

## Effect of Operating Conditions and Split Ratio for Lactic Acid Purification by Short Path Evaporation System

Andrea Komesu<sup>a,b\*</sup>, Johnatt Oliveira<sup>c</sup>, Luiza H. S. Martins<sup>d</sup>, Rubens Maciel Filho<sup>b</sup>, Maria Regina Wolf Maciel<sup>b</sup>

<sup>a</sup>Department of Ocean Sciences (DCMar), Federal University of São Paulo (UNIFESP), Zip: 11070-100, Santos-SP, Brazil.

<sup>b</sup>School of Chemical Engineering, University of Campinas (UNICAMP), Box: 6066, Zip: 13083-970, Campinas-SP, Brazil.

<sup>c</sup>Institut of Health Sciences, Nutricion School, Federal University of Pará (UFPA), Zip: 66075-110, Belém-PA, Brazil.

<sup>d</sup>Centre Of Natural Sciences and Technology, State University of Pará (UEPA), Zip: 66095-015, Belém-PA, Brazil.

[andrea\\_komesu@hotmail.com](mailto:andrea_komesu@hotmail.com)

An increasing interest for discovery new environment-friendly sources of chemicals has been observed due to the current concerns related to the cost and environmental impact of fossil-based chemicals. One important technological platform is the production of bio-based chemicals by fermentation, such as lactic acid (LA). In this work, LA was produced by fermentation using sugarcane molasses without pretreatment as carbon source and *Lactobacillus plantarum* inoculum. Traditionally, several steps are needed after fermentation to produce the final LA product. By not using organic solvents and not produce gypsum, short path evaporation system (SPE) is an alternative separation process to purify the LA. Evaporator temperature (from 116 to 164 °C) and condenser temperature (from 13 to 22 °C) were studied aiming to determine the best operating conditions for SPE. This evaluation to obtaining maximum LA purity and recovery can be made either in the distillate or in the residue stream. In the range of study, the product obtained at the distillate stream using evaporator temperature of 141 °C and condenser temperature of 17.6 °C presented the richest lactic acid fraction (~70 wt%) with recovery of ~55 %. Using split ratio (mass of residue/ mass of distillate) of 1.5, the residue stream presented ~22 wt% of LA fraction with ~52 % of recovery. In addition, results were compared with previous works using different distillation processes. The comparison was performed based on Purification Performance Index (PPI).

### 1. Introduction

Lactic acid (LA), also known as milk acid, is the most widely occurring carboxylic acid in nature. It was firstly isolated in 1780 by a Swedish chemist, Carl Wilhelm Scheele, but it was firstly produced commercially by Charles E. Avery at Littleton, Massachusetts, USA in 1881 (Ren, 2010). The major parts of LA are used for the synthesis of the polylactic acid (PLA) and in the food industry. LA is also used in pharmaceutical industry and cosmetics as well as in chemical industry. Global LA demand is expected to grow annually by 15.5% to reach 1,960.1 kilo tons by 2020 (Abdel-Rahman and Sonomoto, 2016).

LA can be produced either by chemical synthesis or by fermentation. A small amount is produced by chemical synthesis using acetaldehyde as a starting material (Biddu et al, 2016) where a racemic mixture of the two forms LA (D(-) and L(+)) is produced (Lasprilla et al., 2012). Production by fermentation is an important technological biomass-based platform, which has attracted much attention from the researches because it is an attractive process in terms of its environmental impact, high product specificity, and, additionally, the production of optically pure L- or D- LA, which has been shown to affect the physical and mechanical properties of PLA (Komesu et al., 2017).

Fermentation substrates to LA production, such as corn starch, beets, sugarcane, wheat, sugarcane molasses and others, are based on local availability (Biddu et al, 2016). In Brazil, sugarcane molasses is an agro-industrial by product generated from sugar industry. During the sugar production, approximately 17.9 million tons of molasses are generated as by-product (Haully et al., 2003). By the fact that it is cheap and abundant, the use of sugarcane molasses as raw material for LA production is of great potential.

Traditionally, several steps are needed after fermentation to produce the final LA product (Biddu et al., 2016) and this makes the process expensive. To address this problem, efficient and viable separation technologies are needed.

Short path evaporation (SPE) or molecular distillation is a nonconventional unit operation of diffusional mass transfer indicated for separation of homogeneous liquid mixtures with low volatility, high molecular mass and thermally sensitive (Komesu et al., 2016). The unit operation uses gravity force to promote a thin film on the evaporating cylinder (evaporator), usually with a wiping element that mixes and distributes the liquid over the whole evaporator surface (Fregolente et al., 2007). It has been recognized as a promising technology mainly because its low evaporation temperature and short residence time, which minimize problems with thermal decomposition (Komesu et al., 2013). In addition, SPE can avoid some of the drawbacks of the traditional purification steps, such as gypsum formation and disposal (Biddu et al., 2016).

The use of SPE to recover LA from fermentation broth was the subject of previous works (Komesu et al., 2013; Komesu et al., 2014). In these works were evaluated the influence of operational conditions of the SPE on the dependent variables, that is, lactic acid purity and recovery at distillate and residue streams. The results showed that condenser and evaporator temperatures were significant variables of the process.

Bearing all this in mind, the purpose of this work was to evaluate the optimal operating conditions to obtain maximum lactic acid purity and recovery in the distillate or in the residue stream. The results were compared with previous works using different distillation processes. Furthermore, the analysis was important to determine which one of the studied systems would be better to use in order to purify the LA.

## 2. Materials and Methods

### Raw Material

Fermentation process was carried out in a 7 L New Brunswick Scientific BioFlo 415 bioreactor. Sugarcane molasses (48 % sucrose w/w) without pretreatment from Costa Pinto Mill (Piracicaba, Brazil) was diluted with distilled water in order to obtain an initial sucrose concentration of 32 g/L approximately. The fermentation medium was enriched with 4 g/L of yeast extract to attend the nutritional requirements of the bacterium. 300 mL of *Lactobacillus plantarum* inoculum was added to the fermenter (from Fundação Tropical de Pesquisa e Tecnologia André Tosello, Campinas, Brazil). The temperature was maintained at 37 °C, pH at 5.0 by adding NaOH and agitation speed at 200 rpm. A pulse of diluted molasses (32 g/L) was carried out after the sucrose had been completely consumed in order to avoid the inhibition of the cell growth by high sucrose concentration as well as to increase of lactic acid end concentration. The total time of fermentation was approximately 30 h. The fermentation product containing about 5 % (w/w) lactic acid was vacuum filtered and centrifuged (5000 rpm for 15 min at room temperature) and used as raw material for the investigation of the separation process.

### Short Path Evaporation System

Lactic acid was concentrated in an evaporation system composed by a short path evaporator (SPE), Model Pope 2 Wiped Film Still, manufactured by Pope Scientific Inc. (Saukville, WI, USA). A schematic diagram of the apparatus is shown in Figure 1. Feed raw material (about 40 g at room temperature) was pumped into the still by using a peristaltic metering pump Cole Palmer Masterflex model 77200-60 with the flow rate of 14 mL/min. A rotor containing diagonally slotted wiper blades in a heated vertical tube, wiped the incoming liquid circumferentially as well as downward, as a dynamic highly mixed thin film. The rotor was kept in 750 rpm. The incoming liquid evaporated an evaporation surface of 0.033 m<sup>2</sup> (or 0.35 ft<sup>2</sup>) heated by a jacketed with an electric heating system (Komesu et al., 2017). SPE has two condensers, one located internally and other externally to the evaporator. The external condenser was added to the original Pope system (Komesu et al., 2013). The distance between the evaporator and the internal condenser is 17 mm. During the experiments performed in this work, operating conditions ranged from 116 to 164 °C for evaporator temperature, from 13 to 22 °C for condenser temperature, and the external condenser was fixed at -5 °C. The vacuum system is composed of a mechanical pump (Edwards AGD, UK), keeping the pressure at 1 kPa. Vacuum control was achieved by means of bleed valves in the vacuum line. These valves had adjustable leaks for vacuum control. The vacuum path includes a cold trap which was continuously fed with liquid nitrogen (-196 °C) to prevent stray light material from entering the vacuum pump. The volatile components condensed as distillate and light streams, while heavier components were collected as residue. The streams were collected in glass flasks and were analysed by liquid chromatography to determine lactic acid purity (Komesu et al. 2017).

### Determination of Lactic Acid Purity

Analyses of the raw material and products were performed in an equipment of high performance liquid chromatography (HPLC), Agilent model 1260, equipped with UV detector (UV/vis) connected in series with the

chromatography column Bio-Rad Aminex, model HPX-87H (300 x 7.8 mm). The equipment was controlled through OpenLab software. Sulfuric acid solution with 5 mM was used as mobile phase at flow rate of 0.6 mL/min. The column temperature was kept constant at 37 °C. An injection volume of 25 µL was used in each run. For lactic acid detection and quantification, the wavelength of 215 nm was used in the UV detection system (Komesu et al., 2013). The lactic acid purities were determined using the calibration curve (regression coefficient of 0.99987) obtained with standard solutions of DL-Lactic acid 90 % supplied by Sigma-Aldrich (St Louis, Missouri, EUA). The identification of the substances peaks in the chromatogram profiles was performed by comparison of their retention times with standard substances.

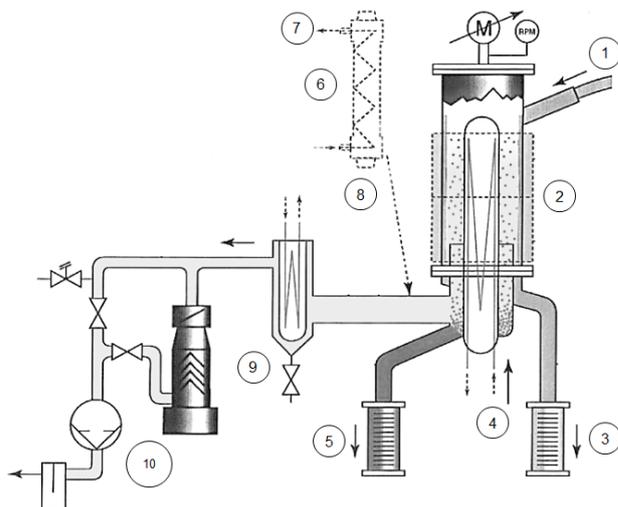


Figure 1: Schematic diagram of evaporator; (1) Feed; (2) Electric jacket; (3) Residue; (4) Coolant; (5) Internal condenser distillate; (6) External condenser; (7) Coolant; (8) External condenser distillate (light); (9) Cold trap; and (10) Vacuum pump; By permission from Pope Scientific, Inc., Saukville, WI, USA (adapted) (Komesu et al. 2017)

### 3. Results and Discussions

Optimal operating conditions aiming to the maximum lactic acid purity and recovery can be made either in the distillate or residue stream. The lactic acid purity (LA) and recovery (Rec) were calculated according Eq(1) and Eq(2), respectively:

$$LA_i (\%) = \frac{m_{\text{lactic acid},i}}{m_i} \quad (1)$$

In which  $i$  is the index for residue or distillate and  $m$  is the residue or distillate mass (g).

$$Rec_i (\%) = \frac{m_i \times LA_i (\%)}{\sum_{i=1}^3 m_i \times LA_i (\%)} \quad (2)$$

In which  $i$  is the index for residue or distillate or light,  $m$  is the residue or distillate or light mass (g) and  $LA_i (\%)$  is the lactic acid purity in residue or distillate or light.

Figures 2 and 3 show the lactic acid purity and recovery on distillate stream varying the condenser temperature and evaporator temperature, respectively. From Figures 2 and 3, it can be seen that, increasing the condenser temperature, the purity increases. Similarly, the purity increases with evaporator temperature, which was expected, because the increment of temperature enlarged the evaporation rate (Chen et al., 2012). The maximum lactic acid purity was 89.71 % using feed flow rate of 14 mL/min, agitation of 750 rpm, condenser temperature of 22 °C and evaporator temperature of 163.7 °C. Although the purity was high, the lactic acid recovery was 14.27 %. Considering the low recovery obtained, this operation condition cannot be considered the optimum of the system. In addition, working with higher evaporator temperature is not recommended because LA can be decomposed in other products (water, hydroxyl, propionic acid, acrylic acid, acetaldehyde, carbon dioxide and formate).

The intersection of the lactic acid purity and lactic acid recovery curves in Figures 2 and 3 show an internal condenser temperature of 17.6 °C and evaporator temperature of 141 °C. In this operating conditions, the

distillate stream show ~70 % of lactic acid purity with ~55 % of recovery. This result can be considered the optimal of the system in the operating range studied.

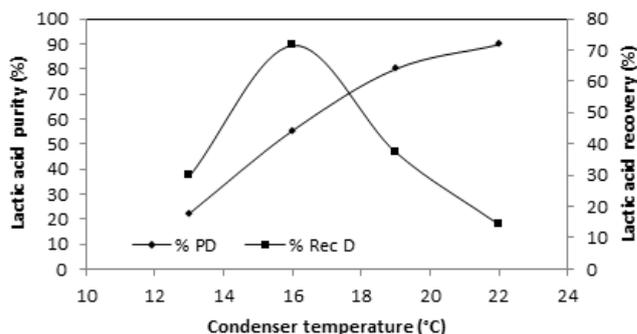


Figure 2: Lactic acid purity (% PD) and recovery (% Rec D) on distillate stream varying the condenser temperature

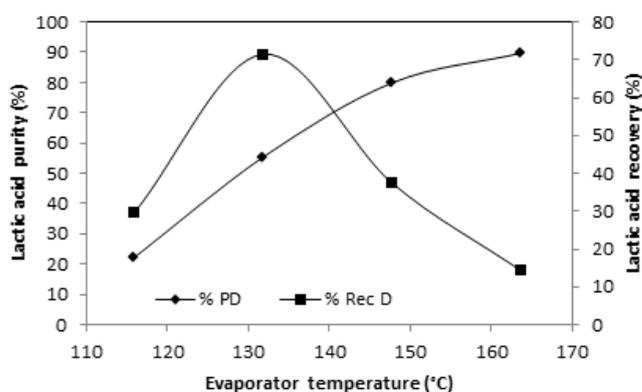


Figure 3: Lactic acid purity (% PD) and recovery (% Rec D) on distillate stream varying the evaporator temperature

The lactic acid purity in residue stream can be studied using the split ratio defined by Eq(3):

$$\text{Split ratio} = \frac{\text{mass residue (g)}}{\text{mass distillate (g)}} \quad (3)$$

The split ratio is an important parameter to evaluate the SPE process, since it incorporates the effects of evaporator temperature and feed flow rate, facilitating the analysis of the results. In addition, another advantage of the split ratio is that the results can be used directly in the scale up of the equipment (Martins, 2006).

The lactic acid purity and recovery in residue stream varying the split ratio can be seen in Figure 4. It is observed from Figure 4 that the lactic acid purity in residue decreased while split ratio increased. Lactic acid purities of ~35 wt% can be achieved by split ratio lesser than 1. In addition, lactic acid recovery on residue stream increased while split ratio increased. Recovery over 90% can be obtained with split ratio of 6.7.

The best results of high lactic acid purity as well as high recovery considering the residue stream were obtained using a split ratio of approximately 1.5. In this split ratio, the residue stream presented lactic acid purity of ~22 wt% and recovery of ~52 %.

Obtaining maximum purity and recovery on the residue stream or on distillate stream depends on the operating conditions used. In the process design to purify lactic acid, the designer will have to choose between obtaining higher concentrations of lactic acid or losing less lactic acid to another stream. If the purity of lactic acid is considered more important than its recovery, the optimum operating condition will be that obtained for the distillate stream.

The knowledge of the optimal operating conditions is crucial for the design of a separation strategy (Martins, 2006). In addition, the results obtained from these experiments are promising because with one step of evaporation and low temperature it was possible to concentrate the lactic acid from fermentation broth. In addition, technical grade lactic acid (70 %) achieved in this work can be used as an acidulant in vegetables (food grades).

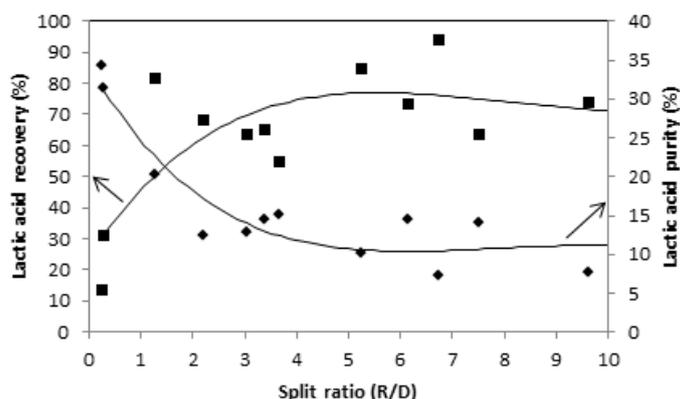


Figure 4: Lactic acid purity and recovery on residue stream varying the split ratio

### 3.1 Purification Performance Index Evaluation

Table 1 shows results obtained in this work and in previous one using different distillation processes. Comparing the results, the highest lactic acid concentration was obtained in this work using SPE, in which lactic acid was concentrated in 18 times. In coupled process (SPE and reactive distillation) and in reactive distillation (RD), lactic acid was concentrated in 4.7 and 2.4 times, respectively.

Table 1 Lactic acid concentration using different separation processes

Separation process	Lactic acid feed	Lactic acid concentration	Reference
Short path evaporation (SPE)	Fermentation	18 Ci	This work
SPE-RD	Commercial	4.7 Ci	Komesu et al., 2016
Reactive distillation (RD)	Commercial	2.4 Ci	Komesu et al., 2015

Ci= lactic acid initial concentration in the feed.

Winkelkemper and Schembecker (2010) developed key performance indicators, as Purification Performance Index (PPI<sub>j</sub>), for rating purification on basis of single step purity improvement. The proposed indicators do not require complete mass and energy balances and can be applied from the beginning of experimental investigation (Winkelkemper and Schembecker, 2010). PPI<sub>j</sub> is calculated according Eq(4) and it was used in order to evaluate the best separation and purification strategy between: SPE, RD and coupled process (SPE-RD). The PPI calculated for each separation process is shown in Table 2.

$$PPI_j = \frac{\tanh^{-1}(2x_{out,j} - 1) - \tanh^{-1}(2x_{in,j} - 1)}{\tanh^{-1}(2x_f - 1) - \tanh^{-1}(2x_0 - 1)} \quad (4)$$

in which  $x_{out,j}$  is the purity at the outlet of a step;  $x_{in,j}$  is the purity at the inlet of a step;  $x_f$  is the final purity, at the end of the complete process;  $x_0$  is the initial purity, before the downstream process; and  $j$  is the purification step  $j$ .

Table 2 Purification Performance Index (PPI) for separation processes

Separation process	$x_{out,j}$	$x_{in,j}$	$x_f$	$x_0$	PPI (%)
Short path evaporation (SPE)	0.8971	0.0471	0.90	0.0471	99.39
Reactive distillation (RD)	0.2632	0.1096	0.90	0.0471	20.47
SPE-RD	0.2197	0.0471	0.90	0.0471	33.43

$x_{out,j}$ =purity at the outlet of a step;  $x_{in,j}$  = purity at the inlet of a step;  $x_f$  = final purity, at the end of the complete process;  $x_0$  = initial purity, before the downstream process; and  $j$  = purification step  $j$ .

It was assumed that the purity to be achieved is 90 wt % ( $x_f$ ), and the initial purity of lactic acid obtained by fermentation process is ~5 wt % ( $x_0$ ). According to Table 2, higher PPI was obtained using SPE, followed by coupled process and RD. Then, SPE is the best strategy for lactic acid purification based on PPI. On the other hand, the coupled process is worse than using only SPE step. So, an increase number of separation steps do not mean purity increase. The advantages of using SPE are: high levels of lactic acid purification are

achieved, it does not use solvent, it reduces the risk of lactic acid thermal decomposition and no further purification is needed. Finally, for a better evaluation, an economic analysis should also be performed.

#### 4. Conclusions

The purification of the lactic acid fermentation product was conducted by using the short path evaporation system (SPE). For tests were used: feed flow rate of 14 mL/min, stirring of 750 rpm, pressure of 1 kPa and was varied the evaporator temperature from 116 to 164 °C and the condenser temperature from 13 to 22 °C. The evaluation of optimal operating conditions to obtaining maximum lactic acid purity and recovery can be made either in the distillate or residue stream. In the range of study, the product obtained at the distillate stream using evaporator temperature of 141°C and condenser temperature of 17.6°C presented the richest lactic acid fraction (~70 wt%) with recovery of ~55 %. Using split ratio (mass of residue/ mass of distillate) of 1.5, the residue stream presented ~22 wt% of lactic acid fraction with ~52 % of recovery. Based on the results, it can be concluded that lactic acid concentration can be successfully performed by using a SPE. Purification Performance Index (PPI) was calculated in order to comparing three separation processes: SPE, reactive distillation (RD) and SPE-RD. SPE was the technology with higher PPI, followed by SPE-RD and RD. Therefore, SPE is the best option for lactic acid separation and purification between the technologies studied.

#### Acknowledgements

The authors are grateful to the financial support from São Paulo Research Foundation (FAPESP), Projects n° 2015/12783-5 and 2008/57860-3 and CNPq.

#### References

- Abdel-Rahman M.A., Sonomoto K, 2016, Opportunities to overcome the current limitations and challenges for efficient microbial production of optically pure lactic acid, *J. Biotechnol.*, 236, 176-192.
- Biddy M.J., Scarlata C., Kinchin C., 2016, Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential; NREL/TP-5100-65509, NREL: Oak Ridge, TN.
- Chen L., Zeng A., Dong H., Li Q., Niu C., 2012, A novel process for recovery and refining of L-lactic acid from fermentation broth, *Bioresour. Technol.*, 112: 280–284.
- Fregolente L.V., Fregolente P.B.L., Chicuta A.M., Batistella C.B., Maciel Filho R., Maciel M.R.W., 2007, Effect of operating conditions on the concentration of monoglycerides using molecular distillation, *Chem. Eng. Res. Des.*, 85(A11), 1524–1528.
- Haully M.C. de O., Oliveira A. R. de, Oliveira A. S. de., 2003, Produção de ácido láctico por *Lactobacillus curvatus* em melaço de cana-de-açúcar, *Semina: Ciências Agrárias*, 24(1), 133 (in portuguese).
- Komesu A., Martins Martinez P.F., Lunelli B.H., Maciel Filho R., Wolf Maciel M.R., 2015, Lactic acid purification by reactive distillation system using design of experiments, *Chem. Eng. Process*, 95, 26-30.
- Komesu A., Martins P.F., Lunelli B.H., Morita A. T., Coutinho P.L.A., Maciel Filho R., Wolf Maciel M.R., 2013, Lactic acid purification by hybrid short path evaporation, *Chemical Engineering Transactions*, 32, 2017-2022.
- Komesu A., Martins P.F., Oliveira J., Lunelli B.H., Maciel Filho R., Wolf Maciel M.R., 2014, Lactic acid purification by hybrid short path evaporation, *Chemical Engineering Transactions*, 37, 367-372.
- Komesu A., Oliveira J.A.R., Martins L.H.S., Wolf Maciel M.R., Maciel Filho R., 2017, Lactic acid production to purification: a review. *Bioresources*, 12 (2), 4364-4383.
- Komesu A., Oliveira J.A.R., Wolf Maciel M.R., Maciel Filho R., 2016, Separation of lactic acid from diluted solution by hybrid short path evaporation and reactive distillation. *J. Chem. Eng.*, 10, 271-276.
- Komesu A., Wolf Maciel M.R., Alves de Oliveira, R., Maciel Filho R., 2017, Influence of residual sugars on the purification of lactic acid using short path evaporation, *Bioresources*, 12(2), 4352-4363.
- Komesu A., Wolf Maciel M.R., Oliveira J., Martins L.H.S., Maciel Filho R., 2016, Purification of lactic acid produced by fermentation: focus on non-traditional distillation processes, *Separation & Purification Reviews*. DOI: 10.1080/15422119.2016.1260034
- Lasprilla A.J.R., Martinez G.A.R., Lunelli B.H., Jardini A.L., Maciel Filho R., 2012, Poly-lactic acid synthesis for application in biomedical devices — A review, *Biotechnol. Adv.*, 30, 321-328.
- Martins, P.F., 2006, PhD Thesis, University of Campinas, Campinas, Brazil (in Portuguese).
- Pope Scientific Inc., 2017, Wiped Film Stills <<http://www.popeinc.com/#&panel1-2>> accessed 1.02.2017.
- Ren, J., 2010, Biodegradable Poly (Lactic Acid) Synthesis, Modification, Processing and Applications, 1st ed.; Springer: New York.
- Winkelkemper T., Schembecker G., 2010, Purification performance index and separation cost indicator for experimentally based systematic downstream process development, *Sep. Purif. Technol.* 72, 34–39.