Swing processes for solvent regeneration in liquid-liquid extraction of succinic acid

Lisette M.J. Sprakel, A.F.M. Holtkamp, R. Bassa, B. Schuur*

University of Twente, Faculty of Science and Technology, Sustainable Process Technology Group, the Netherlands

ABSTRACT

Solvent regeneration processes for liquid-liquid extraction of succinic acid (HSuc) from aqueous streams were investigated. Tri-*n*-octyl amine (TOA) and tri-*n*-octyl phosphine oxide (TOPO) in methyl isobutyl ketone (MIBK) showed good extraction. For 20 wt% TOA in MIBK, addition of pentane at anti-solvent-to-solvent ratio of 1 (vol/vol) decreased K_D from 10.2 to 0.46, applying ethane at 30 bar decreased K_D to 0.45 and increasing the temperature to 60 °C decreased K_D to 1.6. Evaporation of MIBK from a solvent of 40 wt% TOA in MIBK decreased K_D from 10.2 to 4.0. For these processes, capital investments and energy requirements were calculated for 10 kiloton per year at a concentration factor of 5. Costs of all processes to obtain the product at maximum solubility are less than evaporation (2600 kJ/kg product at maximum solubility). A combination of a swing in diluent and temperature results in higher product concentrations after back-extraction, and reduced the energy input to obtain the pure HSuc to 19 MJ/kg. The ethane-based process is most effective with 13 MJ/kg to obtain the pure HSuc product. Although additional capital investments for compressors and pumps are required, only 110 days of production are required for return on investments.

1. Introduction

Liquid-liquid extraction (LLX) can be an efficient, environmentally friendly and economical process for the separation of acids from aqueous streams [1–3], e.g. to recover organic acids from aqueous waste streams and fermentation broths [4]. For a reasonable acid production a neutral pH is required for the fermentation broth, which is challenging for recovery of succinic acid as the acid will mostly be in deprotonated form. Also, production of acids itself will decrease the pH of the broth, decreasing production and thus *in situ* removal of produced acids would be advantageous [3]. Especially in the case of low solute concentrations, similar boiling points of components or thermal decomposition of one (or more) of the components, LLX can be an efficient alternative to distillation.

For an efficient process based on LLX, not only a good extraction but also an effective and easy recovery of the solvent is required [5,6]. The step that can be made in the distribution coefficient K_D between the extraction and regeneration step is even more important than a high K_D in the extraction step. There are various options for solvent regeneration. Evaporation of the acid would be the easiest solution in the case of an acid with a sufficiently low boiling point. However, when the boiling point of the acid is too high, as is the case for succinic acid (HSuc), other options for regeneration must be applied, typically through back-extraction. Examples of regeneration methods include temperature-swing, diluent-swing, pH-swing, acid displacement and precipitation or crystallization [7,8]. In the case of HSuc the initial regeneration process can be followed by crystallization through evaporation of water to obtain the final product. Two possible options without additional formation of byproducts to enhance the back-extraction are diluent-swing regeneration and temperature-swing regeneration, or combinations of these [5]. Diluent-swing may be realized by either adding or removing (a part of) a diluent, which results in a decrease of the acid distribution. Next to adding a liquid diluent, also a pressure-swing regeneration, in which a pressurized gas is applied as an anti-solvent, may be applied. Addition of diluent aims at decreasing the polarity of the solvent mixture to decrease the acid distribution.

To study on the use of diluent or temperature swing for solvent regeneration, extraction of HSuc was selected as case study, because HSuc is an example of a carboxylic acid that can be produced via green routes in a fermentation based process in which glucose is consumed [9,10]. Next to that, being derived from renewable sources, HSuc is a potential green platform chemical [11–13] and it is an important raw

Nomenclature

Symbol		HAB	Acid-base complex (-)
		K	Equilibrium constant (-)
		K_a	Acid-dissociation constant (-)
		n	Number of acids in acid-base complex (-)
A,HA	Acid (-)	pK_a	Acidity (-)
$\bar{A}$	Acid in organic phase (-)	K_D	Distribution coefficient ((mol/L)/(mol/L)),(-)
$[A]$	Concentration of acid (-)	$\frac{K_D}{K_D'}$	Ratio of distribution coefficient in forward and backward-
$[\bar{A}]$	Concentration of acid in organic phase (-)		extraction step (-)
B	Base (-)	K_m	Physical extraction constant (-)
c_0	Initial concentration (mass fraction, -)	T	Temperature (°C)
E	Extraction factor, defined as $E = K_D \frac{S'}{F}$ (-)		

material for several products in industry, such as plastics, solvents and products for the food and pharmaceutical industry [14]. Due to the low acid concentration in the fermentation broth [15], the costs for the downstream processing of the HSuc product stream can be up to 50–70% of the total costs for the production based on the fermentation process [15]. The price of HSuc is roughly 1500 € per ton [16] and therefore, for a fermentation based process to be competitive with the petrochemical based processes, energy and cost efficient processes are required. Hence the industrial relevance of this example [17].

In this research various solvent regeneration strategies have been investigated, all resulting in aqueous solutions of HSuc to be further purified by crystallization, and regenerated solvent that can be sent back to the LLX process to recover HSuc from the aqueous feed stream. The general process scheme, displayed in Fig. 1, consists of the extraction column, the regeneration column and the crystallization column to further purify the concentrated acid stream. In this study the crystallization step is left out of consideration as it will be the same for all processes, and in all processes the final product is a concentrated acid solution that is ready for the crystallization operation.

For several temperature and diluent-swing based processes the swing in the distribution ratio between the extraction and back-extraction step was studied by determining liquid-liquid equilibria before and after the swing in conditions. Processes based on the most promising solvent systems with the largest swing in acid distribution were modeled with Aspen Plus to compare capital investments and required energy input.

2. Theory

In liquid-liquid extraction (LLX) of acids, where the aqueous phase that contains a low concentration of acid is contacted with a solvent phase, the acid distribution K_D between the solvent phase and the aqueous phase is defined in eq (1), where the overbar indicates compounds in the solvent phase.

$$K_D = \frac{[\bar{HA}]}{[HA]} \tag{1}$$

To regenerate the acid from the solvent, a ratio in the acid-distribution between the extraction step and the regeneration step as large as possible is desired, see Eq. (2).

$$\frac{K_D}{K_D'} = \frac{K_{D,\,extraction\ step}}{K_{D,\,back-extraction\ step}} \tag{2}$$

A solvent typically consists of a diluent and a complexating agent (B), such as long-chain tertiary amines [18–21], phosphine oxides and phosphates [2,22,23] to increase the distribution of acid by complex formation with the acid molecules. Complex formation strongly depends on the temperature and medium in which it takes place [18,21,24], therefore a temperature-swing or diluent-swing of active and inactive diluents may be applied to achieve a high $\frac{K_D}{K_D'}$.

3. Materials and methods

3.1. Chemicals

All chemicals were used without further purification and purchased from Sigma Aldrich (HSuc, ≥99%, trioctylamine (TOA, 98%, ρ = 0.809 kg/m³), trioctylphosphine oxide (TOPO, 99%), 1-octanol (> 99%, ρ = 0.830 kg/m³), heptane (99%, ρ = 0.684 kg/m³), pentane (≥99%, ρ = 0.626 kg/m³) and MIBK (≥99%, ρ = 0.802 kg/m³)).

3.2. Experimental methods

3.2.1. Unpressurized liquid-liquid equilibria (LLE)

Unpressurized LLE experiments were performed in 10 or 20 mL glass vials. The aqueous phase and organic phase were mixed in these vials for at least 6 h in the shaking bath. After the equilibration, the phases were allowed to settle and samples were taken from the aqueous phase and analyzed with HPLC. Organic phase compositions were calculated based on a mass balance.
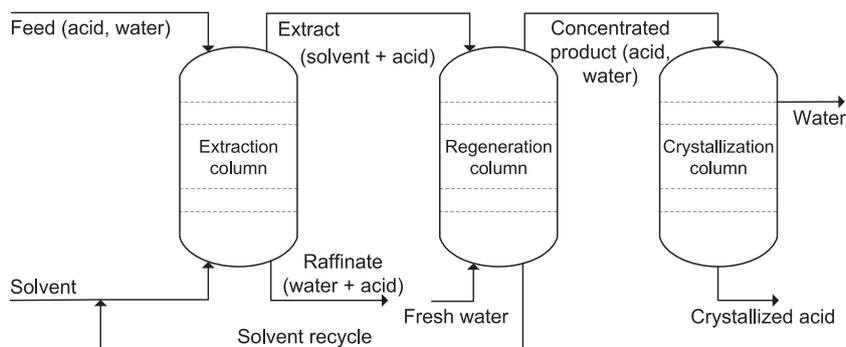

Fig. 1. Schematic overview of a separation process based on liquid-liquid extraction with an extraction column and a regeneration column. The concentrated product of acid in water is further purified by crystallization.

3.2.2. Pressurized liquid-liquid equilibria

The setup to perform LLE experiments under high gas pressures consisted of a vessel (0.25 L, maximum pressure of 60 bar) with a heating/cooling jacket and a mechanical stirrer. Before the experiment the aqueous and organic phase were loaded in the vessel which was then closed. To maintain the pressure, the vessel was connected through a pressure regulator to a gas supply vessel within the setup that can be refilled from the gas supply vessel that is located outside. Before a sample was taken the mechanical stirrer was stopped and the mixture was allowed to settle for 30 min. Samples of the aqueous phase were taken through a tap that is connected to the bottom of the vessel. Organic phase compositions were calculated based on a mass balance.

3.3. Analytical methods

3.3.1. HPLC

The concentration of acid in the aqueous phase was determined using High-Performance Liquid Chromatography (HPLC) on an HPLC Agilent 1200 series with RI detector (accuracy > 99%) and a Hiplex-H column. The mobile phase was 5 mmol/L H_2SO_4 at a flowrate of either 0.6 or 1 mL/min.

3.4. Simulation methods

The modeled processes can be described with four types of process configurations. For the process of temperature-swing regeneration no additional equipment is required and this process is described in Fig. 1. The process of diluent-swing regeneration with distilling of a part of the active diluent before the regeneration column is shown in Fig. 2a and the process in which an inactive diluent is added to the solvent before the regeneration column and distilled off after the regeneration column is shown in Fig. 2b. In both diluent-swing processes an extra distillation column is required to distill off a part of the diluent [5]. For the process of pressure-swing regeneration in which a gas is applied as an anti-solvent, the conceptual process scheme is shown in Fig. 2c. In this case the solvent regeneration column is replaced by a vessel to reduce the pressure of the stream leaving the regeneration column to be able to recycle the gas. For this process also additional compressors (i.e. one for the gas feed of the process and one in the recycle loop) and a pump are required for the pressurization of the streams.

To evaluate and compare the processes, the required energy is calculated relative to a reference case in which the water is evaporated through quadruple effect evaporation to increase the concentration of acid in the product stream. The initial acid concentration is assumed to be 0.012 in mass fraction and a commercial scale production of 10 kta is assumed. The raffinate mass fraction of the extraction columns equaled

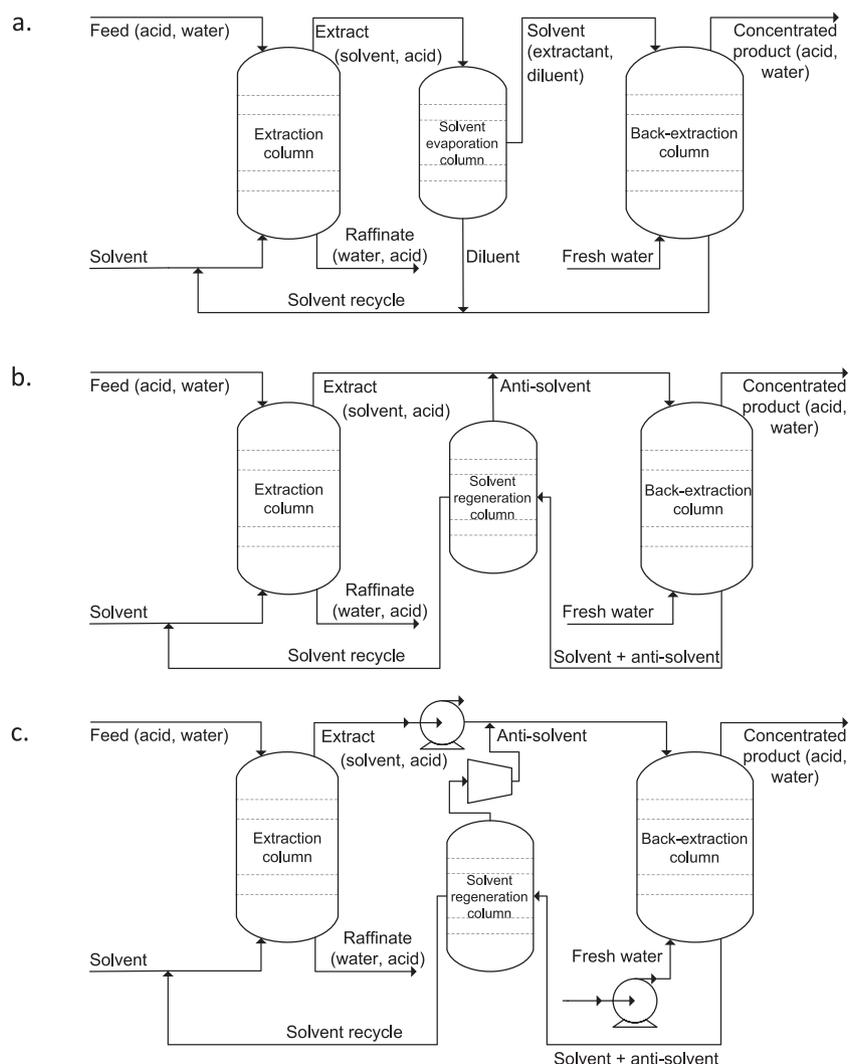**Fig. 2.** Schematic overview of diluent-swing based LLX processes with **a)** diluent-swing by evaporation of a part of the diluent, **b)** diluent-swing by addition of a liquid anti-solvent and **c)** diluent-swing by pressurized gaseous anti-solvent.

0.001. If allowed by the acid distribution ratios, the product stream contained the maximum concentration of HSuc that is soluble at 20 °C, i.e. a mass fraction of 0.061 [25]. At 60 °C the maximum solubility is a mass fraction of 0.22. These concentrations were taken for the product streams of the designed LLX processes [25]. Further upgrading of the product is performed by crystallization, which was not included in the modeling as crystallization is also part of the reference case process based on evaporation of the water. For an equal comparison of the energy required in each of the processes, the energy requirement for evaporation and crystallization to obtain a pure product (weight fraction of 0.995) from the product after extraction and back-extraction is included in the economic evaluation.

The acid mass fraction remaining in the organic phase after the back-extraction (and sent back to the extraction) was assumed to be 0.0005. The ingoing and outgoing concentrations of the streams of both the extraction and regeneration columns were calculated as well as the minimum solvent-to-feed ratio $\left(\frac{S'}{F'}\right)_{min}$, making use of short-cut calculations. $\left(\frac{S'}{F'}\right)_{min}$ of an extraction process can be determined using eqs (3) and (5) that were taken from de Haan et al. [26]. Where X_{in} (= $\frac{x_{in}}{1-x_{in}}$, with x the mass fraction) is the weight ratio in the feed stream, X_{out} the weight ratio in the raffinate and Y_{in} the ingoing weight ratio of the extract stream. The apostrophes indicate the solute free phase flows. The number of theoretical equilibrium stages N_{ts} was calculated with the Kremser equation, eq (6), assuming low concentrations and constant K_D [26]. In this equation extraction factor E is defined as $E = K_D \frac{S'}{F'}$.

For the reference case it is assumed that a quadruple-effect evaporator can be applied to save 75% of the energy duty for evaporation [27,28]. For the energy calculations no heat integration was assumed for these processes and the price of a MWh of energy based on natural gas was estimated to be € 35 [29], which is based on data from the year 2016 but still a reasonable assumption for the current situation considering the low inflation of the past two years.

$$\frac{S'}{F'}_{min} = \frac{X_{in} - X_{out}}{Y_{out,\,max} - Y_{in}} \tag{3}$$

$$Y_{out} = \frac{X_{in} - X_{out}}{\frac{S'}{F'}} + Y_{in} \tag{4}$$

$$Y_{out,max} = K_D \cdot X_{in} \tag{5}$$

$$N_{ts} = \frac{\ln\left[\left(\frac{x_{in} - \frac{y_{in}}{K_D}}{x_{out} - \frac{y_{in}}{K_D}}\right)\left(1 - \frac{1}{E}\right) + \frac{1}{E}\right]}{\ln E} \tag{6}$$

Aspen Plus V10 modeling software was applied to model the three processes as well as the reference case in which the NRTL method was applied for the calculation of the distillations and flash columns for the evaporators. The required solvent flows, number of stages and product concentrations of the extraction operations were calculated with the shortcut calculations of eqs (3)–(6) using the distribution ratios that were measured and not using Aspen Plus. The capital expenses required for these extraction columns were estimated with the Aspen Plus Aspen Process Economic Analyzer based on the calculated flows and required number of stages in combination with a default packed column. Distillations were simulated using RadFrac, by optimizing the variable 'bottoms to feed ratio' in the software to match the bottom flowrate and composition that was calculated based on the measured K_D values and calculated minimum S/F ratios. For the modeling of the distillation of water from the aqueous solutions of HSuc for the reference case and the additional distillation required for upgrading of the product in case a too low product concentration was obtained after regeneration only 3 stages were applied and no reflux (i.e. simple evaporation of the water),

whereas evaporation of MIBK and pentane was applied using 10 stages and a reflux ratio of 1.5. Multi-effect four stage evaporators were modeled as a series of flash columns (Flash2) and connected heat exchangers over a decreasing pressure range from 1.7 to 0.3 bar, for the modeling of the reference case of water evaporation from the aqueous HSuc feed stream to obtain the concentrated product. By defining the vapor fraction of the first flash column, the fraction of water evaporating in the multi-stage evaporator could be adjusted. Flash2 and Flash3 columns were applied for the splitting of the aqueous and organic phase in the modeling of the extraction and back-extraction columns. The capital investments for each process were calculated with the Aspen Process Economic Analyzer.

4. Results and discussion

4.1. Effect of solvent composition on succinic acid distribution

Applications of long chain tertiary amine mixtures in MIBK and 1-octanol have been reported for the extraction of HSuc from aqueous streams [5,18,30], and also long chain phosphine oxides, e.g. trioctylphosphine oxide (TOPO), are used for carboxylic acids extraction in general, including for HSuc [2,31]. Therefore, the initial mapping of solvent effects to identify possibilities for diluent swing was performed with solvents based on trioctylamine (TOA) and trioctylphosphine oxide (TOPO). Some diluents commonly applied in carboxylic acid extractions, such as chloroform and toluene, were avoided because of their negative environmental impact, and the effect of solvent composition on the distribution of HSuc was studied with MIBK and 1-octanol.

For extraction of carboxylic acids, generally a maximum distribution of acid is observed for solvents with a tertiary amine composition around 30 vol% (= 28–30 wt%, depending on diluent) [21,32,33], thus in this research the full range of compositions was covered for the TOA-based solvents. Since TOPO is a solid at room temperature and thus problematic solubility and third phase formation can be expected at higher concentrations, experiments are performed at concentrations of TOPO of up to 40 wt%. The results for liquid-liquid equilibrium experiments using 1-octanol as a diluent at 20 °C (initial acid mass fraction c_0 of 0.012 and volume based solvent-to-feed ratio S/F of 1/3) are displayed in Fig. 3a.

For TOA in 1-octanol (Fig. 3a) very high maximum distribution ratios of 42.6 and 42.1 were obtained at 20 and 39 wt%, respectively, similar to distribution ratios obtained for lactic acid [18,34–36]. The graphs show a maximum as a result of on the one hand increasing solvent capacity and solvent affinity for the solute with low and increasing concentration of complexating agent, and on the other hand decreasing solvation ability for the formed complexes at higher concentration of complexating agent. For TOPO in 1-octanol (Fig. 3a) the distribution ratios were much lower, i.e. 0.5 and 0.8 at 20 and 40 wt%, respectively. The observed K_D of HSuc for TOA and TOPO in MIBK are displayed in Fig. 3b. Also here, there is a clear maximum in the K_D of HSuc with increasing TOA concentration in MIBK and these values for MIBK are lower compared to those previously discussed for 1-octanol. Previously reported K_D-values for HSuc extraction with the commercially available long chain tertiary amine mixture Alamine 336 (2–25 wt%) in MIBK by Tamada et al. [18] are approximately 6 at a free aqueous acid mole fraction of 0.012. These values are comparable to those in Fig. 3b. A reduction in the K_D was observed for increasing temperature, which is well in line with earlier work by Tamada and King, who extracted HSuc (c_0 = 0.036 weight fraction) with 13 wt% Alamine 336 in MIBK [5].

Based on the strong temperature and compositional dependency of the HSuc distribution, and the knowledge that inert diluents strongly reduce the distribution of acids, approaches will be investigated for both a temperature-swing and to types of diluent swing, i.e. evaporation of diluent or addition of a second, inert diluent. The success of a temperature-swing process is determined by the dependency of K_D on
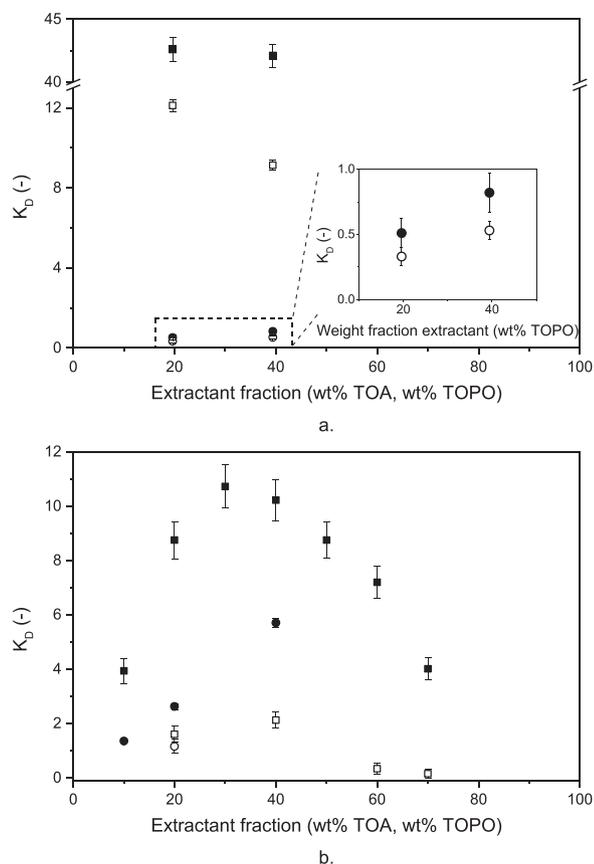
a.

b.

Fig. 3. Effect of solvent composition of complexing agent on the HSuc (c_0 = 0.012 mass fraction) distribution at a room temperature of (closed symbols) 20 °C and elevated temperatures of (open symbols) 60 °C (**a**) or 55 °C (**b**) with a volume based solvent to feed ratio of 1/3 for TOA (squares) and TOPO (circles) in **a)** 1-octanol and **b)** MIBK.

the temperature and similarly the success of a diluent-swing process is determined by the dependency of K_D on the volume fraction of complexating agent in the solvent and the ease of evaporation of the diluent or anti-solvent. Moreover, the existence of a maximum in K_D with varying solvent composition is important for the application of a diluent-swing process. With a diluent-swing process by evaporation the volume fraction of TOA is increased, therefore a solvent with a concentration of complexating agent above the maximum should be used as the starting solvent, e.g. 40 wt% TOA in MIBK. Then, upon evaporation of a part of the MIBK, K_D decreases as can be seen for higher

concentrations of TOA in Fig. 3. This is a good approach for a diluent-swing process and based on these results it can be concluded that TOA in MIBK is a promising solvent for a process based on evaporation of a part of the diluent.

4.2. Diluent-swing by addition of anti-solvent

For diluent-swing by addition of anti-solvent, both addition of liquid anti-solvents (section 4.2.1) and gaseous anti-solvents (section 4.2.2) have been investigated.

4.2.1. Addition of liquid anti-solvent

The effect of the volume based anti-solvent to solvent ratio on the distribution ratio of HSuc for a solvent consisting of 20 wt% TOA in 1-octanol is shown in Fig. 4a. These experiments are performed at an elevated temperature of 55 °C because it is expected that otherwise the distribution ratios obtained with TOA in 1-octanol are too high to allow for a sufficient step in K_D in the regeneration step for a viable process [6,37]. In Fig. 4a it is clear that, even at this elevated temperature, the K_D for 1-octanol indeed only decreases from 10 to approximately 2 with addition of anti-solvent to the solvent in a 1:1 vol ratio. The values for K_D at 20 °C are significantly higher (Fig. 3a) and thus a regeneration process based on a diluent-swing alone is expected to be not feasible for this system, in line with statements reported for similar systems [6,37].

Fig. 4b shows the ratio of the acid distribution with and without anti-solvent $\frac{K_D'}{K_D}$, from which it is clear that the effect of anti-solvent to solvent ratio is stronger for MIBK compared to 1-octanol at an elevated temperature of 55 °C as the K_D is decreased from approximately 2.5 to 0.5 already at a volume based anti-solvent to solvent ratio of 0.5.

To study if addition of anti-solvent is a feasible regeneration process for HSuc extraction with the diluent MIBK, distribution ratios were measured at 20 °C for various (volume based) anti-solvent to solvent ratios and different compositions of the MIBK-based solvent, see Fig. 5 in which absolute K_D (Fig. 5 a–c) as well as the ratio between the distribution coefficients with and without anti-solvent is shown (Fig. 5 d–f). Especially for a solvent consisting of 20 wt% TOA in MIBK there is a strong decrease of K_D, already at low anti-solvent to solvent ratios (Fig. 5a and d). The difference between applying pentane or heptane is only small. For mixtures of TOPO (Fig. 5b and c) the absolute values of K_D are lower and also the decrease with increasing anti-solvent to solvent ratio is less strong than with TOA based solvents (Fig. 5e and f). In this case a mass based composition is applied as TOPO is a solid. The effect on K_D is similar for solvents that contain either 10 wt% or 20 wt% TOPO.

a.

b.
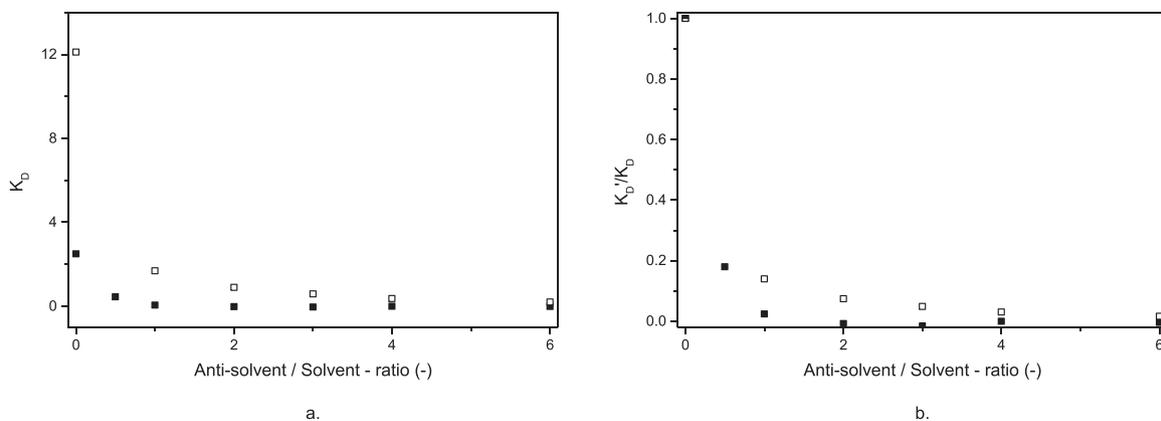
Fig. 4. Effect of anti-solvent / Solvent –ratio on the acid distribution of succinic acid (initial acid mole fraction c_0 = 0.012 and volume based solvent-to-feed ratio S/F of 1/3) for addition of anti-solvent heptane to solvent consisting of 20 wt% TOA in 1-octanol (open symbols) and MIBK (closed symbols) at an elevated temperature 55 °C, with **a)** the acid distribution of succinic acid K_D and **b)** the ratio of the distribution with and without anti-solvent $\frac{K_D'}{K_D}$.
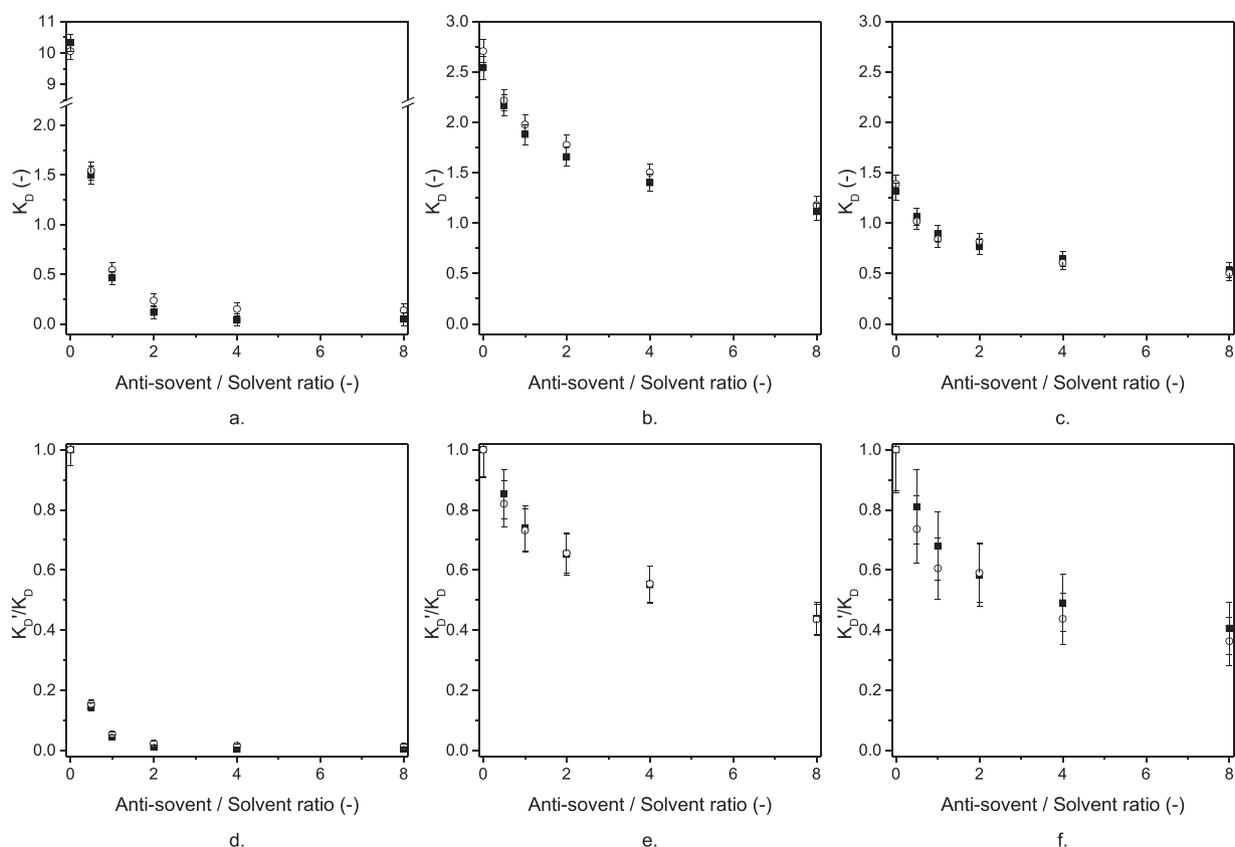
Fig. 5. Effect of anti-solvent / solvent ratio on distribution of succinic acid ($c_0 = 0.012$ mole fraction) at 20 °C with heptane (open symbols) and pentane (closed symbols) as anti-solvents, solvent-to-feed ratio of 1/3 and the solvent phase consisting, with in the top row (**a, b** and **c**) K_D and in the bottom row (**d, e** and **f**) the ratio of acid distribution with and without anti-solvent $\frac{K'_D}{K_D}$ of **a + d**) 20 wt% TOA in MIBK, **b + e**) 20 wt% TOPO in MIBK and **c + f**) 10 wt% TOPO in MIBK.

4.2.2. Addition of gaseous anti-solvent

Three types of gases were investigated as potential anti-solvents, i.e. methane, ethylene and ethane. There is no data available for their solubility in either TOA or MIBK so for an estimate of their solubility in the solvent phase the solubility in the organic solvent 1-octanol as well as the solubility in water based on literature is shown in the first two columns of Table 1. Ethane and ethylene show significantly higher solubility in 1-octanol, but also increased water solubility at both 1 atm and 30 bar, which especially for ethylene may have a counter effect.

The composition of the liquid phase of 1-octanol and MIBK upon pressurization with methane and ethane was also predicted at 20 °C and 1 or 30 bar using Aspen Plus V10 and the UNIFAC model, see Table 1. The calculated mass fractions for gas solubility are over predicted, compared to the literature values for 1-octanol, but ethane clearly shows a larger solubility for both methods and is thus expected to be more promising as an anti-solvent. As expected, the calculated mass fractions for gas solubility in the diluent at the elevated pressure of 30 bar are significantly higher than at 1 bar. For both methane and ethane the solubility in MIBK compared to 1-octanol is relatively similar. The solubility of ethane of 634 g/kg MIBK is comparable with an anti-solvent to solvent ratio of approximately 2, and when related to results of Fig. 4 a significant effect of the diluent-swing with gaseous anti-solvent may be expected.

LLE experiments were performed for each of the solvent mixtures based on TOA and TOPO in MIBK with methane at a pressure of 30 bar as the anti-solvent, the results are displayed in Fig. 6. A sample of the composition of the aqueous phase was taken directly after liquid-liquid equilibration, before applying the methane pressure of 30 bar (t = 0 h). Then, after t = 2, 4 and 6 h of pressurization the concentration of the aqueous phase was also determined. The measured initial K_D (7.9, see Fig. 6a) for 20 wt% TOA in MIBK without anti-solvent is lower than

reported in Fig. 5 ($K_D = 10.2$), this may be a result of small differences in solvent-to-feed ratio, room temperature or equilibration/settling time for the experiments with gases since all samples had to be taken in the course of one day. The results in Fig. 6 clearly indicate that equilibrium was always achieved within 2 h. The effect of methane on K_D is stronger for TOA-based solvents (Fig. 6a and b) than for TOPO-based solvents (Fig. 6c and d). The relative change in K_D is similar for 20 wt% TOA in MIBK (Fig. 6a) and 10 wt% TOA in MIBK (Fig. 6b). When ethylene was applied as an anti-solvent for the TOPO-based solvent (Fig. 6c) there was no significant increase in K_D compared to methane, while for the TOA-based solvent (Fig. 6a) the effect on K_D was significantly stronger than with methane. Upon applying ethane the decrease in K_D is again stronger (Fig. 6a) and even comparable to the effect of the anti-solvents pentane and heptane (Fig. 5a), when the anti-solvent to solvent ratio of approximately 2 based on the maximum solubility (Table 2) is assumed.

4.3. Combined effect of pressure-swing and temperature-swing

In an attempt to improve the performance of the methane based pressure-swing regeneration this process was combined with a temperature-swing in which the temperature was increased from 20 °C to 60 °C in the regeneration step, see Fig. 7. The effect of temperature itself is very strong (time = 0 h) for both TOPO-based and TOA-based solvents, as was also seen in Fig. 3, and the additional effect of the applied methane pressure is only very small (time = 6 h). Therefore, it can be assumed that combining an additional pressure-swing process with a temperature-swing based process is not worth the additional investment costs of the pressurization.

Table 1
Solubility and critical point of selected gases [38,39].

Gas	Solubility in water (g/kg) at 1 atm[a]	Solubility in water (g/kg) at 30 bar[a]	Solubility in 1-octanol (g/kg) at 1 atm[a]	Modeled solubility in 1-octanol (g/kg) at 1 bar	Modeled solubility in 1-octanol (g/kg) at 30 bar	Modeled solubility in MIBK (g/kg) at 1 bar	Modeled solubility in MIBK (g/kg) at 30 bar	Critical temperature (K)	Critical pressure (bar)
Methane	0.023	0.71	0.35	4.1	135	3.7	127	190.56	45.99
Ethylene	0.14	3.88	2.8	–		–		282.35	50.4
Ethane	0.057	1.78	4.1	12.6	565	11.4	634	305.32	48.7

[a] literature data [38,39].

4.4. Process considerations

Four swing based LLX processes, i.e. one process based on a temperature-swing and three based on a diluent-swing, were modeled and compared with each other and with the reference case of water evaporation to concentrate the feed stream. The first two diluent-swing processes are both based on a diluent-swing by addition of an anti-solvent (see Fig. 2b) and both processes use a solvent consisting of 20 wt% TOA in MIBK in the extraction step. In process 1, based on the results in Fig. 5, the anti-solvent pentane is added at an anti-solvent to solvent ratio of 1 (vol/vol) to the solvent mixture before entering the regeneration column. After the regeneration column the stream of solvent and anti-solvent is distilled in order to recycle both solvent and anti-solvent to the extraction and regeneration step, respectively. In process 2, the gaseous 'anti-solvent' ethane with a pressure of 30 bar is added at a volume based anti-solvent to solvent ratio of 1 before entering the regeneration column. After the regeneration column the pressure of the stream with solvent and ethane is reduced to recycle the ethane that will need to be repressurized. A value of $K_D = 7.9$ (Fig. 6) was applied in the calculations in order to have a fair comparison with the measurements after applying ethane as anti-solvent. In process 3, a diluent-swing is applied by evaporating a large part of the MIBK (see Fig. 2b) from the solvent mixture that consists of 40 wt% TOA in MIBK in the extraction step in order to reach a TOA volume fraction of 80 wt% before the regeneration column. In process 4, a temperature-swing is applied between the extraction column and the regeneration column, based on the results of Fig. 7. This process is also based on a solvent that consists of 20 wt% TOA in MIBK.

For each of the processes the energy input and output was modeled as well as the investment costs (input and results given in Table 2) for a commercial scale production plant of 10 kta of pure HSuc, with an HSuc mass fraction of 0.012 in the feed. The last column in Table 2 shows the reference case that is based on quadruple effect evaporation of water from the feed stream to obtain the same product. In case $Y_{out,max}$ was larger than the maximum solubility of HSuc, the maximum solubility of HSuc was applied with the corresponding product flow. This means that a lower amount of stages could theoretically be applied in process 1 and 2, this has however only a marginal effect on the economic evaluation.

From Table 2 it is clear that for process 1 and 3, as well as for the reference case of evaporation, the required capital investments are similar. For process 2 the required compressors and pumps strongly increase the capital investments for the process. For the temperature-swing process, process 4, no extra solvent or equipment is required and the required capital investment is thus lower than for the other processes. The energy input required for all unit operations is low compared to the energy input of the distillation columns in process 1 and 3 and extremely low compared to the energy input that would be required if the evaporation would be performed by simple distillation (reboiler duty of 1950 MW and condenser duty of 1820 MW). For processes 3 and 4 the product concentration is lower than that of the other processes, so the required energy input for additional evaporation of water to obtain the same product is also taken into account and shown in Table 2. Based on all these results the energy per kg of product was calculated in which the additional crystallization and evaporation of the water was also included, showing that the energy input per kg product is very low for the ethane-based pressure swing process (process 2), only 21% of the energy input of the quadruple effect evaporation reference process.

In a temperature-swing process there is no increased concentration in the solvent stream by evaporation. Although K_D was reduced from 10.2 to 1.6 for the temperature-swing process, process 4, (see Fig. 3b) and thus a $1/K_D$ of 0.63, this only resulted in a product concentration of only 0.033 at a production rate of 13.4 kg/s based on a solvent-to-feed ratio of 1.5 times $\left(\frac{S}{F}\right)_{min}$. This process therefore also requires additional evaporation and the required energy input is similar to that of the
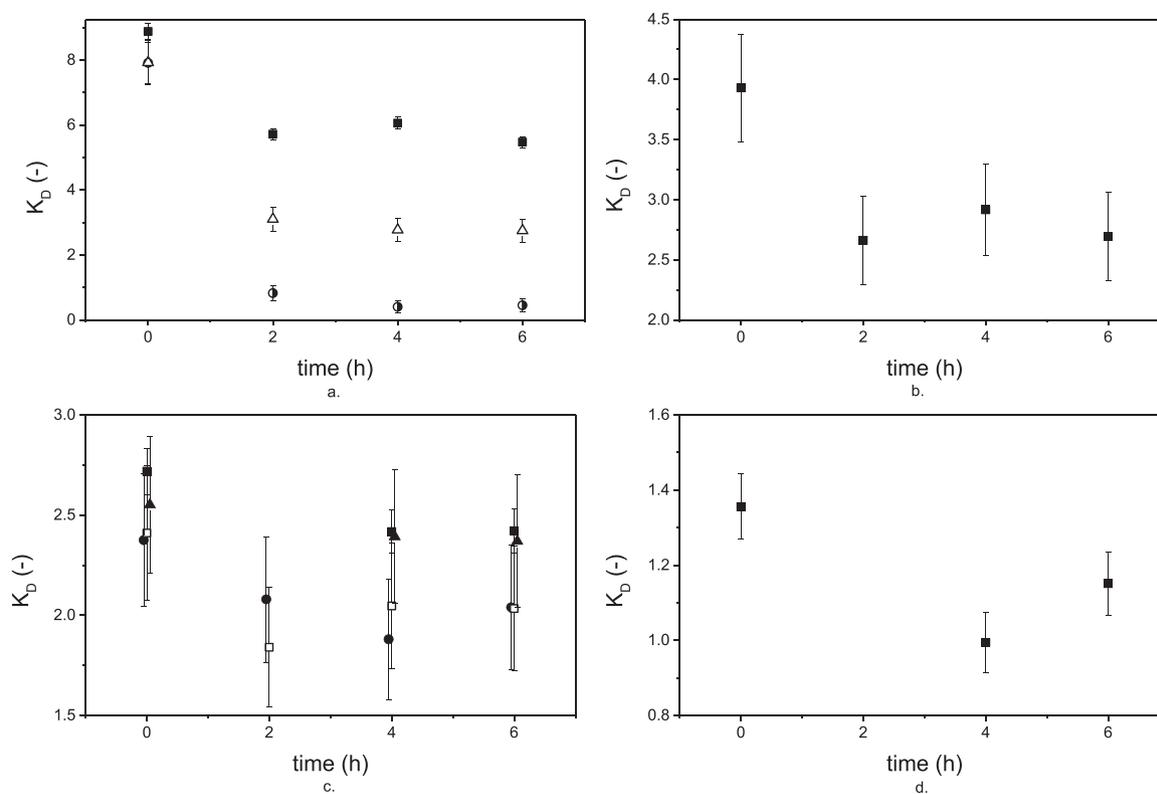
Fig. 6. Effect of applying 30 bar of methane (closed symbols), ethane (half open symbols) and ethylene (open symbols) on the distribution ratio of succinic acid ($c_0 = 0.012$ mass fraction) in LLE at 20 °C and a solvent-to-feed ratio of 1/3 with **a)** 20 wt% TOA in MIBK, **b)** 10 wt% TOA in MIBK, **c)** 20 wt% TOPO in MIBK (x-axis value shifted for graph readability, data points are at 0, 2, 4 and 6 h), and **d)** 10 wt% TOPO in MIBK.

evaporation-based process 3, although the capital investment for process 4 are lower. The return on investments was defined as the number of days of production required at which the additional investments of capital required for compressors and pumps compared to the four-stage evaporator are paid back by the decreased operational costs. No depreciation was assumed as the return on investment time was reached within one year. For the diluent-swing regeneration process (process 2) with pressurized ethane 50 ktons of production (110 days based on 80% operation) are required to fully return all additional capital invested, making the other two cases more interesting for the short-term as their capital investments are similar to that of the evaporation reference case. However, as industrial processes are not designed for operation of less than a year, the ethane-based process with the lowest price per kg of product has a high potential as it will save a large amount of energy and operational costs on the long-term. For the other processes (1 and 3) no significant additional capital investments are required and process 4 requires less capital investments (see Table 2), hence no return on investments was calculated.

As no study on solvent and anti-solvent losses in the process was performed, prices of solvents and gases are not included in the calculations. Furthermore, the solubility of anti-solvent in the aqueous phase is very low and therefore it was assumed that solvent losses do not influence the comparison of the four processes as they will affect all four studied processes in a similar way. For the reference case of evaporation of a part of the water to obtain the more concentrated acid solutions also no thorough study was performed. The rough estimate that was calculated can however be used to compare the other processes since this is just a reference case and the advantage of the diluent-swing processes compared to the case of evaporation is clearly shown. For this conceptual comparison, the effect of more detailed economical factors (e.g. Lang factors, fixed operational costs, variation of feed, solvent and product pricing, solvent losses) are excluded as they are not expected to have a significant and distinguishing effect on the

final comparison of the processes evaluated.

All swing-based regeneration processes are economically viable based on these calculations. The process based on evaporation of pentane seems more viable than those based on evaporation of MIBK and a swing in temperature, as those processes result in lower product concentrations and extra distillation or evaporation is required to obtain the same product.

4.4.1. Opportunities for process improvement

There is an opportunity for improvement of process 3 and 4 by combining both types of swing, since in these calculations process 3 is performed without a temperature-swing in the regeneration. To improve this process, the heat that is required to evaporate the MIBK can be kept in the system to apply also a temperature swing regeneration. With this increased temperature in the regeneration step, (which is basically obtained by less cooling of the streams after the MIBK distillation), there is an increased $1/K_D$ of 6.7 (the inverse of the K_D in Fig. 3b) in the regeneration step, and a water feed in the regeneration of 1.57 kg/s, resulting in a product with a HSuc mass fraction of 0.22. The duty of the regeneration column is 585 kW and the column has 3.8 stages. For the overall process there is a similar total energy input of 6050 kW (17 MJ/kg pure HSuc) and the required equipment is the same, except that there is no need for an extra cooler (95 k€) after the distillation column. The advantage of production at a higher temperature is that also the maximum solubility of the HSuc is increased (to a mass fraction of 0.22) and less water needs to be evaporated in the crystallization step. Including the crystallization step the energy requirement for this combined diluent-swing and temperature-swing process is 6700 kW (19 MJ/kg pure HSuc), which is 31% of the energy input per kg of pure HSuc product required for the benchmark process based on quadruple effect evaporation. Thus, combining the evaporation of diluent with a temperature swing by making use of the heat that is already applied in the MIBK distillation, does increase the viability of

Table 2

Energy requirements and product specifications to evaluate the four different processes (schematically shown in Fig. 1 and Fig. 2) and compare with the reference case of evaporation. The extraction factor E is defined as $E = K_D \frac{S'}{F'}$, for which K_D was converted to a mass fraction based ratio. N_{ts} is the number of theoretical stage in the column. All processes are based on a commercial scale production of 10 kta with a succinic acid mass fraction of 0.012 in the feed.

	Unit	Process 1	Process 2	Process 3	Process 4	Reference case (evaporation)
Model input	Process	anti-solvent pentane	'anti-solvent' ethane	evaporation of diluent	temperature-swing	–
	Schematic	Fig. 2b	Fig. 2c	Fig. 2a	Fig. 1	–
	Extraction column	20 wt% TOA in MIBK	20 wt% TOA in MIBK	40 wt% TOA in MIBK	20 wt% TOA in MIBK	–
	K_D	10.2	7.9	10.2	10.2	
	$\left(\frac{S'}{F'}\right)_{min}$	0.076	0.099	0.077	0.076	
	Extraction factor E	1.45	1.45	1.45	1.45	
	N_{ts}	6.0	6.2	6.0	6.0	
	Back-extraction column					–
	$1/K_D$	2.2	2.2	0.20	0.63	
	S (water) (kg/s)	6.91	6.91	16.7	13.3	
	Extraction factor E	1.52	2.24	1.5	1.5	
	N_{ts}	8.6	5.4	11.7	10.3	
	Solvent regeneration column					
	Feed	4.5 kg/s (TOA + MIBK) 3.5 kg/s pentane		4.5 kg/s (TOA + MIBK)		1 L/s water
	Product details					
	Mass fraction succinic acid	0.061	0.061	0.028	0.033	0.061
	Flow (kg/s)	6.91	6.91	16.7	13.3	6.91
Model output	Equipment cost (installed)					
	Extraction column	470 k€	470 k€	470 k€	470 k€	–
	Back-extraction column	140 k€	120 k€	165 k€	130 k€	–
	Solvent regeneration / Distillation column	830 k€	–	760 k€	–	–
	Flash column	–	120 k€	–	–	740 k€ (= total of 4 columns)
	Compressors	–	1900 k€	–	–	–
	Coolers	75 k€	110 k€	155 k€	180 k€	895 k€
	Pump	–	19 k€	–	–	–
	Total	1500 k€	2900 k€	1600 k€	780 k€	1600 k€
	Distillation	(anti-solvent pentane)	–	(MIBK to 20 wt%)	–	(evaporates water)
	Reboiler duty Q_{reb}	4500 kW	–	3000 kW	–	–
	Condenser duty Q_{cond}	3500 kW	–	1960 kW	–	–
	Duty (4-stage evaporator)	–	–	–	–	18 MW
	Duty to increase conc. (4-stage evap.)	–	–	5525 kW	–	–
	Energy input					
	Pump	–	75 kW	–	–	–
	Compressor	–	0.65 kW	–	–	–
	Recycle compressor	–	250 kW	–	–	–
	Cooler/heater	960 kW	270 kW	1050 kW	4800 kW	–
	Flash vessel	–	105 kW	–	–	–
	Regeneration column	12 kW	95 kW	74 kW	60 kW	–
	Total energy input	8970 kW	800 kW	6100 kW (with further evaporation 11,600 kW)	4900 kW	18 MW (based on 4-stage evap.)
Energy calculations	Energy for production					
	Energy per kg product (no heat int.)	1300 kJ/kg	120 kJ/kg	360 kJ/kg (w. further evap. 1680 kJ/kg)	370 kJ/kg (w. further evap. 1230 kJ/kg)	2600 kJ/kg
	Duty cost per ton product at maximum solubility	13 €	1.1 €	3.6 € (w. further evap. 16 €)	3.5 € (w. further evap. 12 €)	26 €
	Total energy per kg pure acid incl. crystallization	36 MJ/kg (58% of evaporation)	13 MJ/kg (21% of evaporation)	44 MJ/kg (70% of evaporation)	35 MJ/kg (56% of evaporation)	62 MJ/kg
	Production required for return on investments compared to evaporator	–	50 kton, 2000 h, 110 days (80% production)	–	–	

the process, however this process still requires more energy than the ethane-based process that requires only 21% of the energy input of the quadruple effect evaporation benchmark.

The process of diluent-swing by addition of pentane could theoretically also easily be combined with a temperature swing by increasing the temperature of the anti-solvent and thereby the temperature in the regeneration column. However, the improvement based on this will only be very small and result in similar process economics, since the K_D of HSuc is already strongly decreased by the addition of pentane.

5. Conclusion

Swing processes for regeneration of solvent in liquid-liquid extraction processes were compared using temperature-swing and/or a diluent-swing. In the case of a solvent consisting of 20 wt% TOA the effect of anti-solvent was stronger than for 20 wt% TOPO in MIBK in liquid-liquid equilibria measurements for LLX of succinic acid (HSuc) from aqueous streams, reducing K_D from 10.2 to 0.46 already at a volume based anti-solvent-to-solvent ratio of 1. An increase of temperature to 60 °C without diluent-swing decreased K_D to 1.6. Applying a gaseous
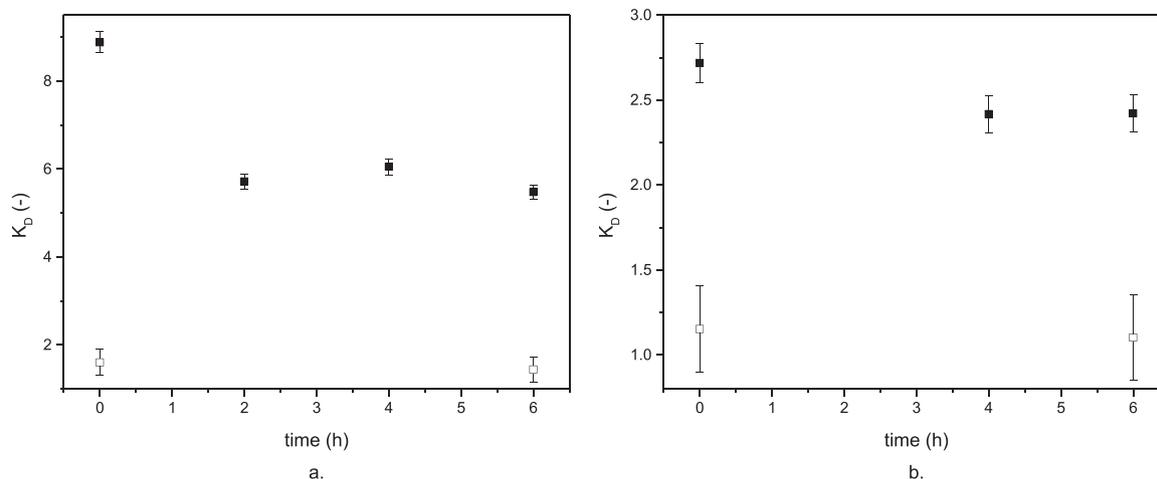
Fig. 7. Effect of temperature on distribution of HSuc ($c_0 = 0.012$ mole fraction) at 20 °C (closed symbols) and 60 °C (open symbols) under methane pressure (t > 0), a solvent-to-feed ratio of 1/3 and the solvent phase consisting of **a)** 20 wt% TOA in MIBK and **b)** 20 wt% TOPO in MIBK.

anti-solvent is promising because of the easy removal by reducing the pressure and no requirement of an additional distillation column. Extra equipment in the form of compressors and pumps is however required. Applying ethane at a pressure of 30 bar with 20 wt% TOA in MIBK decreased K_D from 7.9 to 0.45. This is comparable to the effect of the liquid anti-solvent pentane.

A temperature swing-based process and three diluent-swing based processes were compared and their capital investments and energy required for operation were predicted using Aspen Plus. All processes, based on either a temperature-swing, evaporation of the diluent MIBK or addition of pentane or ethane as anti-solvents, were more promising than the reference process based on quadruple effect evaporation of the water. Combining a swing in temperature with a swing in diluent strongly improves the process and results in higher product concentrations and the calculated energy input per kg pure acid product is only 31% (19 MJ/kg pure acid) of that of benchmark process. The process based on an ethane pressure-swing requires only 110 days of production to fully return the additional capital invested for compressors and a pump. This is the most effective process considering reduction of energy demand as the energy required for operation is 21% (13 MJ/kg) of what would be required for the quadruple effect evaporation of the water.

References

[1] 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.

[2] T. Hano, M. Matsumoto, T. Ohtake, K. Sasaki, F. Hori, Y. Kawano, Extraction equilibria of organic acids with Tri-n-octylphosphineoxide, J. Chem. Eng. Jpn. 23 (1990) 734–738.

[3] C.S. López-Garzón, A.J.J. Straathof, Recovery of carboxylic acids produced by fermentation, Biotechnol. Adv. 32 (2014) 873–904.

[4] X. Shan, W. Qin, Y. Dai, Dependence of extraction equilibrium of monocarboxylic acid from aqueous solutions on the relative basicity of extractant, Chem. Eng. Sci. 61 (2006) 2574–2581.

[5] J. Tamada, C. King, Extraction of carboxylic acids with amine extractants. III: Effect of temperature, water coextraction, and process considerations, Ind. Eng. Chem. Res. 29 (1990) 1333–1338.

[6] V.H. Shah, V. Pham, P. Larsen, S. Biswas, T. Frank, Liquid–liquid extraction for recovering low margin chemicals: thinking beyond the partition ratio, Ind. Eng. Chem. Res. 55 (2016) 1731–1739.

[7] L.J. Poole, Novel Regenerated Solvent Extraction Processes for the Recovery of Carboxylic Acids or Ammonia from Aqueous Solutions Part I. Regeneration of Amine-carboxylic Acid Extracts, (2008).

[8] C.J. King, J.N. Starr, L.J. Poole, J.A. Tamada, Regeneration of carboxylic acid extracts, in: T. Sekine (Ed.), Process Metallurgy, Elsevier, 1992, pp. 1791–1796.

[9] B. Cok, I. Tsiropoulos, A.L. Roes, M.K. Patel, Succinic acid production derived from carbohydrates: an energy and greenhouse gas assessment of a platform chemical toward a bio-based economy, Biofuel. Bioprod. Bior. 8 (2014) 16–29.

[10] N. Shen, Y. Qin, Q. Wang, S. Liao, J. Zhu, Q. Zhu, H. Mi, B. Adhikari, Y. Wei, R. Huang, Production of succinic acid from sugarcane molasses supplemented with a mixture of corn steep liquor powder and peanut meal as nitrogen sources by Actinobacillus succinogenes, Lett. Appl. Microbiol. 60 (2015) 544–551.

[11] A. Cukalovic, C.V. Stevens, Feasibility of production methods for succinic acid derivatives: a marriage of renewable resources and chemical technology, Biofuel. Bioprod. Bioref. 2 (2008) 505–529.

[12] I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky, A. Springer, Succinic acid: a new platform chemical for biobased polymers from renewable resources, Chem. Eng. Technol. 31 (2008) 647–654.

[13] T. Werpy, G. Petersen, Top value added chemicals from biomass: results of screening for potential candidates from sugars and synthesis gas, in: U.D.o. Energy (Ed.), National Renewable Energy Laboratory - Pacific Northwest National Laboratory, 2014.

[14] J.G. Zeikus, M.K. Jain, P. Elankovan, Biotechnology of succinic acid production and markets for derived industrial products, Appl. Microbiol. Biot. 51 (1999) 545–552.

[15] Z. Sheng, B. Tingting, C. Xuanying, W. Xiangxiang, L. Mengdi, Separation of succinic acid from aqueous solution by macroporous resin adsorption, J. Chem. Eng. Data 61 (2016) 856–864.

[16] Indicative Chemical Prices A-Z, ICIS, 2018.

[17] Y. Cao, R. Zhang, C. Sun, T. Cheng, Y. Liu, M. Xian, Fermentative succinate production: an emerging technology to replace the traditional petrochemical processes, Biomed. Res. Int. 2013 (2013) 723412-723412.

[18] 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.

[19] L.A. Tung, C.J. King, Sorption and extraction of lactic and succinic acids at pH & pKa1. I. Factors governing equilibria, Ind. Eng. Chem. Res. 33 (1994) 3217–3223.

[20] 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.

[21] C.B. Rasrendra, B. Girisuta, H.H. van de Bovenkamp, J.G.M. Winkelman, E.J. Leijenhorst, R.H. Venderbosch, M. Windt, D. Meier, H.J. Heeres, Recovery of acetic acid from aqueous pyrolysis oil phase by reactive extraction using tri-n-octylamine, Chem. Eng. J. 176–177 (2011) 244–252.

[22] M. Matsumoto, T. Otono, K. Kondo, Synergistic extraction of organic acids with tri-n-octylamine and tri-n-butylphosphate, Sep. Purif. Technol. 24 (2001) 337–342.

[23] G.H. Malmary, F. Monteil, J.R. Molinier, H. Hanine, T. Conte, J. Mourgues, Recovery of aconitic acid from simulated aqueous effluents of the sugar-cane industry through liquid-liquid extraction, Bioresour. Technol. 52 (1995) 33–36.

[24] A.V. Ladesov, D.S. Kosyakov, K.G. Bogolitsyn, N.S. Gorbova, Solvatochromic polarity parameters for binary mixtures of 1-butyl-3-methylimidazolium acetate with water, methanol, and dimethylsulfoxide, Russ. J. Phys. Chem. A 89 (2015) 1814–1820.

[25] Q. Yu, S. Black, H. Wei, Solubility of butanedioic acid in different solvents at temperatures between 283 K and 333 K, J. Chem. Eng. Data 54 (2009) 2123–2125.

[26] A.B. Haan, H. Bosch, Industrial Separation Processes: Fundamentals, Walter de Gruyter, GmbH, & Co., KG, Berlin, 2013.

[27] M.A. Sorour, Optimization of multiple effect evaporators designed for fruit juice concentrate, Am. J. Energy Eng. 3 (2015) 6–11.

[28] R.L. Earle, Unit Operations in Food Processing, 1st ed., (1966) Pergamon, Oxford.

[29] B.B. Katharina Grave, Jose Ordonez, Jakob Wachsmuth, Sil Boeve, Matthew Smith, Torben Schubert, Nele Friedrichsen, Andrea Herbst, Katharina Eckartz, Martin Pudlik, Marian Bons, Mario Ragwitz, Joachim Schleich, Prices and Costs of

EU Energy, European Commission, Ecofys, 2016.

[30] J. Procházka, A. Heyberger, E. Volaufová, Extraction equilibrium of dicarboxylic acids with tertiary amine in single and binary diluents, Sep. Sci. Technol. 39 (2005) 1073–1091.

[31] K.L. Wasewar, Reactive extraction: an intensifying approach for carboxylic acid separation, Int. J. Chem. Eng. Appl. 3 (2012) 249–255.

[32] J.M. Wardell, C.J. King, Solvent equilibriums for extraction of carboxylic acids from water, J. Chem. Eng. Data 23 (1978) 144–148.

[33] 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.

[34] A. Krzyzaniak, B. Schuur, M. Sukumaran, H. Zuilhof, A.B. De Haan, Extractant screening for liquid-liquid extraction in environmentally benign production routes, Chem. Eng. Res. Des. 24 (2011) 709–714.

[35] Z. Li, W. Qin, Y. Dai, Liquid−Liquid equilibria of acetic, propionic, butyric, and valeric acids with Trioctylamine as extractant, J. Chem. Eng. Data 47 (2002) 843–848.

[36] T. Brouwer, M. Blahusiak, K. Babic, B. Schuur, Reactive extraction and recovery of levulinic acid, formic acid and furfural from aqueous solutions containing sulphuric acid, Sep. Purif. Technol. 185 (2017) 186–195.

[37] S.G.G. Amruta Magdum, P.J. Patil, A.V. Patil, A review: reactive extraction of succinic acid form aqueous solution using different extractant, Int. J. Eng. Res. Technol. 10 (2017).

[38] F.L. Boyer, L.J. Bircher, The solubility of nitrogen, argon, methane, ethylene and ethane in normal primary alcohols, J. Phys. Chem. 64 (1960) 1330–1331.

[39] W.M. Haynes, D.R. Lide, T.J. Bruno, CRC Handbook of Chemistry and Physics : a Ready-reference Book of Chemical and Physical Data, CRC Press, Boca Raton, Florida, 2017.