Chemical Engineering & Processing: Process Intensification 139 (2019) 95–102

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

A new concept of liquid membranes in Taylor flow: Performance for lactic acid removal

Alan D. Pérez, Javier Fontalvo*

Universidad Nacional de Colombia - Sede Manizales - Facultad de Ingeniería y Arquitectura - Departamento de Ingeniería Química, Laboratorio de Intensificación de Procesos y Sistemas Híbridos - Grupo de Investigación en Aplicación de Nuevas Tecnologías, Colombia

ARTICLE INFO

Keywords:
Liquid membrane
Taylor flow
Lactic acid removal
Process intensification
Perstraction

ABSTRACT

A liquid membrane in Taylor flow regime is a novel alternative kind of contact in three-phase flow for liquid membranes that preserves the advantages of conventional emulsion liquid membranes while overcomes the stability problems of emulsion systems. As a proof of concept, this work presents experimental results of a liquid membrane in Taylor flow for lactic acid removal. Several operating conditions, such as injection times, delay times and flow of the membrane phase were tested for a channel length and inner diameter of 348.8 cm and 2.5 mm, respectively. The lactic acid removal is mainly affected by the driving force of lactic acid concentrations between donor droplets and the membrane interface, and the space-time. Thus, the lactic acid removal process through the liquid membrane in Taylor flow is enhanced at low injection times and high droplet velocity considering that enough space-time is provided. This technology results promising as an alternative to conventional liquid membranes and the intensification of chemical and fermentative processes.

1. Introduction

1.1. Liquid membranes

In a liquid membrane (LM) process three fluid phases are continuously in contact [1]: membrane phase (*M*), donor phase (*D*) and receiving phase (*R*). Membrane phase is an immiscible semipermeable barrier which separates the donor phase from the receiving phase [1,2]. The donor phase contains the solute that is transported from the donor to the receiving phase through the membrane phase. Transport process in liquid membranes involves both liquid-liquid extraction (LLE) and membrane separation in a single device [1]. Usually, the membrane phase is organic [1,2] and comprises a solvent of the LLE process which can include a carrier. When the carrier is within the membrane phase, it reacts spontaneously, rapidly and reversibly with the solute of the donor phase forming a complex which is transported from the *D/M* interphase to *M/R* interphase (facilitated transport), and here, the solute is released to the receiving phase [1].

LMs is a perstraction process that is classified as bulk (BLM), supported (SLM) and emulsion (ELM) liquid membranes according to its configuration [1]. BLMs are commonly used for mass transport and kinetic studies at lab-scale because it is limited by its low specific interface area [2]. SLMs and ELM have potential on applications in industrial scale because they provide large interfacial areas, extraction and stripping are in one stage, simple operation and it is possible to process high quantities of compounds (from donor phase) using small volumes of the membrane phase [1,3]. However, SLMs and ELMs have some stability problems that are limiting their use in industry. On the one hand, during the separation process through a SLM there are losses of the membrane phase components that lead to flux decreasing and the support has to be refilled with the membrane phase [1,2,4]. On the other hand, ELMs require mixing, decantation, and the addition of surfactants to keep stable the double emulsion and, in consequence, drops do not easily break-up to recover the receiving phase [1].

1.2. Taylor flow

Taylor flow (or slug flow) is a type of two-phase flow regime, where a liquid phase flows continuously (continuous phase) within a tube or channel, and there is a periodic occurrence of elongated droplets or bubbles (dispersed phase) within the same channel. Besides geometrical and physicochemical parameters, Taylor flow depends on the flow rate ratio between the continuous and the dispersed phases [5]. The segment of liquid that travels between the droplets (or bubbles) is called slug [5,6]. Taylor flow is characterized by the formation of a toroidal vortex within the slug [5,7,8] and into the droplets [5,9]. In this kind of two-phase flow, heat and mass transfer between the phases is enhanced due to the presence of the internal circulations that helps to renew the

* Corresponding author.
E-mail address: jfontalvoa@unal.edu.co (J. Fontalvo).

https://doi.org/10.1016/j.cep.2019.03.015
Received 2 January 2019; Received in revised form 20 March 2019; Accepted 22 March 2019
Available online 31 March 2019
0255-2701/

Nomenclature

A	Transversal section area of the channel (cm^2)
C_{LA}	Lactic acid concentration (as free LA) at the receiving phase (g/L)
$C_{LA,aq}$	Lactic acid concentration fed at aqueous donor phase (g/L)
$C^*_{LA,aq}$	Lactic acid concentration in equilibria with membrane phase at the side of the aqueous phase (g/L)
$C_{LA\text{-}NA}$	Sodium lactate concentration at receiving phase (g/L)
$C_{LA,out}$	Final lactic acid concentration at the outside of the channel in the donor phase (g/L)
$C^*_{LA,org}$	Lactic acid concentration in equilibria with membrane phase at the side of the membrane phase (g/L)
$C_{LA\text{-}TiOA}$	Concentration of the LA-TiOA complex at membrane phase (g/L)
C_R	Sodium carbonate concentration in the receiving phase (g/L)
LA	Lactic acid
$LA_{complex} = V_R{\cdot}C_R{\cdot}R_{st}{\cdot}(MW_{LA}/MW_R)$	Maximum theoretical amount of lactic acid expected by Eq. (7) at receiving phase (g)
$LA_{free} = C_{LA,out}{\cdot}V_D$	Final amount of lactic acid in the donor phase (g)
LA-TiOA	Complex produced in the reaction between the lactic acid and the tri-iso-octylamine
L_C	Channel length (cm)
LMTF	Liquid membrane in Taylor flow
MW_{LA}	Lactic acid molecular weight
MW_R	Sodium carbonate molecular weight
Q_D	Flow rate of donor phase per injection (cm^3/s)
$Q_{D,Tot}$	Total flow rate when donor phase is injected (cm^3/s)
Q_M	Flow rate of membrane phase (cm^3/s)
Q_R	Flow rate of receiving phase per injection (cm^3/s)
$Q_{R,Tot}$	Total flow rate when receiving phase is injected (cm^3/s)
Ra	Degree of lactic acid removed in the LMTF system
$R_{LA} = Q_D{\cdot}t_{inj}{\cdot}(C_{LA,aq} - C_{LA,out})$	Amount of lactic acid removed from donor phase (g)
R_{st}	Stoichiometric ratio between lactic acid and sodium carbonate in Eq. (7)
$TiOA$	Tri-iso-octylamine
t_{del}	Delay time between injection of the two dispersed phases (s)
t_{inj}	Injection time of each dispersed phase (s)
U_D	Linear velocity of donor phase at injection point (cm/s)
U_R	Linear velocity of receiving phase at the injection point (cm/s)
V_D	Volume of donor phase per injection (cm^3)
V_R	Volume of receiving phase per injection (cm^3)
τ_D	Space-time of the donor droplets (s)
τ_R	Space-time of the receiving droplets (s)

interfaces. Also, there is a high specific interfacial area and a high mass and heat transfer in a liquid film, next to the tube wall, that surrounds the dispersed drops [10,11].

Taylor flow regime can be predicted using the capillary number (Ca) that relates the viscous with interfacial tension forces [12]. The Capillary number is defined as $Ca = U_d^* \mu/\sigma$, where U_d is the mean droplet velocity, μ is the viscosity of the continuous phase, and σ is the interfacial tension between the phases. The values of Ca in Taylor flow are low because the interfacial tension force dominates over the viscous force. Additionally, Ca can be used to predict the hydrodynamic conditions of the system such as the thickness of the liquid film [13], the vortex formation and the bubbles or droplet shape [5,9].

Application of Taylor flow on liquid-liquid extraction has attracted the attention of several researchers due to the enhanced characteristics in mass transfer of this regime flow. Current studies are focused on the influence of the geometry of the channel on mass transfer [14], on the influence of the operating conditions such as flow rate ratio (continuous to dispersed phase) and slug length on mass transfer performance [15], on incorporation of twisted mixers to the channels [16], and on the configuration channel design [17], among others.

1.3. The liquid membrane in Taylor flow regime

In this work, an alternative kind of contact among phases of a liquid membrane has been developed by extending the Taylor flow regimen to a three-phase system [18,19]. In this membrane technology, called liquid membrane in Taylor flow regime (LMTF), the membrane phase is used as a continuous phase (slugs), and the donor and receiving phases are dispersed aqueous phases (droplets). All these phases flow within a channel. The solute (S) is transferred from the donor phase to the membrane phase and, from here, to the receiving phase (Fig. 1).

As a proof of concept of the LMTF, this work presents experimental results of lactic acid removal at several operating conditions such as volumetric membrane phase flow, donor and receiving volumetric injection flow, injection time of the dispersed phases and delay time.

1.4. Description of a liquid membrane in Taylor flow regime

The LMTF operates by injecting a single droplet or several droplets of each aqueous phase. The injection of the dispersed phases (donor and receiving) is carried out by cycles while the membrane phase flows continuously through the channel. Each injection cycle follows the next four steps: First, the donor phase is injected during an injection time of the donor phase (t^D_{inj}, the elapsed time for constant injection flow of the donor phase). Then, the injection of the donor phase is stopped and a delay time (t_{del}, the elapsed time from the end of the injection of the donor phase to the start of the injection of the receiving phase) elapses. Afterward, the receiving phase starts to inject during an injection time of receiving phase (t^D_{inj}, the elapsed time for constant injection flow of the receiving phase), and in the fourth step, the receiving phase injection is stopped and a delay time (t_{del}) elapses again.

A train of droplets of the respective phase is formed during the injection of the donor or receiving phases. Two kinds of slugs, with their respective lengths, are formed during each injection cycle (Fig. 2). There is a slug length between the back cap of the last droplet of a train of droplets of the donor phase and the front cap of the first droplet of the subsequent train of droplets of the receiving phase. Another slug is located within the train of droplets of the same phase (donor or receiving), and its length is given between the back cap of a droplet and the front cap of the subsequent droplet of the same phase.

The velocity of each phase could change and depends on the flow of the membrane phase and the injection flow of each dispersed phase. During delay times, the only phase that is injected is the membrane phase while during injection times both dispersed (donor or receiving)

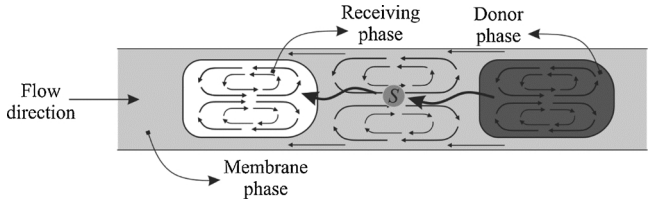

Fig. 1. Scheme for solute (S) transport in a liquid membrane in Taylor flow regime [18].

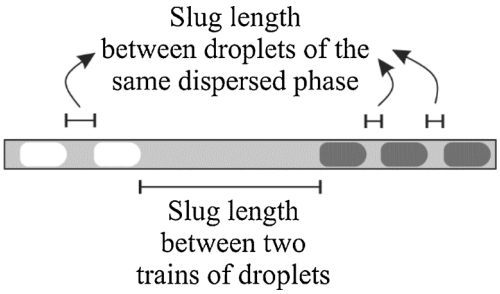

Fig. 2. Scheme of the slug lengths that are formed in the LMTF system [18].

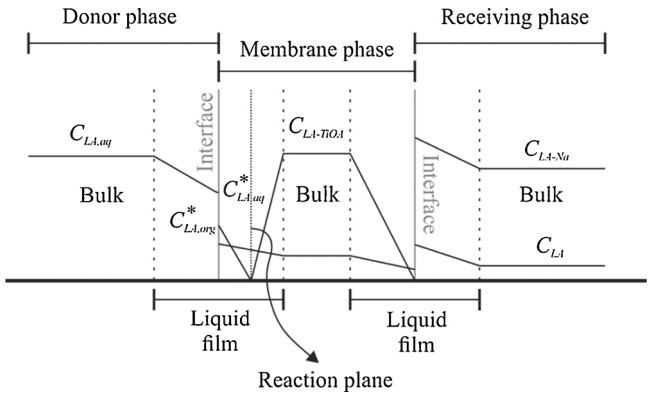

Fig. 3. Lactic acid transport in a liquid membrane in Taylor flow (LMTF) regime with a membrane phase that contains a carrier (TiOA). *D*: Donor phase. *M*: Membrane phase. *R*: Receiving phase (where LA-Na is sodium lactate).

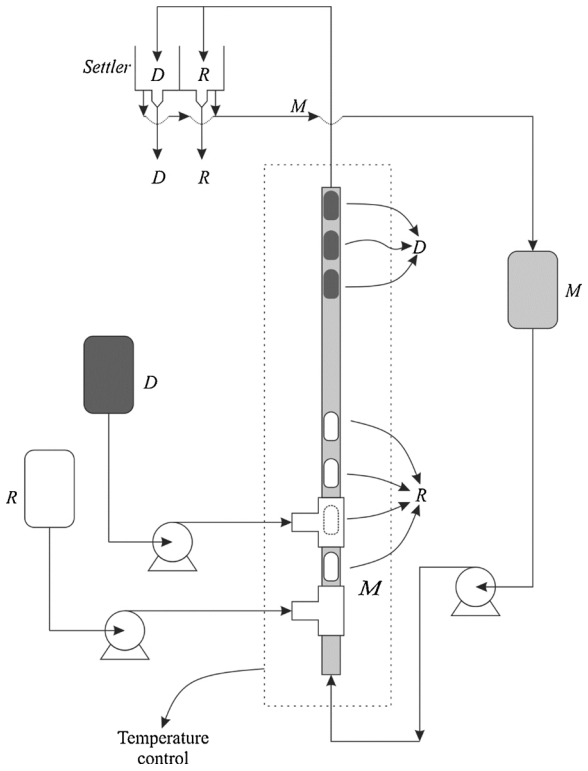

Fig. 4. Schematic experimental set up to carry out the performance test of the liquid membrane in Taylor flow for lactic acid removal [18].

and membrane phases are flowing. Therefore, the total flow during the injection time is higher than the total flow during the delay time, causing changes in velocity for the continuous phase (membrane) and the droplets (donor and receiving).

Table 1
Experimental conditions for lactic acid removal with a LMTF system. Donor flow rate (Q_D) of 2 mL/min. Capillary numbers (for *D/M* and *R/M*) were calculated as it is shown in [52].

Membrane flow rate, Q_M (mL/min)	Receiving flow rate, Q_R (mL/min)	Injection time, t_{inj} (s)	Delay time, t_{del} (s)	$Ca_{mix,D}$	$Ca_{mix,R}$
4.5	1.16	6	6	0.0030	0.0028
4.5	1.16	12	12	0.0030	0.0028
4.5	1.16	16	16	0.0030	0.0028
6.5	1.03	6	6	0.0042	0.0040
6.5	1.03	12	12	0.0042	0.0040
6.5	1.03	16	16	0.0042	0.0040
8.5	0.73	6	6	0.0054	0.0052
8.5	0.73	12	12	0.0054	0.0052
8.5	0.73	16	16	0.0054	0.0052
9.9	0.70	6	6	0.0063	0.0061
9.9	0.70	12	12	0.0063	0.0061

1.5. Lactic acid extraction

Long-chain aliphatic amines have proved to be efficient for organic acid extraction from aqueous solutions [20–25] where the tertiary amines combined with other organic substances (diluents) have been the most widely used. Diluents are used to improve the physical properties of the organic phase such as density, viscosity, interfacial tension, and the extractive capacity [20,24,26]. Trioctylamine (TOA) and tri-iso-octylamine (TiOA) are common tertiary amines used for organic acid removal from aqueous solutions [27–32]. The tertiary amine reacts with the organic acid in the aqueous/organic interface producing an amine-organic acid complex which favored the extraction process of the organic acid [33,34]. Tertiary amines provide high extraction availability, low water solubility and high selectivity [28,35–38].

Currently, there are several studies for LA extraction where potential extractants have been tested. For instance, tertiary amines and other extractants have been modified by adding functionalized silica compounds that provide higher capacity for extraction of the lactic acid [39]. The ionic liquids are another alternative for organic acid extraction that has been tested for LA removal providing high distribution coefficients [40,41]. *N,N*-didodecylpyridin-4-amine (DDAP) extractant is another potential extractant tested for LA removal that reaches LA extraction till 99% [42].

In perstraction processes, while the solute is transported to the membrane phase it is continuously removed from it by the receiving phase [2]. Hence, it is not necessary to use the extractant with the highest distribution coefficient for the organic acid because perstraction processes are not limited by the thermodynamic liquid-liquid equilibria, unlike the liquid-liquid extraction processes. However, if the perstraction process is used for in-situ removal of the organic acid from the fermentation broth, the toxicity of the membrane phase must be taken into account for selecting of a membrane phase to achieve a good compromise between a high value of distribution coefficient and a relatively low toxicity.

In previous works, both the liquid-liquid equilibria of potential membrane phases for LA removal and the molecular toxicity of these potential membrane phases on the *Lactobacillus casei* ATCC 393 (lactic acid bacteria) have been tested [32,43–45]. In this works, a membrane phase composed by TiOA, 1-dodecanol, and n-dodecane has been used which provides a relative low molecular toxicity on the *Lactobacillus casei* ATCC 393 and a relative high LA extraction capacity [44].

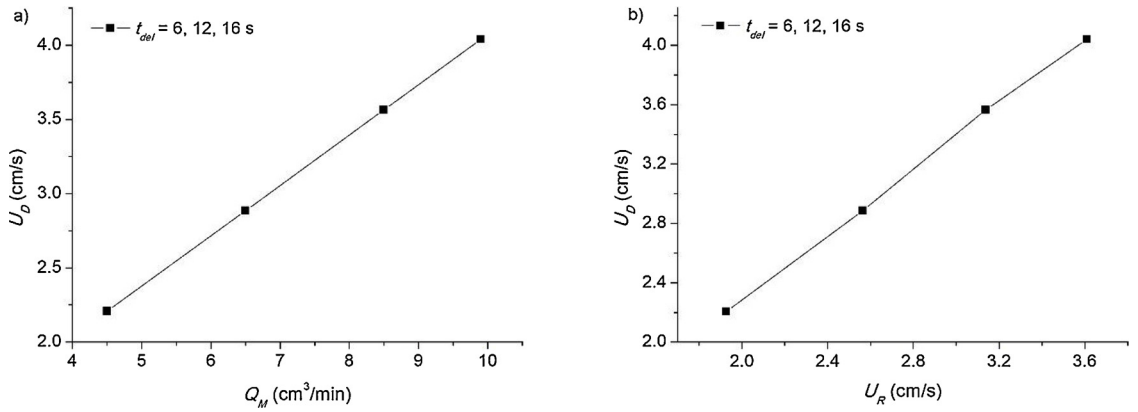

Fig. 5. a) Velocity of the donor droplets at several membrane flow rates. b) Velocity of donor droplets at each corresponding velocity of receiving droplets.

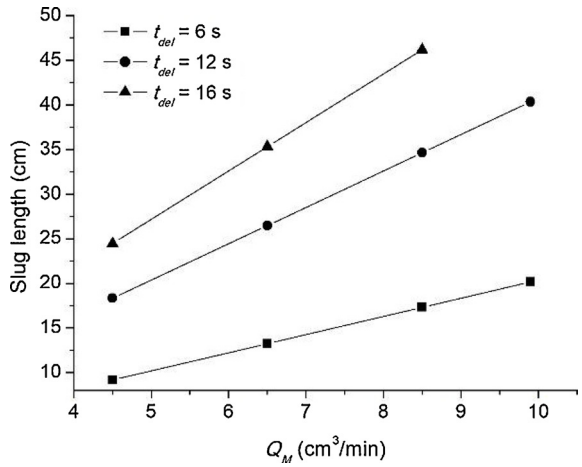

Fig. 6. Slug length between the train of droplets of the donor phase and the subsequent train of droplets of the receiving phase as a function of the membrane flow rate for three delay times. Use Fig. 5 to read donor phase and receiving phase velocities at each membrane flow rate.

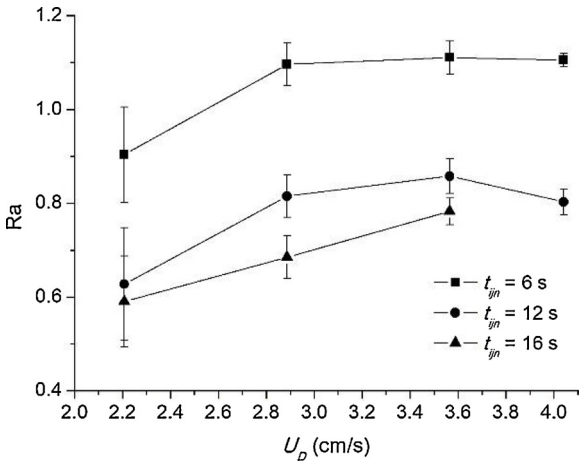

Fig. 8. Degree of lactic acid removal at three injection times as a function of the donor droplet velocity.

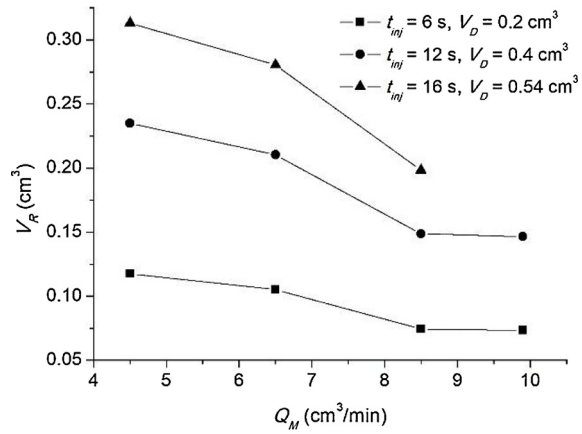

Fig. 7. Injected volumes of the receiving phase at several flow rates of the membrane phase and injection times. Use Fig. 5 to read donor phase and receiving phase velocities at each membrane flow rate.

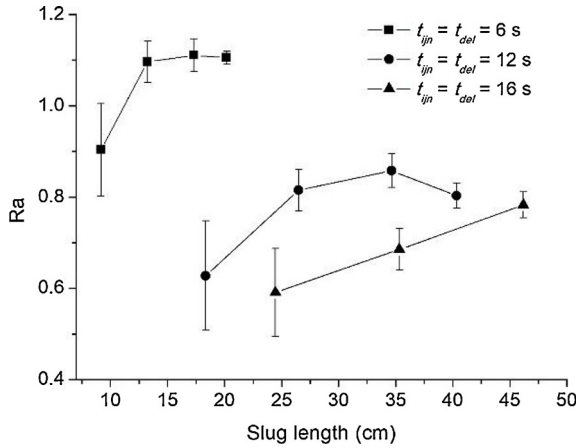

Fig. 9. Effect of the slug length on the degree of lactic acid removal at different injection and delay times.

2. Experimental

2.1. Materials

Tri-iso-octylamine (assay 95%), n-dodecane (assay 99%), 1-dodecanol (assay 98%), sulfuric acid (assay 95–97 %) and sodium carbonate anhydrous (assay 99.5%) were supplied by Merck Millipore. L(+)-lactic acid was supplied by Panreac Química S.A.U. (assay 88.0–92.0 %). The lactic acid, according to the supplier, contains a maximum concentration of metals of 0.001 wt.%. However, HPLC measurements do not show additional peaks besides lactic acid. The purity of lactic acid was assessed by titration with sodium hydroxide of Carlo Herba (assay ≥ 97.0%) using Metrohm automatic titrator (702 SM Titrino, 703 TI Stand). Type I water was used for all aqueous solutions (Barnstead™ Nanopure™).

2.2. Preparation of the phases

The membrane phase is composed by a mixture of tri-iso-octylamine (TiOA), 1-dodecanol and n-dodecane at 10, 40 and 50 vol%, respectively, where the amine is the carrier, dodecanol an active diluent and dodecane an inert diluent [45]. The donor phase was an aqueous solution of lactic acid at 10 g/L prepared from a stock solution of lactic acid at 150 g/L previously heated at 90 °C under total reflux between 8–10 hours for dimer hydrolysis [32,46,47] and it was quantified by titration using Metrohm automatic titrator (702 SM Titrino, 703 TI Stand). The receiving phase was an aqueous solution of sodium carbonate at 2.5 g/L.

2.3. Liquid membrane transport between the phases

The carrier, TiOA, within the membrane phase reacts with lactic acid (LA, which is the solute) of the donor phase in the *D/M* interphase to produce a LA-TiOA complex [45] in the side of the liquid film of the membrane phase where is located the reaction plane [48]. Also, free LA is solubilized into the membrane phase [32]. Both, LA and LA-TiOA complex are transported to the *M/R* interphase where an instantaneous acid-base reaction is carried out between sodium carbonate (of the receiving phase) and LA (Fig. 3). Thus, the receiving phase contains sodium lactate and free LA.

2.4. Experimental setup and calculations

The lactic acid fermentation are commonly carried out in the range of 35–45 °C, where the optimal temperature of the fermentation depends on the strain used [49–51]. Therefore, we previously carried out several LA fermentations by *Lactobacillus casei* ATCC 393 in this range of temperatures and the optimal fermentation temperature was 37 °C (not shown). Hence, the experiments for LA removal through the LMTF were carried out at 37 °C.

The experimental setup consists of a transparent polyurethane circular channel with an inner diameter of 2.5 mm and a length of 348.8 cm. This channel was coiled in a vertical length of 45 cm inside of a chamber with a controlled temperature of 37 ± 0.5 °C. In the bottom of the channel, two T-junctions were located at 4 cm each other to inject the donor and receiving phases (Fig. 4). The donor phase (*D*) was injected by a syringe pump (Cole-Parmer® Touch Screen Infuse/Withdraw) setting the injection time, delay time and the flow rate. The receiving phase (*R*) was injected by a gear pump (Ismatec, Reglo-z) with a pump-head (Ismatec Z-186) controlling the injection and delay time by an Arduino Mega interface coupled to a solenoid valve (STNC® - DC 24 V). Donor, receiving and membrane phases outflowed at the top channel to a settler with two compartments (lab-made of polytetrafluoroethylene, PTFE) to independently split the donor and receiving phases from the membrane phase. When the train of donor droplets with membrane slugs are near to leave the channel, the outside of the channel is located in one of the compartments of the settler. By knowing the injection times of each phase it is possible to predict the time when the corresponding phase is going to arrive at the top of the channel and so the liquid is driven to the corresponding compartment of the settler (donor or receiving). In each compartment, the corresponding aqueous phase is separated from the membrane phase and the membrane phase is recirculated to the inlet of the LMTF system.

A HPLC pump (Waters 501) was used to continuously feed the membrane phase (*M*) at the bottom of the channel and, after decantation at the top of the channel, it was recycled. Samples of the donor and receiving phases were taken from each container in the settler during an experiment until their LA concentrations were constant (30 to 50 min). Both aqueous phases were constantly purged from their respective containers in the settler. Lactic acid concentrations were measured by HPLC with an ORH-801 column (Chrom Tech), an aqueous solution of 0.01 N of sulfuric acid for the mobile phase, and a RI detector at 45 °C [32].

Several flow rates of the membrane phase, and of the dispersed phases (donor and receiving) were tested at several injections (t_{inj}) and delay times (t_{del}). For every single experiment, the injection times of donor and receiving phases were the same. The operating conditions for each experiment are shown in Table 1.

The total flow when donor ($Q_{D,Tot}$) and receiving ($Q_{R,Tot}$) phases are injecting is calculated taking into account the flow of the continuous phase (Q_M) as is shown below:

$$Q_{D,Tot} = Q_M + Q_D \tag{1}$$

$$Q_{R,Tot} = Q_M + Q_R \tag{2}$$

The average velocity of each phase was calculated as follows:

$$U_D = Q_{D,Tot}/A \tag{3}$$

$$U_R = Q_{R,Tot}/A \tag{4}$$

where A is the transversal area of the channel. The space-time of the dispersed phases was calculated taking into account the time from the injection point (bottom of the channel) to the outside of the channel (this distance corresponds to the channel length, L_C).

$$\tau_D = L_C/U_D \tag{5}$$

$$\tau_R = L_C/U_R \tag{6}$$

The degree of LA removed in the LMTF (*Ra*) is defined as the ratio between the amount of LA removed from donor phase (R_{LA}) and the total amount of LA acid that theoretically can be accepted in the receiving phase ($LA_{complex}$ + LA_{free}), Eq. (8). LA in the receiving phase is accepted as sodium lactate ($LA_{complex}$) and as free LA acid. The maximum theoretical amount of LA as sodium lactate ($LA_{complex}$) depends on the stoichiometry of Eq. (7), while the amount of free LA depends on the final amount of LA in the donor phase (LA_{free}).

$$2\ CH_3\text{-}CH(OH)\text{-}COOH + Na_2CO_3 \rightarrow 2\ CH_3\text{-}CH(OH)\text{-}COO\text{-}Na^+ + H_2CO_3 \tag{7}$$

$$Ra = \frac{R_{LA}}{LA_{complex} + LA_{free}} \tag{8}$$

In the receiving phase, the sodium lactate is first formed till the sodium carbonate is exhausted, and the additional LA is transferred to the receiving phase as a free LA. At the top of the channel the maximum theoretical amount of free LA (LA_{free}) in the receiving phase is close to the concentration of LA in the donor phase. Thus, the final concentration in the donor phase was used as the maximum theoretical amount of free LA (LA_{free}) in the receiving phase in Eq. (8). *Ra* is related to the amount of LA transported but it is limited by thermodynamics. Thus, if the LA activity in the donor and receiving phases are equal at some point within the channel the LA mass transfer ceases. However, in this paper, as a shortcut, instead LA activities we have used LA concentrations and thus the LA activity coefficient is the unity for both donor and receiving phases. Thus, the maximum value of *Ra* can be slightly higher than one because actually LA activity coefficients are slightly different from one which corresponds to non-ideal aqueous phases. On the other hand, *Ra* also includes the flow rates of donor and receiving phases (nomenclature section).

3. Results and discussion

3.1. Flow characterization

Figs. 5–7show the hydrodynamic behavior of the LMTF system regarding droplet velocity, slug length (between donor and receiving phases) and injected volume of the dispersed phases at the tested experimental conditions presented in Table 1. Fig. 5a shows that the velocity of the donor droplets increases as the membrane flow rate rises,

regardless of both delay and injection times. For all operating conditions, the velocity of the droplets of the receiving phase was lower than the velocity of the droplets of the donor phase (Fig. 5b), due to an also lower flow rate of the receiving phase. In the LMTF system can be expected a difference of velocities between the donor droplets and receiving droplets because their physical properties differ as density, viscosity, and interfacial tension. The density of the aqueous phases was measured experimentally at 25 °C, achieving similar values of 1.0013 and 1.0239 kg/m^3 for donor and receiving phases, respectively. In contrast, experimental values for viscosity are different at 25 °C, being 1.17 and 0.7669 mPa·s for donor and receiving phases, respectively. Thus, the donor phase has higher shear stress that allows the droplet to travel faster with an increase of the membrane flow rate than the receiving phase in co-current flow. Goldsmith and Mason [8] have shown that a high viscosity difference produces a high droplet velocity in a liquid-liquid Taylor flow system, and in an additional study, it was observed that more viscous droplets move faster than less viscous ones [53]. On the other hand, the interfacial tension between the membrane phase and the respective dispersed phase (donor or receiving) also have a direct effect on the capillary number and the shape of the droplets [5]. Both, interfacial tension and viscosity influence the hydrodynamic behavior of the phases in Taylor flow regime. The ratio between these properties (σ/μ) is called interfacial velocity, and it has been related to the stability of droplet formation in Taylor flow [8,54,55]. The interfacial tension of receiving and donor phases were not experimentally measured in this work. According to previous CFD simulation that we performed (not shown) it was observed that at the low viscosity ratios (dispersed/membrane) of these experiments, lower than the unit, the influence of the interfacial tension on the interfacial velocity is negligible. Also, the interfacial velocity around the droplets in the organic film is higher at low viscosity ratios than at high viscosity ratios.

For the membrane phase, high flow rates produce high injected volumes and whereby the slug length is also high (Fig. 6). On the other hand, for a fixed flow rate of the membrane phase, a high delay time involves a high injected volume of the membrane phase as well, risen the slug length and producing a higher slope in Fig. 6 as delay time rises.

The volume of the receiving phase per injection cycle increases as the injection time rises for constant membrane and donor flow rates (Fig. 7). On the contrary, the volume of the receiving phase decreases as the membrane flow rate rises for a constant delay time. For injection times of 6, 12 and 16 s, the injected volumes of the donor phase were 0.2, 0.4 and 0.54 cm^3, respectively. For a constant membrane flow rate, the injected volume of the donor phase was higher, between 41 and 63%, than the injected volume of the receiving phase.

3.2. Performance of the LMTF

The behavior of LA transported from donor to receiving phase is shown as a function of the donor droplet velocity, and the slug length in Figs. 8 and 9, respectively. The degree of LA removal increases as the velocity of the donor droplet rises (Fig. 8). At high donor droplet velocities, the LA concentration at the interphase renews faster than at low velocities [56,57]. Also, the higher the velocity of the donor droplets is, the higher the mixing caused by the vortex [55] will be, reducing stagnant zones within the slugs. Additionally, it is observed that *Ra* is almost constant at high velocities of donor droplets, where the LA mass transport is at its maximum.

The removal process of LA through the LMTF depends on two factors. The driving force of LA concentrations between donor droplets and the membrane interface (*D/M*), and the space-time (Eqs. 7 and 8) of the droplets in the channel. High values of *Ra* are expected for high mass transfer rates and high space-times. At low droplet velocities, the mass transfer is low, but the space-time is high. At high droplet velocities the mass transfer is high, but the space-time low.

Since the space-time is inversely proportional to droplet velocity, for a constant channel length of 348.8.cm, the separation process achieves a maximum *Ra*, which occurs at a velocity of 3.5 cm/s (Fig. 8). Thus, despite the high velocities, which provide high mixing for the LA transport, the space-time of the donor phase was not long enough to reach values of *Ra* close to one (except for a $t_{inj} = 6$ s). Solute concentrations within the slug, between the donor droplets, are higher in short slugs than within long ones which have been observed for conventional liquid-liquid Taylor flow [58]. Short slugs lengths (slugs between the donor droplets) are achieved with low droplet velocities which depend on the membrane flow rate (Figs. 5a and 6). Therefore, the driving force between the LA concentration of the donor droplets and the membrane slugs increases as the donor droplet velocity rises (high slug lengths between donor droplets), and thus the value of *Ra* also increases (Fig. 8). However, at high droplet velocities (> 3.5 cm/s) the mass transfer of LA is limited by the space-time of the donor and receiving phases, and a limited *Ra* is achieved.

According to the initial slope of *Ra* at each injection time (Fig. 9), the slug length has a higher impact at low injection times than at high injection times. It is because, when low injection times (that provides low injection volumes) are used the amount of solute that can be transported to membrane phase is lower compared to high injection times, therefore, the driving force between donor phase and membrane phase is higher at low injection times generating a higher slope of *Ra* vs. slug length. On the other hand, *Ra* increases till achieving a maximum value at an optimal slug length, because beyond this point (which is the same points where the velocity of the donor droplets is beyond 3.5 cm/s in Fig. 8) there is not long enough space-time for LA removal.

The abovementioned means that the degree of LA removal is enhanced with an increase of the slug length because a high driving force is induced. Nevertheless, exist a limiting value of the slug length, regarding the mass transfer [59], if it is provided a long enough space-time. When the slug length is too high, stagnant zones can appear between the vortex in the slug and the droplet which decrease the mass transfer between the droplet and the slug [7,60]. Consequently, there is an optimum slug length that produces a maximum *Ra* (Fig. 9) for given injection and delay times.

LA that is transported to the receiving phase as sodium lactate requires a lower space-time than LA that is received as a free acid because of the instantaneous reaction and high driving force in the former case [61]. Thus, *Ra* can also be enhanced if a low volume of receiving phase and a high concentration of sodium hydroxide is used.

Susanti et al [48] study the LA removal using an extraction process in Taylor flow without back-extraction. They found a 100% removal for a space-time of 90 s. In this study, a *Ra* of 1 is found for a residence time of 80 s where extraction and back-extraction occur simultaneously. However, between both studies there are differences in flow rates, channel length and diameter, organic phase composition and concentration, thus this comparison has to be performed with caution.

4. Conclusions

The lactic acid removal in a liquid membrane in Taylor flow regime (LMTF) was measured at several membrane flow rates, injection times of the dispersed phases and delay times. Also, the hydrodynamic behavior of the LMTF was measured as a function of these parameters. LMTF showed that is potentially useful for removal of LA acid from aqueous solutions.

The degree of LA removal (*Ra*) through the LMTF systems depends on the driving force of LA concentrations between donor droplets and the membrane interface (*D/M*), and the space-time of the phases within the channel. The LA removal among the phases is enhanced by low injection times and high velocity of dispersed phases, which produces long space-times and high mass transfer driving forces. Also, there is an optimal value of slug length for a given injection and delay times to achieve the maximum value of *Ra*.

The LMTF is a potential technology for industrial applications that

preserves the advantages of conventional emulsion liquid membranes while overcomes the stability problems of emulsion systems. LMTF can be integrated to other systems and enables the intensification of chemical and fermentative processes.

Funding

This research was financial supported by National University of Colombia-Manizales under projects 23,097 and 28046, and by Colciencias under call 647. Departamento Administrativo de Ciencia, Tecnología e Innovación (Colciencias) - Colombia.

Acknowledgements

We sincerely acknowledge to engineers Oriana Sánchez, Diana Amaya and Eduvier Arango for your experimental support.

References

[1] V.S. Kislik, Liquid Membranes Principles & Applications in Chemical Separation & Wastewater Treatment, 1st ed., Elsevier B.V., Amsterdam, 2010.
[2] R.D. Noble, S.A. Stern, Membrane Separations Technology: Principles and Applications, 1st ed., Elsevier, Amsterdan, 2003.
[3] N.M. Kocherginsky, Q. Yang, L. Seelam, Recent advances in supported liquid membrane technology, Sep. Purif. Technol. 53 (2007) 171–177.
[4] A. Pérez de los Ríos, F.J. Hernández-Fernández, F. Tomás-Alonso, J.M. Palacios, G. Víllora, Stability studies of supported liquid membranes based on ionic liquids: effect of surrounding phase nature, Desalination 245 (2009) 776–782.
[5] T. Taha, Z.F. Cui, Hydrodynamics of slug flow inside capillaries, Chem. Eng. Sci. 59 (2004) 1181–1190.
[6] T.C. Thulasidas, M.A. Abraham, R.L. Cerro, Flow patterns in liquid slugs during bubble-train flow inside capillaries, Chem. Eng. Sci. 52 (1997) 2947–2962.
[7] G.I. Taylor, Deposition of a viscous fluid on a plane surface, J. Fluid Mech. 9 (1961) 218.
[8] H.L. Goldsmith, S.G. Mason, The flow suspensions through tubes. II. Single large bubbles, J. Coloid Sci. 18 (1963) 237–261.
[9] R. Gupta, S.S.Y. Leung, R. Manica, D.F. Fletcher, B.S. Haynes, Hydrodynamics of liquid–liquid Taylor flow in microchannels, Chem. Eng. Sci. 92 (2013) 180–189.
[10] D. Tsaoulidis, P. Angeli, Effect of channel size on liquid-liquid plug flow in small channels, AIChE J. 62 (2016) 315–324.
[11] A. Ufer, M. Mendorf, A. Ghaini, D.W. Agar, Liquid-Liquid slug flow capillary microreactor, Chem. Eng. Technol. 34 (2011) 353–360.
[12] F.P. Bretherton, The motion of long bubbles in tubes, J. Fluid Mech. 10 (1961) 166–188.
[13] P. Aussillous, D. Quéré, Quick deposition of a fluid on the wall of a tube, Phys. Fluids (1994) 12 (2000) 2367–2371.
[14] M. Sattari-Najafabadi, M. Nasr Esfahany, Z. Wu, B. Sundén, Hydrodynamics and mass transfer in liquid-liquid non-circular microchannels: comparison of two aspect ratios and three junction structures, Chem. Eng. J. 322 (2017) 328–338.
[15] F. Kaske, S. Dick, S.A. Pajoohi, D.W. Agar, The influence of operating conditions on the mass transfer performance of a micro capillary contactor with liquid–liquid slug flow, Chem. Eng. Process. Process Intensif. 108 (2016) 10–16.
[16] O. Jafari, M. Rahimi, F.H. Kakavandi, Liquid-liquid extraction in twisted micromixers, Chem. Eng. Process. Process Intensif. 101 (2016) 33–40.
[17] P. Plouffe, D.M. Roberge, A. Macchi, Liquid-liquid flow regimes and mass transfer in various micro-reactors, Chem. Eng. J. 300 (2016) 9–19.
[18] J. Fontalvo, A.D. Pérez, Membrana Líquida y proceso para realizarlo, Colombian pending patent, Rad. 15-131023.
[19] A.D. Pérez, Desarrollo y evaluación de un sistema de membrana líquida en flujo de Taylor para la remoción de ácido láctico, Master dissertation, Universidad Nacional de Colombia, 2014.
[20] M. Marinova, J. Albet, J. Molinier, G. Kyuchoukov, Specific influence of the modifier (1-Decanol) on the extraction of tartaric acid by different extractants, Ind. Eng. Chem. Res. 44 (2005) 6534–6538.
[21] R. Canari, A.M. Eyal, Extraction of carboxylic acids by amine-based extractants: apparent extractant basicity according to the pH of half-neutralization, Ind. Eng. Chem. Res. 42 (2003) 1285–1292.
[22] Z. Gu, B.A. Glatz, C.E. Glatz, Propionic acid production by extractive fermentation. I. Solvent considerations, Biotechnol. Bioeng. 57 (1998) 454–461.
[23] A.M. Eyal, R. Canari, pH dependence of carboxylic and mineral acid extraction by amine-based extractants: effects of pKa, Amine Basicity, and diluent properties, Ind. Eng. Chem. Res. 34 (1995) 1789–1798.
[24] H. Ziegenfuß, G. Maurer, Distribution of acetic acid between water and organic solutions of tri-n-octylamine, Fluid Phase Equilib. 102 (1994) 211–255.
[25] S.T. Yang, S.A. White, S.T. Hsu, Extraction of carboxylic acids with tertiary and quaternary amines: effect of pH, Ind. Eng. Chem. Res. 30 (1991) 1335–1342.
[26] S. Pandey, S. Kumar, Reactive extraction of gallic acid using aminic and phosphoric extractants dissolved in different diluents: effect of solvent's polarity and column design, Ind. Eng. Chem. Res. 57 (2018) 2976–2987.
[27] G. Malmary, J. Albet, A. Putranto, H. Hanine, J. Molinier, Measurement of partition coefficients of carboxylic acids between water and triisooctylamine dissolved in various diluents, J. Chem. Eng. Data 43 (1998) 849–851.
[28] D.H. Han, W.H. Hong, Water-enhanced solubilities of lactic acid in reactive extraction using Trioctylamine/Various active diluents systems, Sep. Sci. Technol. 33 (1998) 271–281.
[29] D. Yankov, J. Molinier, J. Albet, G. Malmary, G. Kyuchoukov, Lactic acid extraction from aqueous solutions with tri-n-octylamine dissolved in decanol and dodecane, Biochem. Eng. J. 21 (2004) 63–71.
[30] G. Kyuchoukov, A. Labbaci, J. Albet, J. Molinier, Simultaneous influence of active and "inert" diluents on the extraction of lactic acid by means of Tri- n -octylamine (TOA) and Tri- iso -octylamine (TIOA), Ind. Eng. Chem. Res. 45 (2006) 503–510.
[31] W. Qin, Z. Li, Y. Dai, Extraction of monocarboxylic acids with trioctylamine: equilibria and correlation of apparent reactive equilibrium constant, Ind. Eng. Chem. Res. 42 (2003) 6196–6204.
[32] A.D. Pérez, S. Rodríguez-Barona, J. Fontalvo, Liquid–liquid equilibria for Trioctylamine/1-dodecanol/lactic acid/water system at 306.1, 310.1 and 316.1 K: experimental data and prediction, J. Chem. Eng. Data 61 (2016) 2269–2276.
[33] M. Hossain, Mass transfer investigation of organic acid exatraction with trioctylamine and aliquat 336 dissolved in various solvents, Mass Transf. Multiph. Syst. Its Appl. InTech, 2011, pp. 367–388.
[34] K.L. Wasewar, A.A. Yawalkar, J.A. Moulijn, V.G. Pangarkar, Fermentation of glucose to lactic acid coupled with reactive extraction: a review, Ind. Eng. Chem. Res. 43 (2004) 5969–5982.
[35] D. Yankov, J. Molinier, G. Kyuchoukov, J. Albet, G. Malmary, Improvement of the lactic acid extraction. Extraction from aqueous solutions and simulated fermentation broth by means of mixed extractant and TOA, partially loaded with HCl, Chem. Biochem. Eng. Q. 19 (2005) 17–24.
[36] J.A. Tamada, A.S. Kertes, C.J. King, Extraction of carboxylic acids with amine extractants. 1. Equilibria and law of mass action modeling, Ind. Eng. Chem. Res. 29 (1990) 1319–1326.
[37] B. Choudhury, T. Swaminathan, Lactic acid extraction with trioctyl amine, Bioprocess Eng. 19 (1998) 317.
[38] C.S. López-Garzón, A.J.J. Straathof, Recovery of carboxylic acids produced by fermentation, Biotechnol. Adv. 32 (2014) 873–904.
[39] A. Krzyzaniak, M. Leeman, F. Vossebeld, T.J. Visser, B. Schuur, A.B. De Haan, Novel extractants for the recovery of fermentation derived lactic acid, Sep. Purif. Technol. 111 (2013) 82–89.
[40] F.S. Oliveira, J.M.M. Araújo, R. Ferreira, L.P.N. Rebelo, I.M. Marrucho, Extraction of l-lactic, l-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146.
[41] J. Marták, Š. Schlosser, Extraction of lactic acid by phosphonium ionic liquids, Sep. Purif. Technol. 57 (2007) 483–494.
[42] A. Krzyzaniak, B. Schuur, A.B. De Haan, Equilibrium studies on lactic acid extraction with N,N-didodecylpyridin-4-amine (DDAP) extractant, Chem. Eng. Sci. 109 (2014) 236–243.
[43] A.D. Pérez, S. Rodríguez-Barona, J. Fontalvo, Molecular toxicity of potential liquid membranes for lactic acid removal from fermentation broths using Lactobacillus casei ATCC 393, Dyna 85 (2018) 360–366.
[44] A.D. Pérez, V.M. Gómez, S. Rodríguez-Barona, J. Fontalvo, Liquid-liquid equilibrium and molecular toxicity of active and inert diluents of the organic mixture Tri-iso-octylamine/Dodecanol/Dodecane as potential membrane phase for lactic acid removal, J. Chem. Eng. Data (2019) submited.
[45] A.D. Pérez, S. Rodríguez-Barona, J. Fontalvo, Liquid–Liquid equilibria of lactic acid/water solutions in Tri-iso-octylamine/dodecane/1-dodecanol at 306.1, 310.1, and 316.1 K. experimental data and prediction, J. Chem. Eng. Data 64 (2019) 603–610.
[46] M. Matsumoto, T. Takagi, K. Kondo, Separation of lactic acid using polymeric membrane containing a mobile carrier, J. Ferment. Bioeng. 85 (1998) 483–487.
[47] D. Yankov, J. Molinier, J. Albet, G. Malmary, G. Kyuchoukov, Lactic acid extraction from aqueous solutions with tri-n-octylamine dissolved in decanol and dodecane, Biochem. Eng. J. 21 (2004) 63–71.
[48] J.G.M. Susanti, B. Winkelman, H.J. Schuur, J. Yue Heeres, Lactic acid extraction and mass transfer characteristics in slug flow capillary microreactors, Ind. Eng. Chem. Res. 55 (2016) 4691–4702.
[49] G. Chronopoulos, A. Bekatorou, E. Bezirtzoglou, A. Kaliafas, A.A. Koutinas, R. Marchant, I.M. Banat, Lactic acid fermentation by Lactobacillus casei in free cell form and immobilised on gluten pellets, Biotechnol. Lett. 24 (2002) 1233–1236.
[50] O. Sejong, R. Sungsue, S. Jaehun, K. Sangkyo, B. Yungjin, Optimizing conditions for the growth of Lactobacillus casei YIT 9018 in tryptone-yeast extarct- glucose Medium by using response surface methodology, Appl. Environ. Microbiol. 61 (1995) 3809–3814.
[51] P.S. Panesar, J.F. Kennedy, C.J. Knill, M. Kosseva, Production of l(+) lactic acid using Lactobacillus casei from whey, Braz. Arch. Biol. Technol. 53 (2010) 219–226.
[52] A.D. Pérez, B. Van der Bruggen, J. Fontalvo, Study of overall mass transfer coefficients in a liquid membrane in Taylor flow regime: calculation and correlation, Chem. Eng. Process. - Process Intensif. 134 (2018) 20–27.
[53] G.F. Teletzke, H.T. Davis, L.E. Scriven, Wetting hydrodynamics, Agressologie 23 (1988) 989–1007.
[54] H.V. Nickens, D.W. Yannitell, The effects of surface tension and viscosity on the rise velocity of a large gas bubble in a closed, vertical liquid-filled tube, Int. J. Multiph. Flow. 13 (1987) 57–69.
[55] J.D. Tice, A.D. Lyon, R.F. Ismagilov, Effects of viscosity on droplet formation and mixing in microfluidic channels, Anal. Chim. Acta 507 (2004) 73–77.
[56] M.N. Kashid, D.W. Agar, S. Turek, CFD modelling of mass transfer with and without chemical reaction in the liquid-liquid slug flow microreactor, Chem. Eng. Sci. 62 (2007) 5102–5109.

[57] N. Aoki, S. Tanigawa, K. Mae, A new index for precise design and advanced operation of mass transfer in slug flow, Chem. Eng. J. 167 (2011) 651–656.
[58] C. Butler, E. Cid, A.M. Billet, Modelling of mass transfer in Taylor flow: investigation with the PLIF-I technique, Chem. Eng. Res. Des. 115 (2016) 292–302.
[59] M. Mendorf, D.W. Agar, Scale-up of capillary extraction equipment, Chem. Ing. Tech. 83 (2011) 1120–1124.
[60] J. Fontalvo, Ma G. Vorstman, J.G. Wijers, J.T.F. Keurentjes, Heat supply and reduction of polarization effects in pervaporation by two-phase feed, J. Membr. Sci. 279 (2006) 156–164.
[61] R. Juang, S. Lee, R. Shiau, Mass-transfer modeling of permeation of lactic acid across amine-mediated supported liquid membranes, J. Membr. Sci. 137 (1997) 231–239.