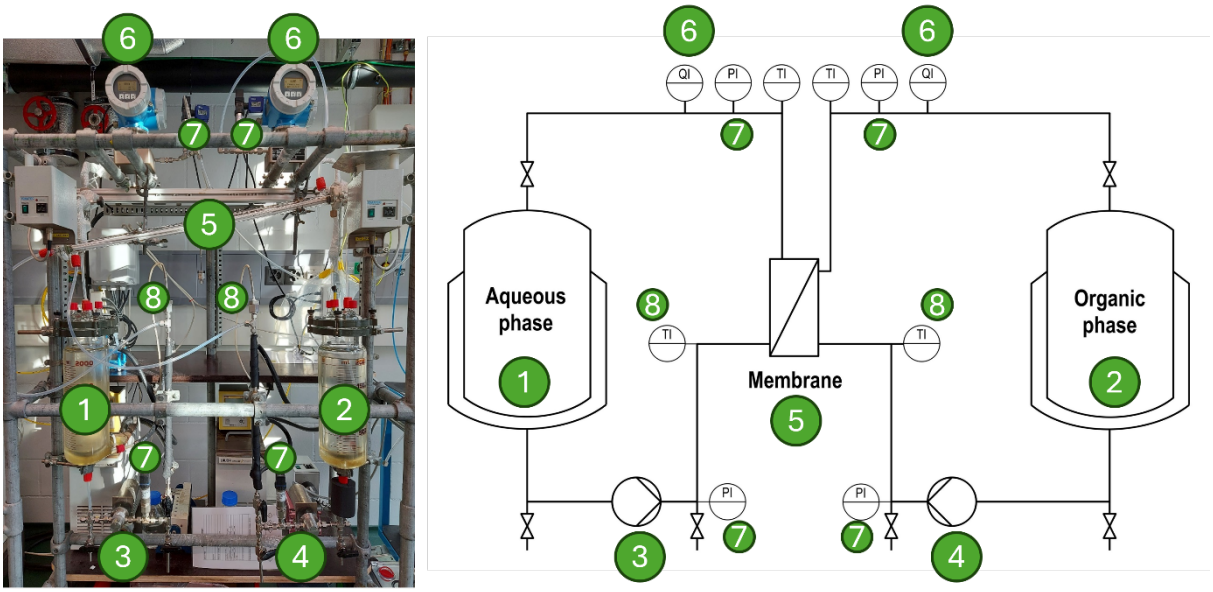


Figure 5. Membrane extraction setup. a) Setup at the HLS facility, b) schematic representation of the membrane extraction setup in batchwise.

In the ME process, the feed (aqueous phase) is added to one vessel (1), while the solvent (organic phase) is added to the other vessel (2). The flow rate for each phase is set in the gear pump between 5 and 60 L/h (3 and 4 feed and solvent, respectively). On the outlet side of each gear pump there is a pressure sensor (7 on bottom) to monitor the pressure of each phase before it enters the membrane extraction module (5). Just before each phase enters the ME module, there is a temperature sensor (8) to monitor the temperature on the inlet side of the ME module. The feed phase enters the lumen side of the ME module while the solvent phase enters the shell side of the ME module. On the outlet side of the ME module, there are two Coriolis flowmeters (6) and two pressure sensors (7 on top) to monitor flow rate, density, temperature (all by Coriolis flowmeters), and pressure. The feed phase is then returned to the feed vessel, while the solvent is returned to the solvent vessel in a closed loop.

The ME setup is operated in a closed-loop and samples are taken from the feed and/or solvent phase during the experiment to quantify the lactic acid concentration by further analysis. The extraction temperature is set by adjusting the temperature in the jacketed vessels.

2.2 Membrane extraction modules available

Several sizes of PTFE ME modules were used in this project. Figure 6 shows the available modules in detail.

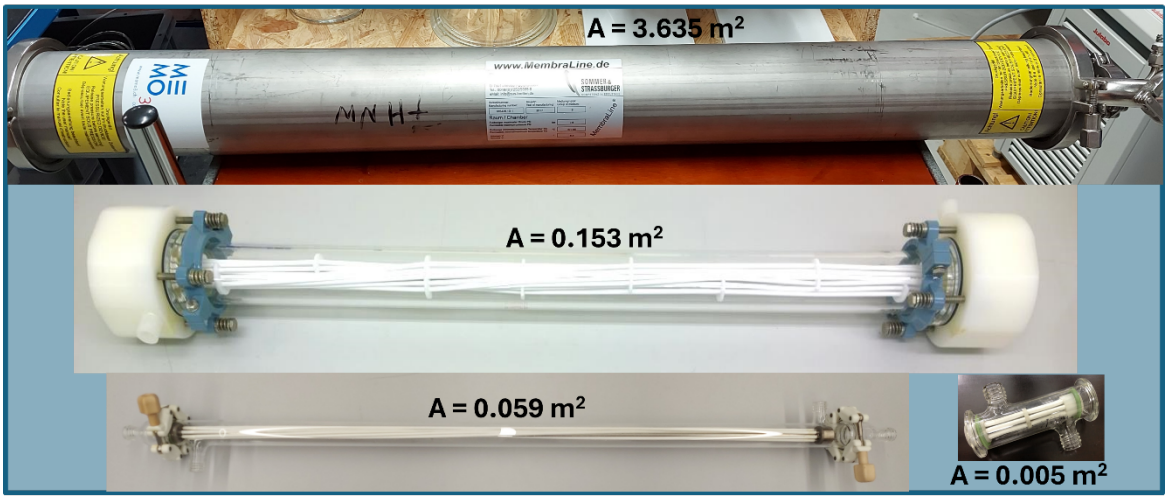


Figure 6. Membrane extraction modules that are available at HLS with different membrane area sizes.

As shown in Figure 6, we had access to different membrane modules for the membrane extraction purposes. The module on top of Figure 6 is an industrial one from Memo3 GmbH and the so far largest membrane extraction module available.

2.3 In-situ lactic acid membrane extraction setup (ATB-Potsdam)

Since we had no access to industrial feedstock at the HLS, we carried out membrane extraction trials at the ATB - Leibniz-Institut für Agrartechnik und Bioökonomie e.V. (ATB) in Potsdam, Germany. At the ATB, several fermenter are available in different sizes and a sound experience with the fermentation of different feedstocks is accessible. We thus transferred one of the membrane extraction modules (with A=0.153 m^2, see Figure 6) to the ATB and installed this in a by-pass installation to a 2 L fermenter (see Figure 7).

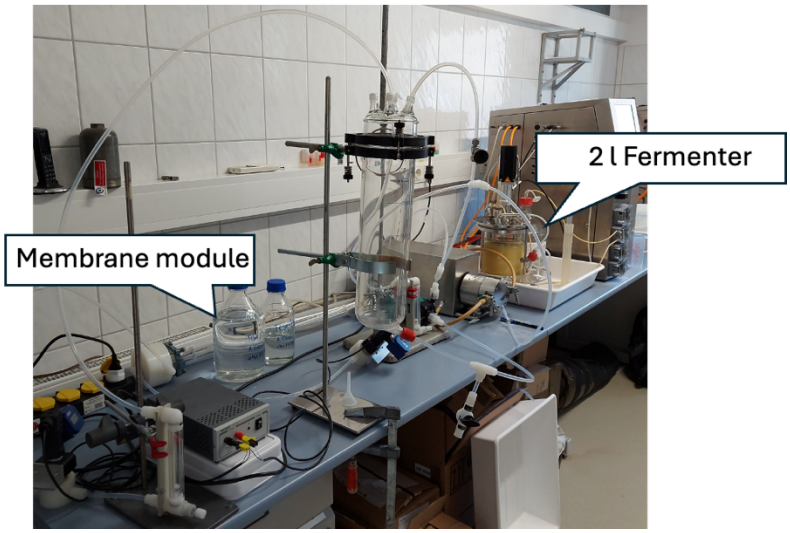


Figure 7. Set-up with Fermenter and Membrane contactor (in by-pass); installed at Leibniz-Institut, Potsdam (ATB)

Over a period of 4 months, several fermentation runs with in-situ removal of lactic acid with membrane contactors where carried out before the membrane module returned to HLS.

3 Procedures and methodology

In order to investigate the feasibility of membrane extraction purposes and to reduce the required amount of feed and solvent, the ME trails are normally carried out in loop operation. Since membrane extraction processes are driven by concentration difference of the target component and thus follow a diffusional mass transfer, typcial saturation and declining functions occur. Depending on the installed membrane area and the process parameters, these curves will end at equilibrium concentration for the dedicated component between the two liquid phases. This equilibrium concentration can be obtained by shaking tests, too. However, here emulsion formation may take place, requiring additional energy and effort to separate the phases e.g. by centrifugation, which is not necessary at all, if ME is applied.

At the HLS, there is a test set-up available which allows to test all kinds of available modules (see Figure 6) with feed and solvent amounts from 0.2 L to 50 L (see Figure 5)

For every test run, both the feed and the dedicated solvent will be filled into the feed tanks. Then, the dedicated membrane module will be installed and connected to the feed and solvent tank via flexible pips. Gear pumps are available to provide a continuous, pulsation- free operation.

Temperature, pressure and flow measurements are installed to monitor the process conditions during the experiments. All data will be transferred to a PC and thus are available for further data treatment.

By running the two liquid phases through the installed membrane module, it can be detected visually, whether the membrane extraction process runs as desired, if no phase transfer from the one to the other phase is obtainable. This can be indicated either by the (rapid) formation of an emulsion or a fast change of the liquid level in the feed tanks.

If this does not take place in the first couple of minutes during the operation, the experiment can be continued further.

Depending on the applied membrane module (size) and process parameters, the time until the equilibrium is reached can vary from a couple of minutes to a couple of days (see eq. 1). However, longer extraction times are not a disadvantage in this investigation status, since the slow but constant change in concentration leaves enough time for detailed analysis (=sampling) and the process stability can also be examined over a longer period of time (=measure for the process stability in general).

The mass transfer for a dedicated component can be described as following (eq. 1, expressed for lactic acid)

$$\frac{dm_{LA,feed}}{dt} = \dot{m}_{LA} = K_{ov} \cdot A \cdot \Delta C \qquad \text{Eq. 1}$$

Where $m_{LA,feed}$ is the mass of LA in the feed phase, t is the operating time, K_{ov} is the overall mass transfer coefficient, A is the available membrane area, and ΔC is the difference in concentration of LA between the two phases (=driving force).

By dividing the specific mass flow dm/dt by the installed membrane area and plot this via the dedicated driving force, a line of origin can be generated from which the slope represents the K_{ov} value (see Figure 8).

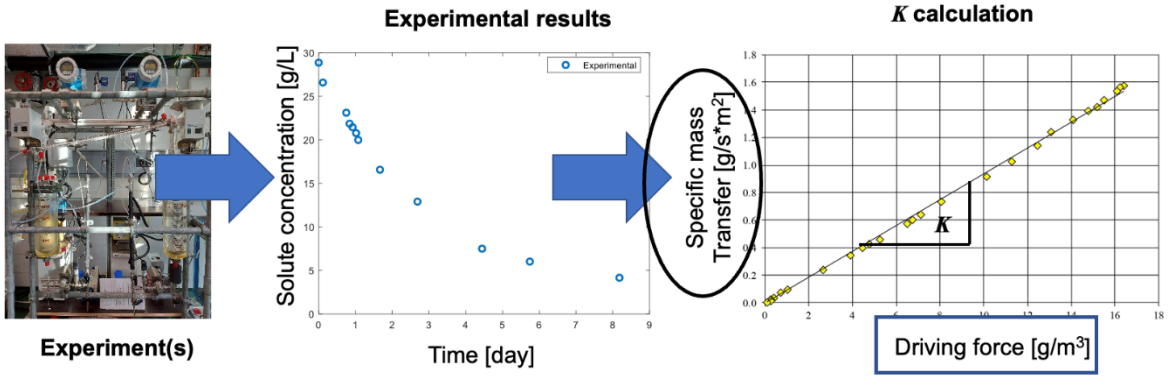


Figure 8. Derivation of the K_{ov}-value for a dedicated membrane extraction.

Thus, the overall mass transfer coefficient can be used to describe the dedicated extraction under the applied conditions – and to benchmark and quantify the membrane extraction trials, which are carried out under different process conditions. The results in this report are therefore based on the obtained K_{ov}-values (unless otherwise mentioned).

More further information see also [1,2].

4 Results and discussion

4.1 Membrane supported extraction with model solutions

Lactic acid (LA) extraction involves capturing/removal of LA from an aqueous source (feedstock), such as a model solution, whey, or fermentation broth, by contacting it with an organic solvent. This solvent must be immiscible with water and non-toxic to the LA-producing microorganism if the extraction is performed directly in a fermentation process. Long-chain aliphatic amines are particularly effective for extracting organic acids from dilute solutions [7,11]. Typically, tertiary amines are combined with diluents to improve the physical properties of the organic phase, such as density, viscosity, interfacial tension, and extraction capacity [11].

Diluents can be inert or active: inert diluents are non-polar compounds that improve physical properties, while active diluents (modifiers) contain polar groups that stabilize the acid-amine complex, thereby promoting the extraction process [3]. The selection of an appropriate solvent for LA extraction depends on its ability to efficiently remove LA from the fermentation broth and its toxicity to the specific microorganism involved. In general, longer alkyl chain alcohols are less toxic to bacteria and n-alkanes are potentially non-toxic to the bacteria [12–14].

4.1.1 Solvent screening

From the scientific literature review, tri-n-octylamine (TOA) has been identified as a suitable carrier which, when combined with diluent, provides a solvent mixture suitable for LA extraction. Therefore, several diluents were tested in combination with TOA by measuring distribution coefficient and solvent toxicity (molecular and phase levels). The distribution coefficient provides information on the ability of the solvent to extract LA, while the toxicity measurement quantifies the extent to which the solvent affects the growth of *Lactobacillus Plantarum* DSMZ 2648), which is a commercial lactic acid bacteria.

For the distribution coefficient measurements, a known volume and concentration of LA was placed in contact with the solvent in a flask and agitated for about one hour. Afterwards, the mixture was allowed to settle for approximately 10 to 18 hours. A sample of the feed phase was then taken to quantify the LA concentration after extraction. Then the distribution coefficient is calculated as the ratio between the LA concentration in the solvent phase with the LA concentration in the feed phase (both after extraction).

Since the solvent interacts with the microorganism through two main routes—direct contact between cells and the solvent at the aqueous-organic interface (phase toxicity) and the presence of soluble organic solvent in the aqueous broth (molecular toxicity)—both toxicity effects were quantified. Toxicity tests involved cultivating LA bacteria in a fermentation broth saturated with the appropriate solvent (molecular level) and exposing LA bacteria in a fermentation broth to the solvent during the growth process (phase level). Finally, the amount of LA produced by the bacteria was quantified and compared with LA cultivation without any solvent contact. According to the toxicity classification of *J. Marták et al*. [14], an used to evaluate the solvent toxicity on LA bacteria in previous work [15],organic solvents are divided into three groups based on their toxicity to microorganisms. They are considered non-toxic if the production rate is above 75%, moderately toxic if the production rate is between 25% and 75%, and toxic if the production rate is below 25% relative to a control fermentation. In Table 1 are summarized the experimental results of solvent screening in terms of distribution coefficient, molecular and phase level toxicity.

Table 1. Distribution coefficients, molecular and phase level toxicity obtained with different solvents. Extraction of 20 mL of 0.68 M LA aqueous solution with 20 mL organic phase containing 20 wt% TOA. Toxicity tests were performed on 72 h LA fermentation. Experiments performed at 25 °C. Information is also available in [2].

Diluent used with 20 wt% TOA	Distribution coefficient of LA [-]	Molecular level toxicity** [%]	Phase level toxicity** [%]
2-ethyl-1-hexanol	15.1	26.7	22.7
n-octanol	14.6	0	0
n-decanol	12.7	96	26.7
Tributylphosphate	10.7	64	24
MIBK	8.8	0	0
n-dodecanol	7.1	70.7	36.7
TOA*	0.1	78.7	24

*Pure compound
** LA produced related blank

From the experimental results shown in Table 1 the solvent comprised by 20 wt% of TOA

in decanol is recommended as the solvent for in-situ extraction, because offers a good compromise between extraction efficiency and toxicity.

In addition, an alternative green solvent based on TOA and a mixture of a deep eutectic solvent (DES) consisting of 60 mol% thymol and 40 mol% menthol was investigated as a potential solvent for LA membrane extraction in collaboration with the TU Graz. The partition coefficient of different mixtures of TOA in the DES was investigated (Figure 9).

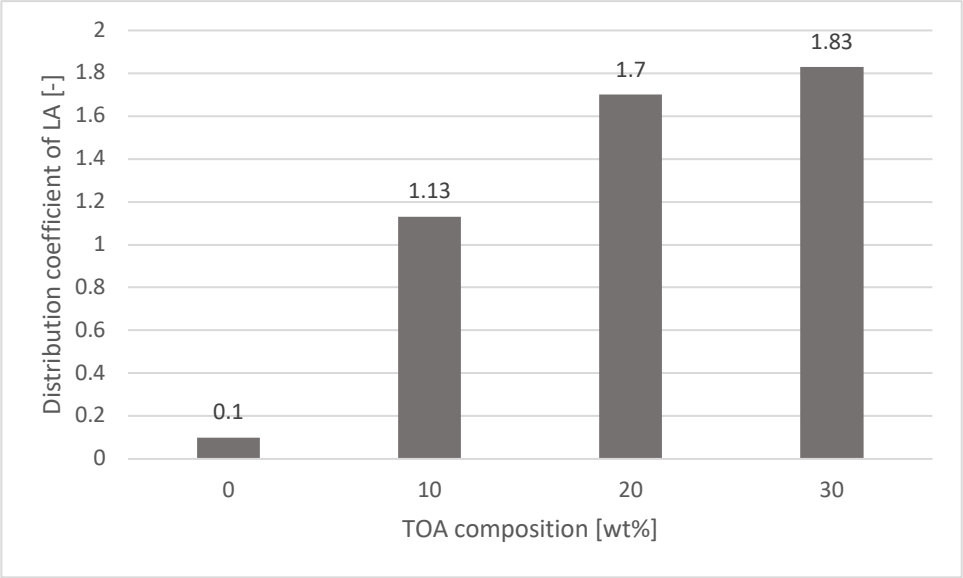


Figure 9. Distribution coefficient obtained for different TOA (wt%) compositions in thymol (60 mol%) - menthol (40 mol%) DES. Extraction of 1 mL of 2.5 wt% LA aqueous solution with 1 mL organic phase. Experiments were performed at 25 °C.

It was observed that the investigated TOA/DES mixtures provide a lower LA distribution coefficient than the TOA/decanol mixture. However, the higher the TOA composition of the TOA/DES, the higher the LA distribution coefficient.

After solvent screening, the TOA/decanol solvent showed the best compromise between distribution coefficient and low toxicity to lactic acid bacteria. Therefore, TOA/decanol is the most promising solvent for extraction of LA from whey source, and TOA/DES could be a second choice, despite of having a lower performance than TOA/decanol but being a greener alternative. However, it is necessary to test this solvent on the LA membrane extraction performance, which is the aim of the next subsection.

4.1.2 Lactic acid membrane extraction test

With a selected system TOA/decanol (20 wt% / 80 wt%) and TOA/DES (10 wt% / 90 wt%), LA membrane extractions experiments were performed from an aqueous lactic acid solution (without biomass) to the solvent phase using the ME setup in Figure 5. The typical LA membrane extraction concentration profile can be observed in Figure 9 where the LA concentration decreases in feed phase while the LA concentration increases in solvent phase until the LA is completely removed or until the solvent is saturated with LA.

The LA membrane extraction experiments were performed at 25°C with the LA solution (feed) flowing in the lumen side of the LA membrane extraction module while the solvent flowed in co-current in the shell side. Samples from the feed phase were taken over the time and by acid-base titration the LA concentration was quantified. Depending on the solvent/feed ratio (S:F), the LA can be diluted or concentrated in the solvent phase. For example, in Figure 9, when an S:F ratio of 1:2 was used, the LA concentration in the solvent phase (organic phase) increased to 2.25 wt%, which is the initial LA concentration on the feed of 0.6 wt%. On the other hand, for the LA membrane extraction with TOA/DES (Figure 10), the LA concentration of the feed phase decreased from 21 g/L (about 2.1 wt%) to 11 g/L in 3 h when the solvent phase was completely saturated with LA (using an S:F ratio of 1:2). LA saturation did not occur in the TOA/decanol solvent because the composition of TOA for this is higher than the composition of TOA in the TOA/DES solvent.

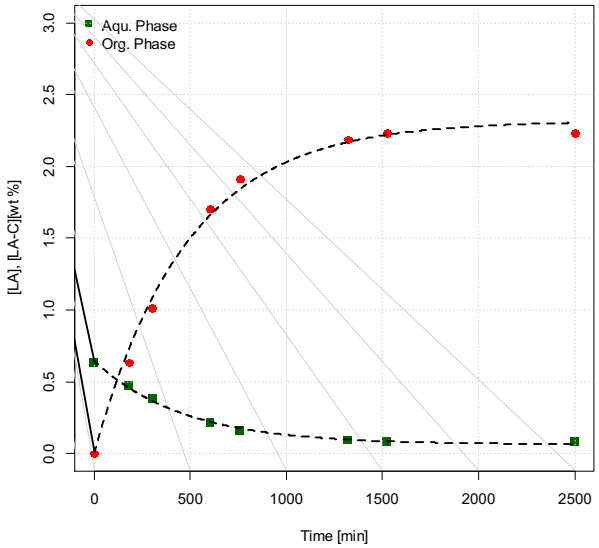


Figure 9. Typical LA membrane extraction experimental and prediction results for TOA/decanol.

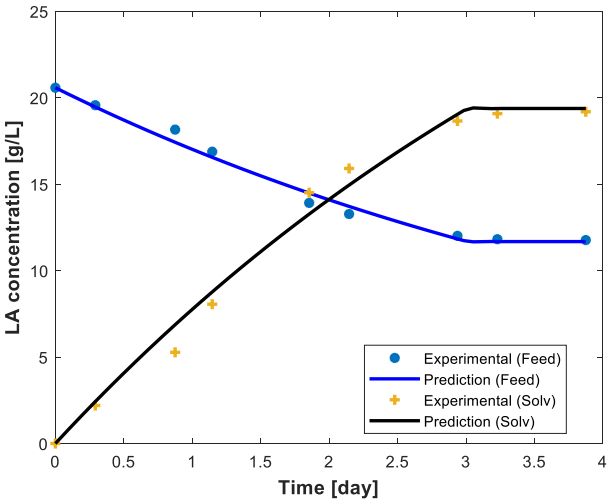


Figure 10. Typical LA membrane extraction experimental and prediction results for TOA/DES.

For each LA membrane extraction experiment, the K_{ov}-value was calculated using the methodology shown in Figure 8. The K_{ov}-value for the TOA/decanol was in the range of $2.2*10^{-7}$ m/s, while the K_{ov}-value for the TOA/DES was $2.3*10^{-8}$ m/s.

LA membrane extraction was also tested using model solution at different pH buffered with NaOH (Figure 11) during about 6 days. It was observed that at pH 5, the LA concentration in feed phase decreased by 15% (from 1 wt% to 0.85 wt%) in 8000 minutes, while at pH 2, the LA concentration decreased by 80% (from 1 wt% to 0.2 wt%) in the same 8000 minutes. This confirms that the pH in the LA feed solution drastically affects the LA membrane extraction. On the other hand, it also confirms that the LA membrane extraction is proposed to be as shown in Figure 1 when the pH is decreased. This is due to the fact that at low pH, LA is mostly in the protonated form, which is the LA form that is extracted by the TOA.

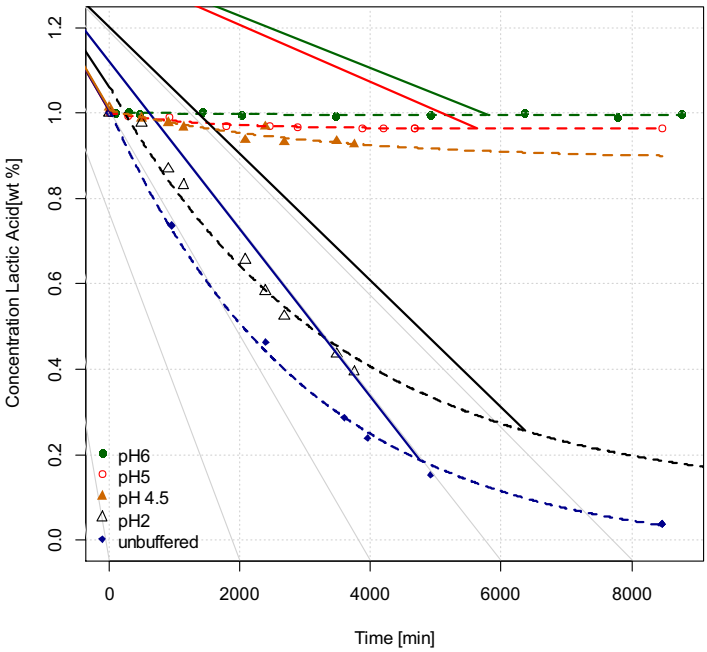


Figure 11. LA membrane extractions with 1 wt% LA buffered with NaOH to pH 6, 5, 4.5, 2 and unbuffered (right).

One additional insight from the LA membrane extraction experiments, shown in Figure 11, is that at 1 wt%, LA provides a sufficiently low pH to promote LA extraction, with almost 90% of LA being extracted.

Later in this project the performance of ME for other carboxylic acids (see Table 2) was investigated, too.

Table 2. Membrane extraction of mandelic, itaconic, lactic and succinic acids in a PTFE-ME module with an available area of 0.06 m2 using TOA/decanol as solvent at a solvent/feed ratio of 1:1. The extraction temperature was maintained at 25 ºC.

Carboxylic acid	**K_{ov}-value [m/s]**
Succinic acid	3.4*10-8
Itaconic acid	5.7*10-8
Lactic acid	5.2*10-8
Mandelic acid	1.7*10-7

As Table 2 shows, the obtained K_{ov} values for the different carboxylic acids vary from $3.4 \cdot 10^{-8}$ m/s to $1.7 \cdot 10^{-7}$ m/s. Thus, under equal process conditions, this means a membrane area that is up to 5 times larger for the same amount of extracted acid at the lowest K_{ov}-value compared to the highest K_{ov}-value. It is particularly advantageous here, however, that the highest K_{ov}-value could be determined for mandelic acid, one of the most valuable representative of the carboxylic acid group.

4.2 Membrane supported extraction with industrial process streams

A characterization (Table 4) of the whey waste products has been performed. There are two sources of whey. The whey waste from Prolactal is mainly spent mother broth left over from lactose crystallization processes. The NÖM whey, which comes from the production of several cheeses and other dairy products that involve partial fermentation of milk.

Table 4. Sour and sweet whey characterization.

Industry	Type	Description	Quantity [t/a]	DM-content [wt%]	Lactose [wt%]	Ash [wt%]	pH
Prolactal	sweet whey	Spent mother broth from crystallisation	10.000 - 25 000	18 -25	12,5 -17,5	4,5 - 7	5,5 - 6,5
NÖM	sour whey	Cottage & other cheeses,	40.000	5,7 - 7	4,6 - 5,5	0,6-0,8	3,4 - 4,6

As mentioned before, the sweet whey contains about 8 wt% of LA, while the ash content can reach up to 7 wt%. This whey waste was used for the fermentation experiments as it was aimed in the project.

Since the TOA/decanol solvent showed the best results for LA with low toxicity, it was tested in an in-situ LA membrane extraction experiment conducted in collaboration with the *Leibniz-Institut für Agrartechnik und Bioökonomie* (ATB) in Potsdam, Germany. Two parallel fermentations were performed (one with pH control at optimum pH by addition of NaOH and the other with in situ LA membrane extraction). The fermentation broth for both fermentations was prepared from sweet whey and inoculated with the same lactic acid bacterial strain (A359). The fermentations were carried out by 30 hours following the pH over time as can be seen in Figure 12.

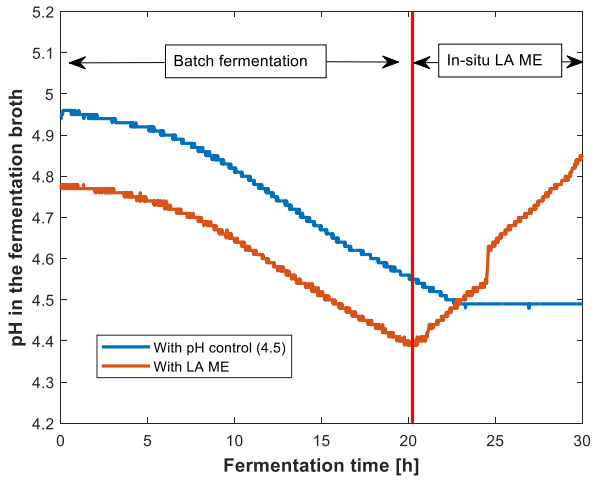


Figure 12. pH evolution over the time for two parallel fermentations at 30 °C, using sweet whey as fermentation broth and inoculated with the same lactic acid bacteria strain from ATB (A359). Fermentation with blue line was performed with pH control at pH 4.5 by adding NaOH (20%) in a 1 L fermenter, while fermentation of red line it was performed with no pH control from beginning up to the hour 20, and from hour 20 until the hour 30 with in-situ LA membrane extraction using TOA/decanol as solvent (solvent-to feed-ratio of 1:0.8) with 2 L fermenter and a PTFE-membrane extraction module of 0.15 m^2.

It was evident that once the ME started (20 hours in the red line in Figure 12), the pH not only stopped decreasing (due to the production of LA), but immediately started to decrease from a pH of 4.4 (at the time of 20 hours) to a pH of 4.85 (at the time of 30 hours), which is almost the initial pH of the fermentation (4.78). This experiment showed not only that it is possible to extract LA in-situ from the fermentation broth, but also that the pH of the fermentation broth can be manipulated by the amount of LA acid extracted.

The next in-situ LA fermentation was performed to maintain the pH of the fermentation broth at around pH 5 (Figure 13) and run it for longer time than the preliminary in-situ LA membrane extraction experiment. The in-situ LA extraction ran for 7 days. After 7 days of in-situ LA, the microorganism was still active, and the final amount of LA was 21 g. Moreover, when the LA fermentation was coupled with a conventional liquid-liquid extraction (using the same solvent as the in situ LA membrane extraction, TOA/decanol) instead of the membrane-assisted extraction, the amount of LA obtained at the end of the fermentation was less than 0.7 g, due to the reason that the solvent was in direct contact with the microorganism and produced a severe toxic effect on the microorganism [2].

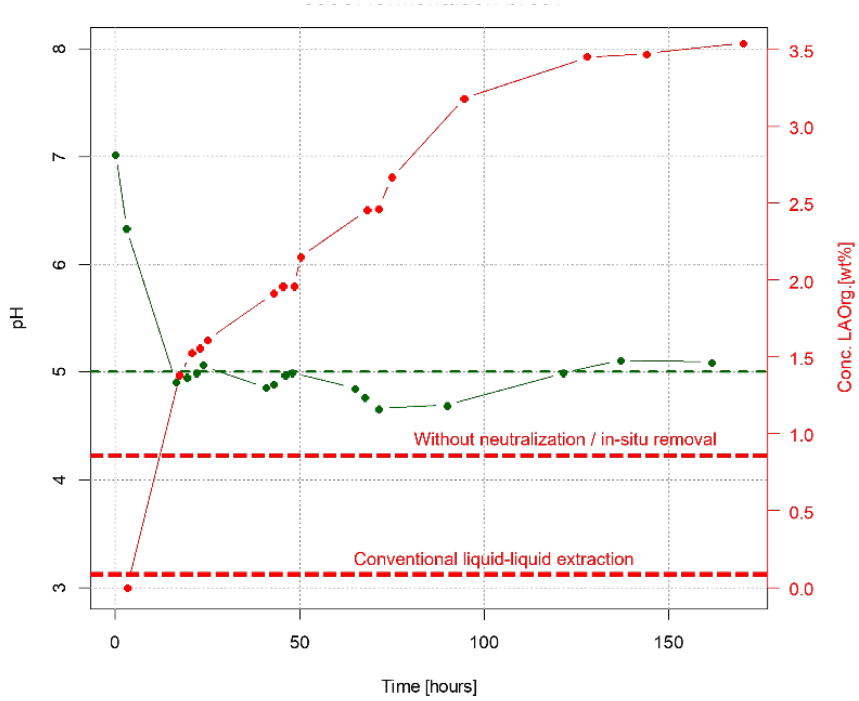


Figure 13. In-situ membrane extraction of LA from a fermentation broth of 0.7 L. The volume of solvent used (TOA/decanol) was 0.7 L. The membrane area of the ME module was 0.059 m^2. The microorganism used was *Lactobacillus plantarum* (DSMZ 2648). The fermentation was maintained at 37 °C for 7 days. The green dotted line is the measured pH of the fermentation broth, while the green dashed line is the set pH of the fermentation. The red dotted line is the LA concentration in the solvent (for the ME process), while the red dashed lines are the LA concentration obtained in the fermentation without any extraction or neutralization of LA, and the fermentation coupled with a conventional liquid-liquid extraction using the same solvent as the ME process. Based on [2].

This result was compared with the amount of LA obtained in a batch fermentation without LA extraction or neutralization, which provides about 5.6 g of LA at the end of the fermentation. This means that 3.75 times more LA mass can be obtained with the in-situ LA process compared to conventional batch fermentation (see Figure 14).

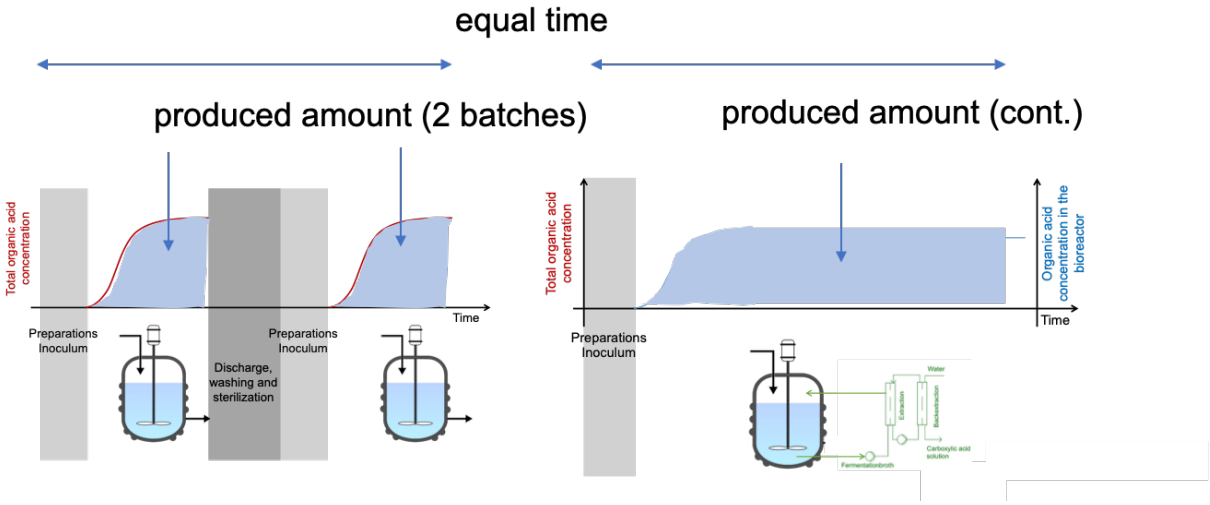


Figure 14. Consequences on batch LAC fermentation (at optimal pH value for microorganisms) vs. continuous fermentation with in-situ recovery of LAC with membrane contactors (at lower pH = improved direct LAC extraction)

As shown in figure 14, a continuous fermentation with in-situ LAC extraction with membrane contactors show several advantages with respect to operation: There are less start-up and shut-down and cleaning procedures for the fermentor required and the total amount of LAC obtained is larger even if the fermentation is operated at lower pH (less optimal for microorganism growth and LAC production, but improved for LAC direct extraction).

Due to the novelty of this technology approach, this process combination was never been tested so far and thus should be investigated in pilot-scale in the nearer future.

After in-situ LA membrane extraction, the membrane extraction module was successfully cleaned (Figure 15). For this purpose, 1 L of a conventional acidic cleaning solution for ceramic membranes was passed through the module for about 30 minutes, and for sterilization, 1 L ethanol was passed through the same module for a 15 minutes. Afterwards, the ME module was used for another in-situ LA membrane extraction experiment.

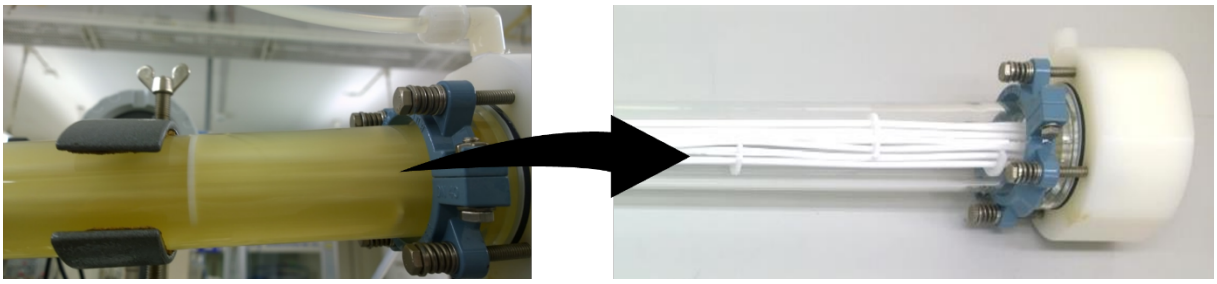


Figure 15: Membrane extraction module during fermentation (left) and after cleaning and sterilization (right).

In addition, the overall mass transfer coefficient (K_{ov}-value) of the LA membrane extraction using TOA/decanol and TOA/DES was calculated for different LA feedstocks (such as model solution, fermentation broth and sweet whey) at 22 °C as shown in Table 3.

Table 3. K_{ov}-values obtained at 22 °C for LA membrane extraction using TOA/decanol (20wt%/80wt%) and TOA/DES solvents under optimum conditions with different feedstocks.

Solvent	Feed	D** [-]	K_{ov} [m/s]
TOA/decanol	Model solution	0.18	$2.2*10^{-7}$
TOA/decanol	Fermentation broth	0.18	$1.9*10^{-7}$
TOA/decanol	Sweet whey	0.18	$1.4*10^{-7}$
TOA/DES	Model solution	0.141	$2.3*10^{-8}$

*DES: 60 mol% of thymol and 40 mol% of menthol. **D: LA Distribution coefficient

It was shown that the quantification of the K_{ov}-value for LA transport may differ from that measured with model solutions compared to real streams such as fermentation broth and sweet whey (compared to the K_{ov}-value for the model solution, the K_{ov}-values for fermentation broth and sweet whey were 24% and 36% lower, respectively). This may be because the model solution contains only water and LA, while the real stream contains many more substances, such as salts, proteins, ash, etc., which can cause different interactions between molecules and change the pH.

4.3 Optimization

4.3.1 Flow, Temperature and different solvents impact

Two parameters were investigated to optimize LA membrane extraction using TOA/decanol solvent. The extraction temperature (Figure 16 left) and the flow rate (Figure 16 right) of both phases (feed and solvent). Initially, ME experiments were performed at extraction temperatures from 25 to 35 °C, and the obtained K_{ov}-values slightly decreased from $2.18*10^{-7}$ m/s (at 25 °C) to $1.8*10^{-7}$ m/s (at 35 °C). On the other hand, different flow rates were tested under similar conditions (Figure 15, right) and no effect of the flow rate (of either phase) from 6 to 50 kg/h was observed on the extraction performance of the LA membrane, giving a K_{ov}-value of $2.2*10^{-7}$ m/s.

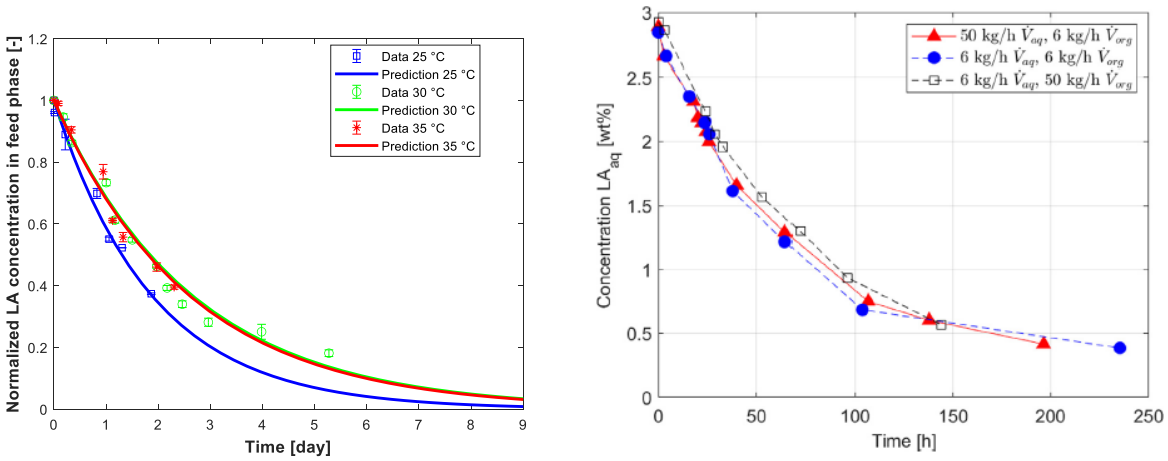


Figure 16: Optimization of the extraction performance of the LA membrane by the extraction temperature and the flow rate (taken from [1]) of both phases (feed and solvent) with TOA/decanol solvent. Experiments to evaluate the extraction temperature (left) were performed at a flow rate of 14 kg/h for solvent and 20 kg/h for feed, and a solvent-to-feed ratio of 1:2, using a 0.059 m^2 ME module. Experiments to evaluate the flow rate (right) were performed at an extraction temperature of 25 °C, and a solvent-to-feed ratio of 1:1.16, using a 0.059 m^2 ME module.

The extraction performance of LA membranes was also optimized using the TOA/DES solvent, in terms of the TOA composition, the solvent flow rate, and the extraction temperature. Compositions of TOA ranging from 10 wt% to 50 wt% were investigated, while extraction temperatures ranging from 20 to 50 °C were also investigated. The flow rates investigated ranged from 3 kg/h to 22 kg/h. The TOA/DES composition and extraction temperature were optimized by using Stavex for Design of Experiments (DoE) and by analyzing its dependence on the distribution coefficient and solvent viscosity.

The optimization results from Stavex provide an optimal TOA composition of 10 wt% at an extraction temperature of 50°C. Therefore, the LA membrane extraction experiments were performed at these conditions for different solvent flow rates to verify that the system was operating with the correct hydrodynamics. In addition, an experiment was performed at 20°C under the same conditions to verify the results of the Stavex optimization. The experimental results are summarized in Figure 17. It was verified that 50 °C (gray columns in Figure 16) as extraction temperature gives a higher K_{ov}-value than 20 °C (black column in Figure 17). In addition, a solvent flow rate between 12 and 18 kg/h was found to provide optimal hydrodynamics for LA membrane extraction using TOA/DES as solvent.

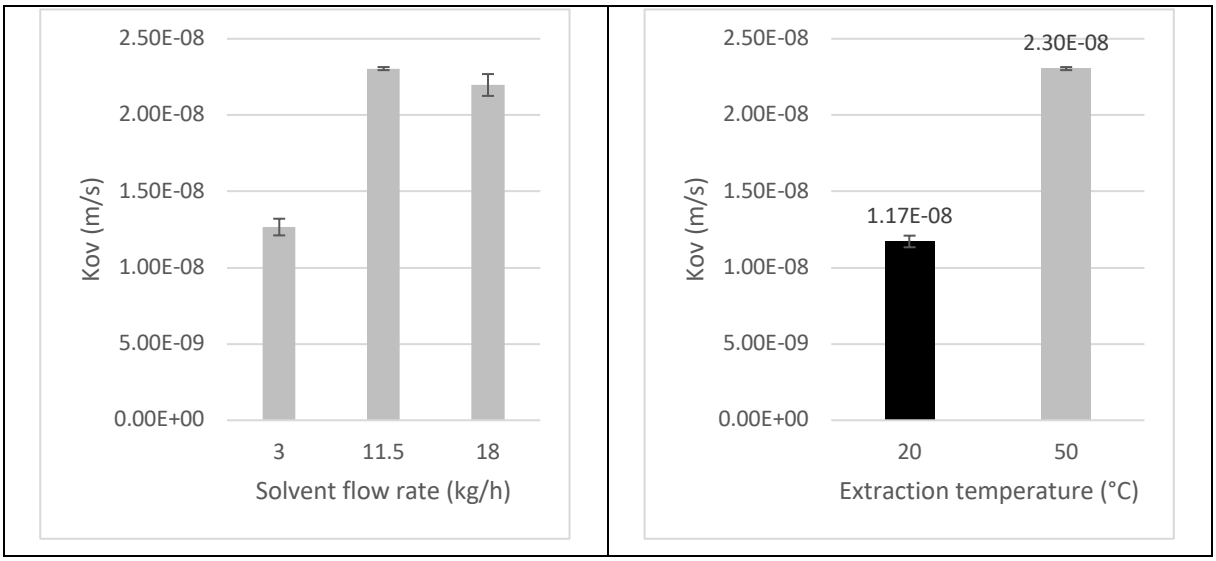


Figure 17. K_{ov}-values obtained for LA membrane extraction using 10 wt% TOA in DES at different flow rates and extraction temperatures with a 0.06 m^2 PTFE-ME module. Feed phase: aqueous LA solution at 20 g/L intial concentration

4.3.2 LA productivity impact on in-situ LA membrane

The effect of pH on the membrane area required for in-situ LA membrane extraction was evaluated for two different LA productivities (1 g/l*h^{-1} and 0.3 g/l*h^{-1}) as shown in Figure 18. The first finding was that the membrane area required per cubic meter of fermenter to extract LA increased exponentially from pH 4 to pH 5 for both LA productivities evaluated. In addition, the membrane area required per cubic meter of fermenter was 32.6 times higher for an LA fermentation with a productivity of 1 g/l*h^{-1} than for an LA fermentation with an LA productivity of 0.3 g/l*h^{-1}. This finding is expected since, as shown in Figure 1, the optimal pH for LA extraction does not match the pH required for LA fermentation. Consequently, when calculating the required membrane area for high LA productivity, the m²/m³ value is significantly large. However, when LA productivity is low, the m²/m³ value decreases because the LA production rate matches the LA extraction rate.

pH	4	4.5	5
m²/m³	300	700	2500

pH	4	4.5	5
m²/m³	9.2	21.4	76.5

Figure 18. Effect of pH during in-situ LA membrane extraction of two fermentations with different LA productivities. 1 g/l*h^{-1} on the left and 0.3 g/l*h^{-1} on the right.

Reasonable conditions for scaling up in-situ LA membrane extraction can be achieved by operating the fermentation at pH 4 with an LA productivity of 0.3 g/l*h^{-1}, since the m²/m³ is reduced to the minimum, 9.2 m²/m³ in Figure 18.

4.3.3 pH-shift into the LA membrane extraction process

To increase the efficiency of in-situ product removal, a strategy of integrating LA membrane extraction with electrochemical pH adjustment has been proposed. This approach allows LA fermentation to occur at its optimal pH, while the membrane extraction process operates at an ideal extraction pH. Anodic electrolysis is used to adjust the pH of the fermentation broth prior to extraction in the membrane module, lowering it from neutral to increase extraction efficiency. In addition, the cathodic reaction is used to raise the pH of the aqueous stream used for back-extraction of the loaded organic phase [16].

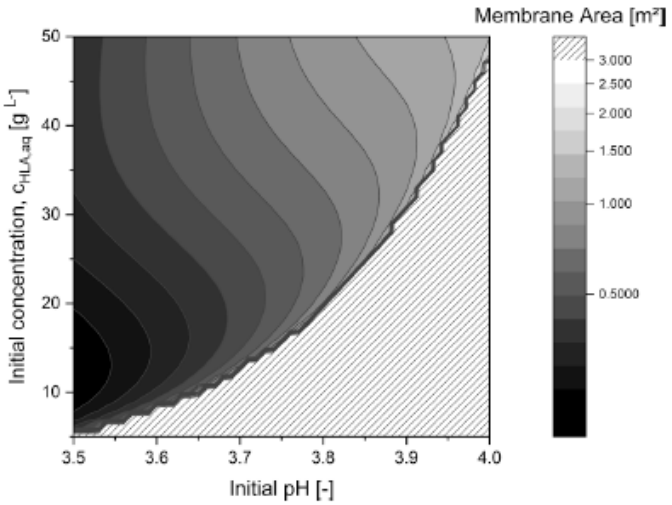


Figure 19. Membrane area required for the LA membrane extraction, dependent on the pH and total LA concentration on the 10 L of fermentation broth (with a LA productivity of 2 g/l*h^{-1}).

Two significant trends are evident in Figure 18: The decreased membrane area required at low acid concentrations and the pronounced effect of pH. The reduced membrane area required at lower concentrations can be attributed to a higher amine-acid ratio. This increase in the enhancement factor offsets the reduction in driving force, resulting in higher mass transfer rates. This underscores the effectiveness of reactive extraction with tertiary amines, especially in scenarios requiring in-situ extraction of lactic acid from dilute solutions [16].

In general, the findings obtained in this project require further investigation, especially with respect to a scaling-up into pilot scale. However, since membrane processes are generally easier to scale up than other separation processes and the results are promising, it is likely that the investigations will be continued in the near future.

5 Conclusions

The proposed methodology for finding a suitable ME system for LA extraction from fermentation broth was successful in all requirements as follows:

- From solvent screening TOA/decanol mixture was found with a good compromise between LA extraction capability (99% of LA extraction) and low toxicity (allowing 96% of LA production) to lactic acid bacteria (*Lactobacillus Plantarum* DSMY 2648).
- Favorably selection and evaluation of a mechanically, thermally, and chemically stable membrane that provides sufficient membrane area (ME modules from 0.05 m^2 to 3.6 m^2, as shown in Figure 6) and porosity (50%) for contact between the selected solvent and the source of lactic acid (model solution, whey, or fermentation broth).
- Effective lactic acid ME performance evaluation (achieving optimum K_{ov}-value of 2.2*10^{-7} m/s) using multiple feedstocks (from LA solution to sweet whey) and solvents, including optimization of operating conditions (such as flow rate, extraction temperature and solvent composition).
- Promising evaluation of the LA membrane extraction for the in-situ extraction of LA from the fermentation broth (7 days of in-situ continuous LA extraction, with a LA productivity 3.75 times higher as compared a conventional batch fermentation at same conditions).

In-situ membrane extraction of LA from a sweet whey fermentation broth showed that both LA yield and productivity could be increased in 3.75-fold as compared to the conventional batch fermentation

process, while increasing the fermentation time resulted in a higher amount of LA produced (21 g of LA in 7 days in 700 mL of fermentation broth, instead of 5.6 g of LA obtained in the conventional batch LA fermentation).

The ME technology for lactic acid recovery from the Austrian industry dairy waste streams can be implemented as a partial treatment of these streams to add value to the waste by recovering lactic acid.

Through modeling results it was shown that it is not necessary to reduce the LA concentration in the fermentation broth to a minimum during in-situ LA membrane extraction in order to promote LA production by the microorganism, while extending the fermentation time leads to an increase in the amount of LA, which is only limited by the lifetime of the microorganisms, but not by their inhibition by LA concentration. This then leads to a reduction in the membrane area required for the implementation of the ME technology, making the in-situ LA membrane extraction approach more affordable.

However, it must be mentioned that without pH adjustment between fermentation and extraction, the required membrane area is currently far too large for the process to be considered economical for lactic acid (up to 2500 m^2/m^3 without pH-adjustment).

It could be shown, that for some applications like extraction of succinic or mandelic acid the required membrane area to even pilot such processes is in the range of less than 10 m^2/m^3 (9.2 m^2/m^3) - thus, further investigations are strongly recommended.

Thus, these project`s findings are useful to be applied to similar challenges from Swiss industries like dairy and cheese production – or for production of high added value carboxylic acids from fermentation broth with in-situ recovery by membrane extraction.

6 Outlook and next steps

The knowledge gained from the development of this project leads us to propose here the next steps for the application of the proposed technology:

- Identify dairy industries in Switzerland where the innovative approach of this project could meet their needs to manage dairy waste streams while valorizing the waste
- Investigate the membrane extraction of other carboxylic acids than lactic acid with a higher commercial value to make the implementation of dairy waste valorization by in-situ ME extraction even more attractive.
- Piloting of the in-situ membrane extraction of carboxylic acids with commercially available ME modules.
- Resolving the conflicting pH requirements in fermentation and extraction through the use of hydrolysis technology driven by green excess energy (“pH-shift”) in order to reduce the required membrane area for the direct extraction of carboxylic acids and thus reduce the initial investment costs

7 National and international cooperation

Within this ERA-Net project, HLS had a strong exchange and cooperation with Memo3 GmbH regarding module design and potential scale-up as well as input on membrane module cleaning. This cooperation did exist already before the start of this project and actually continues also in other fields of membrane contactor technology, especially in the field of gas-transfer (for e.g. microalgae cultivation).

In addition, we were able to expand the already existing contacts with TU Graz – which led to joint publications (see next chapter) in the field of liquid-liquid extraction.

We are thankful for the support from Dr. Venus and his team at Leibniz Institute ATB in Potsdam for the fermentation of whey towards lactic acid and the successful integration of the membrane contactors to his fermenters. We appreciate his feedback to our technology, which was regarded as very innovative downstream technology for fermentations in general and for the lactic acid in particular.

8 Publications

Peer reviewed papers:

- Mass transfer analysis and kinetic modeling for process design of countercurrent membrane supported reactive extraction of carboxylic acids, A Gössi, W Riedl, B Schuur, Chemical Engineering Science: X 13, 100119
- In-situ recovery of carboxylic acids from fermentation broths through membrane supported reactive extraction using membrane modules with improved stability, A Gössi, F Burgener, D Kohler, A Urso, BA Kolvenbach, W Riedl, B Schuur, Separation and Purification Technology 241, 116694
- Electrochemical membrane-assisted pH-swing extraction and back-extraction. Marcel Gausmann, Angelo Gössi, Franziska Bertram, Wolfgang Riedl, Boelo Schuur, Andreas Jupke. Separation and Purification Technology 289 (2022) 120702

Oral presentation and posters in conferences:

- Up-whey- Upstream processing von Lactose-Molke für Plattform-Chemikalien und Energieproduktion; Bioenergieforschung in der Schweiz: Mehrwert schaffen, neue Ansätze erforschen, über den Tellerand blicken, Mai 2021, online (Bioenergieforschung in der Schweiz)
- Continuous in situ lactic acid extraction from sweet whey fermentation broth using a tubular membrane contactor, Demmelmayer, P., Pérez, A., Riedl, W. & Kienberger, M., 26 Sept 2022 (International Solvent Extraction Conference 2022: ISEC 2022 - Chalmers University of Technology in Göteborg, Gothenburg, Sweden).
- Upstream processing of lactose whey for bulk chemicals and energy production, Paul Demmelmayer, Michael Mandl, Marlene Kienberger, Stefan Pflügl, Regina Kutscha, Angelo Gössi, Alan Pérez & Wolfgang Riedl, 18 Jan 2023 → 20 Jan 2023. Oral presentation (7 Mitteleuropäische Biomassekonferenz, Graz, Austria).
- Emulsionsfreie Flüssig-Flüssig Extraktion von Milchsäure mittels Membrankontaktoren und DES, Paul Demmelmayer, Alan Pérez, Marlene Kienberger & Wolfgang Riedl, 22 Feb 2023. Poster presentation (Jahrestreffen der DECHEMAI-Fachgruppen Extraktion und Mischvorgänge, Frankfurt am Main).
- Upstream Processing of Lactose whey for bulk chemicals and energy production, Energy research conference, November 2020, Biel.
- Further Improvements in Lactic Acid Membrane Extraction: Introducing Deep Eutectic Solvents for an Emulsion-free, Non-toxic direct extraction. A. Pérez, P. Demmelmayer, M. Kienberger, W. Riedl, Accepted in Euromembrane 2024 (September 8-12 / 2024).

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10 Appendix

Attached please find the poster “Upstream Processing of Lactose whey for bulk chemicals and energy production” (Energy research conference, November 2020, Biel)