SEPARATION

of

WASTE-DERIVED VOLATILE FATTY ACIDS

from

FERMENTED WASTEWATER

E. REYHANITASH

DISSERTATION

Separation of waste-derived volatile fatty acids from
fermented wastewater

E. Reyhanitash

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DISSERTATION

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Introduction

CHAPTER

1

1. General introduction

Nowadays, the origin of most of the materials used by a person everyday can be traced back to petroleum. This makes petroleum the very central point around which a person's daily life is orbiting. The obvious downside of this close relationship is a quicker depletion of petroleum resources. The consequences of this depletion can even be as catastrophic as turning petroleum into a tool that creates tension between various communities around the world. An example of essential petroleum-derived materials is polymers. They are the major building blocks of the world we have built in the 21st century and call it home. Volatile fatty acids (VFAs), fatty acids of six or fewer carbon atoms [1], are among the ingredients of common polymers. They serve as food and feed preservers as well. To reduce reliance on petroleum resources, one may start with reducing petroleum-derived chemicals that are in high demand. Reducing of course means proposing an alternative resource and production route. VFAs are produced at tremendous rates mainly by petrochemical routes [2], and therefore, they seem to be good candidates. Acetic, propionic and butyric acids are the most common VFAs, and at a total production rate of about 11.5×10^6 t/a, they account for about 50 % of the global short organic acids (up to C_6) market.[2] The current capacity of anaerobic digestion in Europe is about 9×10^6 t/a of organic fraction of municipal solid waste.[3, 4] Assuming that municipal solid waste is entirely convertible to glucose, and a high glucose to acetic acid yield of 0.8 g/g is achievable [2], biological acetic acid can be produced at a rate of 7.2×10^6 t/a. This value clearly shows that, by utilizing only the waste streams that are generated in Europe as fermentation feed, a very large fraction of the global acetic acid demand can potentially be met.

A great deal of study has been invested on assessing various alternative resources and production routes for VFAs, and they seem to have reached a common conclusion that waste streams and fermentation are promising alternative resources and production route respectively.[1, 2, 5-7] Utilizing waste as the resource comes with an extra bonus which is replacing the approach of treatment to meet environmental regulations with treatment to produce value-added chemicals. Fermentation is a potential route to produce various chemicals at a low cost and high efficiency. [8] Furthermore, since numerous types of microorganisms are available to be used for fermentation, a wide variety of chemicals can be produced by fermentation.[2, 9] In the literature, several examples of production of VFAs by fermentation have been reported with resources ranging from industrial wastewater to newspaper waste.[5-7, 10, 11]

An unfortunate limitation of fermentation is the low VFA content of the resulting broths, as the initial waste streams are often poor in carbon. This limitation poses a major bottleneck to a process that is to deliver highly concentrated waste-derived VFAs. This necessitates implementation of a separation technique that is robust and economic at the same time. The presence of water next to the compound of interest when it has a higher boiling point than that of water introduces a great energy penalty to any thermal process, as a result of the tremendous heat of vaporization of water. As fermentation broths are no exceptions, a separation technique aiming at the removal of their water content may not be economically feasible. Therefore, any single-step operation such as distillation is eliminated from our list of potential candidates. The simplest form of a multi-step operation consists of a first step in which VFAs are temporarily transferred into a carrier, and a second step in which VFAs are separated from the carrier. Figure 1 gives a conceptual view of a two-step operation for recovery of VFAs from a fermentation broth.

Figure 1. A conceptual two-step operation for recovery of VFAs from a fermentation broth

Although the second step has to perform a thermal operation to recover high purity VFAs from the carrier, its nature is dictated by the nature of the separation practice conducted in the first step. An affinity separation technique is an ideal practice for the first step. Affinity separation techniques are able to selectively separate the compound of interest with a minimal interaction with the undesired accompanying compounds. The reason behind their success is introduction of a tailored molecular interaction between a separating agent and the compound of interest, referred to as affinity. The separating agent has to be regenerated after attracting the compound of interest to unload it and be reused. Therefore, a proper operation of the second step is critical (see Figure 1). Depending on the type of the waste stream used for fermentation, the resulting broth may contain other accompanying compounds than water such as minerals. The effect of such impurities on the selectivity and capacity of the affinity agent can be drastic.

Liquid-liquid extraction (LLX) and adsorption are the most common affinity separation techniques. LLX uses a solvent as the separating agent to attract the compound of interest, i.e. extraction, that is to be released afterwards, i.e. solvent regeneration. The second separation step in which solvent regeneration is performed can be a distillation or stripping column, or a crystallizer (see Figure 1). The separating agent used for adsorption, the adsorbent, first attracts the compound of interest, i.e. adsorption, and then releases it, i.e. desorption. Since the adsorbent is a solid and cumbersome to transport, adsorption is usually operated with two identical packed columns one of which performs adsorption (1st separation step in Figure 1) while the other undergoes desorption (2nd separation step in Figure 1). Letting a stream of an inert gas through the desorbing packed column or reducing the absolute pressure facilitates desorption. When the compound of interest is in a gaseous solution, circulation of the adsorbent over the course of adsorption/desorption cycles might be considered.[12]

2. Thesis outline

In this thesis, we have employed LLX and adsorption to recover VFAs from fermented wastewater. Next to being poor in VFAs, fermented wastewater always contains significant amounts of salts which can potentially influence separation of VFAs and introduce an extra challenge to this practice. The thesis is assembled in a way that each chapter has an independent story to tell while being a part of the main storyline. Chapters 2 to 7 form two main parts of this thesis: (i) recovery by liquid-liquid extraction (ii) recovery by adsorption. The following section of this chapter gives a short introduction on the chapters and states their roles in the main storyline.

2.1. Recovery by liquid-liquid extraction

2.1.1. Chapter 2. Liquid-liquid extraction-based processes for recovery of carboxylic acids from aqueous solutions

LLX was the first affinity separation technique investigated for this thesis. Many solvents belonging to various solvent families, such as ionic liquids, have been reported to be capable of successfully extracting carboxylic acids from aqueous solutions.[13-17] Furthermore, several patents have taken the basic practice of extraction followed by solvent regeneration to a new level by making novel modifications.[18-23] This chapter gives a comprehensive picture of the reported solvent innovations and novel processes. An extensive set of energy demand calculations was performed on the processes to assess their economic feasibility. When applied to separation of carboxylic acids from an aqueous solution as dilute as fermented wastewater, most of the assessed processes failed to be economically feasible. A process that maintained a high performance at a low VFA content had been proposed by Urbas.[18] Inspired by the novelty of this process and the solvents designed to avoid the drawbacks of conventional solvents, we devised a process for recovery of VFAs from an artificial fermented wastewater. Chapter 4 examines this process.

2.1.2. Chapter 3. Extraction of volatile fatty acids from fermented wastewater

The mechanisms behind extraction of VFAs from an aqueous solution together with the ways the salts dissolved in the aqueous solution interfere with them is extensively studied in this chapter. $[P_{666,14}][Phos]$, an ionic liquid recently proposed for extraction of organic acids [16, 24], was studied for extraction of VFAs. Its main competitor and the state of the art molecular solvent for carboxylic acids, trioctylamine in n-octanol, was examined similarly. Next to $[P_{666,14}][Phos]$ and trioctylamine in n-octanol, three other ionic liquids with the same cation as that of $[P_{666,14}][Phos]$ but different anions were investigated to obtain a complete

picture of possible interactions during extraction. Afterwards, a complicated artificial fermented wastewater containing lactic, acetic, propionic and butyric acids and dissolved salts was employed to assess the performance of $[P_{666,14}][Phos]$ when exposed to an actual fermented wastewater, and compare it with trioctylamine in n-octanol.

2.1.3. Chapter 4. CO₂-enhanced extraction of acetic acid from fermented wastewater

This chapter first examines $[P_{666,14}][Phos]$ by extracting acetic acid, a VFA model compound, from an artificial fermented wastewater. Afterwards, the novel concept of improving extraction with applying CO₂ is adapted to involve the use of $[P_{666,14}][Phos]$. As the benchmark, the state of the art molecular solvent, trioctylamine in n-octanol, was investigated similarly.

2.1.4. Chapter 5. Regeneration of volatile fatty acid-containing $[P_{666,14}][Phos]$

After investigating the extraction capabilities of $[P_{666,14}][Phos]$, this chapter aims at regenerating it to prepare it for being reused for extraction and recover the VFAs. Several techniques from simple evaporation to more complicated reactive regeneration have been assessed. The choice of reactive techniques was inspired by the procedures proposed by some patents for regeneration of molecular solvents and modifying the resulting products.[23, 25-27]

2.1.5. Chapter 6. Solvent selection approach for liquid-liquid extraction with an ionic liquid

This chapter provides an approach to assess the practicality of a LLX-based process involving an ionic liquid. Evaluation of the experimental work carried out for chapters 3, 4 and 5 and the insights gained from them led to preparation of this chapter. This chapter concludes the first part of this thesis focusing on recovery of VFAs by LLX.

2.2. Recovery by adsorption

2.2.1. Chapter 7. Recovery of volatile fatty acids from fermented wastewater by adsorption

This chapter evaluates separation of VFAs from fermented wastewater by adsorption. Four adsorbents including primary, secondary and tertiary amine-functionalized adsorbents and a non-functionalized adsorbent were investigated for this chapter. The same complicated artificial fermented wastewater prepared for Chapter 3 was used as the feed for this chapter. As a result of complication of the feed, only one adsorbent survived the cut. This adsorbent was then comprehensively studied in an adsorption column followed by being exposed to desorption. Temperature-profiled desorption was employed to obtain various fractions of VFAs at high concentrations. The stability of the adsorbent over multiple adsorption-desorption cycles was investigated as well. The feasibility of the established adsorption-desorption procedure from energy demand point of view was assessed as well. The aim was set at drawing streams of pure propionic and butyric acids, and sending lactic and acetic acids back to fermentation to undergo chain elongation and form propionic and butyric acids. The second part of this thesis investigating adsorption to efficiently separate VFAs from fermented wastewater is concluded in this chapter.

2.3. Chapter 8. Conclusions and outlook

The last chapter of this thesis presents a bird's-eye view on the main storyline. It pictures the thesis as two main parts, LLX and adsorption, and states a summarized conclusion for each. It evaluates the approaches taken for each part, and based on their performances, provides a few tools to improve them. Since the first part of this thesis is of a more challenging nature, Chapter 8 dedicates a larger part of its discussion to it. An outlook to assist with a similar line of research to be conducted in the future is presented as well.

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Liquid-liquid
extraction
processes for
recovery of
carboxylic acids
from aqueous
solutions

CHAPTER

2

Abstract

Production of carboxylic acids by fermentation rather than petrochemical routes aims at reducing dependency on petroleum resources. Wastewater streams are potential carbon sources for fermentation. However, their limited carbon content results in low carboxylic acid concentrations (~ 1 wt%) that render separation of waste-derived carboxylic acids challenging. This necessitates implementation of cost-effective separation concepts. The incentive to review liquid-liquid extraction (LLX)-based processes for carboxylic acids was to evaluate their applicability to low carboxylic acid concentrations. Several novel LLX-based processes were assessed in terms of energy demand by simulating their thermal unit operations with Aspen Plus. They were simulated both under their reported conditions and with their initial concentration set to 1 wt%. A process proposed by Urbas that makes use of CO_2 , CO_2 -switchable solvents and low-boiling organic solvents outperformed the others. With a heating duty of about $36 \text{ MJ/kg}_{\text{product}}$, it could recover both volatile and non-volatile carboxylic acids from fermentation broths.

This chapter is based on the article submitted as:

E. Reyhanitash, T. Brouwer, S. R. A. Kersten, and B. Schuur, "Liquid-liquid extraction processes for recovery of carboxylic acids from aqueous solutions", Separation and Purification Reviews.

Nomenclature

LLX:	Liquid-liquid extraction
IL:	Ionic liquid
DES:	Deep eutectic solvent
HBD:	Hydrogen bond donor
HBA:	Hydrogen bond acceptor
HAc:	Acetic acid
Ac ⁻ :	Acetate
HAcr:	Acrylic acid
HLa:	Lactic acid
TBA:	Tributyl amine
TBAH ⁺ :	Tributyl ammonium
[TBAH ⁺][Ac ⁻]:	Tributyl ammonium acetate
DDAP:	N,N-didodecylpyridin-4-amine

Symbols

RCOOH:	Carboxylic acid
MOH:	Alkali solution of an alkaline or alkali earth metal
RCOOM:	Alkaline salt of carboxylic acid
D:	Distribution coefficient
S:	Selectivity
S/F:	Solvent to feed ratio

1. Introduction

Large production and consumption of petroleum-based chemicals and the associated negative effects on our planet has raised concerns worldwide. While resource scarcity was on top of the global list of concerns for decades, according to The Paris Agreement 2015, reduction of emissions has taken the top priority position recently. In addition, to reduce waste to preserve living quality on Earth, circular economy has become a popular topic of research.[1] An extensive number of studies are in progress to discover or improve technologies by which chemicals can be produced from waste. In an attempt to reduce the carbon footprint, production of chemicals from renewable resources is studied extensively as well.[2-8] Fermentation enables production of chemicals from waste and renewable resources with a high efficiency, and potentially at a low cost. Since numerous types of microorganisms are available to be used for fermentation, a wide variety of chemicals can be produced by fermentation, ranging from commodity chemicals to pharmaceutical intermediates.[9-11] A wide variety of carbon sources for fermentation have also been reported, ranging from glucose to industrial wastewater such as chemical, food or paper industry wastewater. [12, 13] Sugar streams isolated from pyrolysis oil can also be fed to a fermenter. [14] While product diversity and feedstock flexibility are among major benefits of fermentation, low product concentration is a major drawback which results in significant downstream costs.[15]

Carboxylic acids are widely used as platform chemicals for synthesis of value-added chemicals and polymers.[16] In the literature, fermentative production of carboxylic acids has been extensively examined.[17-21] Unfortunately, their low concentrations in fermentation broths imposes a significant cost factor on separating them limiting economic feasibility of carboxylic acid production by fermentation.[22-27] To tackle this challenge, effective recovery strategies are needed.

In the literature, various techniques to separate carboxylic acids from aqueous solutions have been reported.[28-31] An important parameter for choosing a suitable separation technique is the carboxylic acid content of the aqueous solution. In 1985, Drake et al. [32] suggested that, for separation of acetic acid (HAc) from an aqueous solution with an acid content of above 50 wt%, distillation may be chosen. When the acid content is below 50 wt%, they proposed liquid-liquid extraction (LLX) as the practical option. Since fermentation broths largely consist of water and only small amounts of carboxylic acids, the chosen separation technique has to target the carboxylic acids rather than the accompanying water to be efficient. Affinity-based separation techniques such as LLX make use of

affinity agents that target the carboxylic acids to selectively separate them. They are often composed of at least two stages:

- (i) Separation of the compound(s) of interest from the feed stream
- (ii) Regeneration of the affinity agent to recover the separated compound(s) and recycle the agent for further separation.

Typically a higher separation capacity can be achieved with LLX compared to other affinity-based separation techniques, and it is applicable to a wider concentration range.[33] The distribution coefficient (D) of a LLX solvent for a carboxylic acid (RCOOH) is defined in equation 1. The selectivity (S) of the solvent for the carboxylic acid in the presence of an accompanying species X (e.g. water) is expressed as the ratio of the distribution coefficients, as shown in equation 2.

$$D_{\text{RCOOH}} = \frac{[\text{RCOOH}]_{\text{Extract}}}{[\text{RCOOH}]_{\text{Raffinate}}} \quad (1)$$

$$S_{\text{RCOOH}} = \frac{D_{\text{RCOOH}}}{D_X} \quad (2)$$

The solvents reported for LLX of carboxylic acids can be divided in two categories:

- (i) Physical solvents
- (ii) Chemical solvents

Physical solvents do not strongly interact with carboxylic acids, and as a result, they do not form complexes with carboxylic acids. Alcohols, esters and ketones are among common physical solvents used for extraction of carboxylic acids.[34] Chemical solvents, however, induce a strong chemical interaction with carboxylic acids which results in formation of solvent–carboxylic acid complexes. Amines and organophosphorus compounds are common chemical solvents often reported in the literature for carboxylic acid extraction.[35, 36] They are usually dissolved in a diluent, as they are typically either solid or highly viscous. Moreover, the presence of a diluent may enhance their distribution coefficients and selectivities for carboxylic acids. Higher distribution coefficients are often achieved with chemical solvents rather than with physical solvents, but as a result, regeneration of chemical solvents is usually more challenging. Due to a weaker nature of their intermolecular interactions with carboxylic acids, regeneration of physical solvents is generally straightforward, although it can still be energy intensive. Furthermore, physical solvents are typically less expensive.[37] The nature of the solvent chosen for extraction together with the nature of the carboxylic acid(s) to be extracted determine the operational window for choosing a suitable solvent regeneration technique.

The following section categorizes the extraction solvents proposed for carboxylic acids as the low-boiling or the high-boiling solvents. An overview of the basic LLX-based process concepts involving either a low-boiling or a high-boiling solvent is presented afterwards.

This article presents a review of innovative processes reported in the (patent) literature for recovery of carboxylic acids as well as a comparison of a selection of them and the basic process concepts. The selected processes were assessed in two steps. First, their energy demand calculations were performed at conditions reported by the author(s). Then, in order to assess their applicability to recovery of carboxylic acids from dilute aqueous streams such as fermented wastewater, they were simulated with an initial carboxylic acid concentrations of 1 wt%.

2. Extraction solvents

The nature of the solvent in terms of being a physical or chemical solvent is often independent of its boiling point. In order to regenerate the extract comprising the solvent, the carboxylic acid and possible co-extracted species by distillation, the boiling point of the solvent, especially with respect to the boiling point of the carboxylic acid, is a critical parameter. Solvents with a boiling point higher than that of the carboxylic acid, i.e. high-boiling solvents, require a different regeneration approach than that often taken for regeneration of solvents with a lower-boiling point, i.e. low-boiling solvents. This important difference is taken as the main categorization criterion for the solvents, with an exception of so called switchable solvents. Switchable solvents respond to an external trigger, e.g. light, electricity, or CO_2 , and, upon switching, may exhibit significantly altered molecular properties including their boiling points. Therefore, they are discussed in a separate subsection.

2.1. High-boiling solvents

After volatile carboxylic acids are extracted with a solvent, regeneration of the solvent can be done by distillation. As a result of their higher boiling point, high-boiling solvents are obtained as the bottom product of the distillation column and the volatile carboxylic acid as the distillate. As the solvent flow is typically much larger than the carboxylic acid flow, the energy demand of such a regeneration procedure is often lower than when the solvent has a lower boiling point than that of the carboxylic acid. A drawback is that possibly co-extracted higher-boiling impurities accumulate in the solvent over the course of extensive extraction-solvent regeneration cycles. In the case of non-volatile carboxylic acids (e.g. lactic acid), high-boiling solvents cannot be regenerated by distillation at all. In such a situation, at least one more unit operation, typically a back-extraction column, is necessary to regenerate the solvent.

2.1.1. Conventional high-boiling solvents

The most common conventional high-boiling solvents for extraction of carboxylic acids are composite solvents comprising large amines or organophosphorus compounds and various high-boiling diluents.[22, 25, 26, 35, 36, 38-43] The composite solvents often have a particular composition tuned to induce a relatively strong affinity for carboxylic acids, leading to an improved distribution coefficient.[44] Their affinity for carboxylic acids is sometimes so strong that their regeneration becomes problematic.[45, 46] A drawback of using a composite solvent in systems including mineral impurity is that the composite solvent tends to interact with the mineral impurity resulting in undesired co-extraction thereof.[23, 47]

2.1.2. Innovations in high-boiling solvents

2.1.2.1. Ionic liquids

Ionic liquids (ILs) have gained much interest in the recent literature on (carboxylic acid) extractions, as they have been shown to possess certain characteristics that appear superior to those of conventional solvents.[48-52] Most importantly, they exhibit higher carboxylic acid distribution coefficients at very low raffinate concentrations, ideal for dilute aqueous streams and leading to lower solvent to feed ratios (S/Fs).[23, 48, 49] Furthermore, their higher boiling/decomposition temperature enables thermal solvent regeneration to be performed in a wider temperature range [53, 54], and their design flexibility makes them capable of meeting various extraction demands.[55, 56] An important element in any extraction process is solvent loss into the raffinate phase, and to limit that, ILs can be designed to be highly hydrophobic and exhibit significant carboxylic acid extraction capacities at the same time (e.g. phosphonium-based ILs).[49, 50, 57] Washing the raffinate phase with a hydrophobic substance (e.g. hexane) to recover any leaching IL may also be devised.[58] ILs have also been used as diluents hosting organophosphorus compounds [59], and even in aqueous two-phase systems.[60]

2.1.2.2. Deep eutectic solvents

Deep eutectic solvents (DESs), often seen as an alternatives to ILs, are made by mixing two or more compounds with high melting points which, upon mixing, form a liquid with a lower melting point than those of the individual compounds.[61-66] The liquid formation is due to the presence of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA) at the same time. Hydrophobic DESs have been only recently applied for extraction of carboxylic acids from aqueous solution.[67] The applied hydrophobic DESs were mixtures of a fatty acid and an ammonium halide. The disadvantage of an ammonium halide-containing DES is a significant leaching of the halide into the raffinate which is due to ion-exchange between the halide and the carboxylate ion. This was observed for phosphonium halide ILs as well.[23] DESs are often created with various molar HBD:HBA ratios. Increasing the molar HBD:HBA ratio has been seen to lower the melting point of a DES, but this does not automatically mean that the boiling point is increased so much that the mixture resembles an IL.[61, 68]

2.2. Low-boiling solvents

Using a low-boiling solvent for extraction resolves the issue of possible accumulation of higher-boiling impurities in the solvent phase. However, it necessitates distillation of the solvent to obtain a pure carboxylic acid stream as the bottom product which may be energy intensive, especially when a large S/F is required.

2.2.1 Conventional low-boiling solvents

Alcohols, ethers, esters, ketones and chlorinated hydrocarbons are common low-boiling solvents reported for extraction of carboxylic acids.[34, 69-75] They are ideal solvent choices for recovery of valuable high-boiling carboxylic acids such as lactic acid and succinic acid.

2.2.2. Innovations in low-boiling solvents

Evaporation of a low-boiling solvent to obtain a pure carboxylic acid stream at the bottom of the distillation column might be cumbersome and/or energy intensive. Schon [76] patented a carboxylic acid extraction process which employs liquefied propylene and/or propane as the solvent to facilitate thermal regeneration of the solvent. With this method, solvent regeneration is realized using a few flash drums operating at low temperatures enabling the use of waste heat as the energy source. The absence of an energy source for flashing will force the propylene and/or propane stream to absorb its heat of vaporization from the surroundings, which will eventually lower their temperature drastically and cause frost formation on them. This suggests that the equipment have to be capable of operating at extremely low temperatures. This process is in particular interesting for separation of acrylic acid (HAcr), as the volatile solvent is flashed at such a low temperature that polymerization of HAcr does not occur anymore. This also enables the liquid HAcr stream to retain a non-volatile polymerization inhibitor. Furthermore, since propylene and/or propane are used to produce acrolein and HAcr, they are usually available at the production plant, and therefore, the need for storing and handling an extra chemical is eliminated.

2.3. Switchable solvents

Switchable solvents belong to a new generation of solvents whose chemical identity (e.g. polar or non-polar) can be reversibly altered by applying an external trigger. [77-79] The external trigger can be a chemical such as CO_2 . Recently, CO_2 -triggered switchable solvents have been applied to extract soy oil from soybeans [80], and lipids and fatty acids from algae.[8, 81, 82] The concept, although at the time not named switchable solvent, had already been considered for HAc extraction by Urbas in 1983.[45]

3. Liquid-liquid extraction processes

Depending on the boiling point and thermal stability of the carboxylic acid of interest, the method used to regenerate a solvent is either distillation (see sections 3.1 and 3.2) or back-extraction (see section 3.3) followed by an additional regeneration step such as distillation or crystallization. In this section, various combinations of standard unit operations are discussed.

3.1. Extraction + distillation with a high-boiling solvent

Applying distillation for solvent regeneration enables production of highly concentrated carboxylic acid streams at the cost of evaporation of either the carboxylic acid or the solvent. Using a high-boiling solvent for extraction, especially when the carboxylic acid content of the extract is limited, is advantageous, as the major part of the energy supplied is spent on evaporation of the carboxylic acid. [83] It should be noted that this applies only to volatile carboxylic acids, as the presence of a non-volatile carboxylic acid (e.g. lactic acid) in a high-boiling solvent requires an alternative solvent regeneration approach (e.g. back-extraction, see section 3.3). Figure 1 shows a process scheme of a LLX-based carboxylic acid recovery process involving a high-boiling solvent and a volatile carboxylic acid.

*Trace amount; can be isolated by further polishing stages.

^a Carboxylic acid.

Figure 1: Basic process scheme for LLX with recovery of high-boiling solvent by distillation.

3.2. Extraction + distillation with a low-boiling solvent

The conventional LLX-based HAc recovery technology involving low-boiling solvents is well established and described in several handbooks such as *Handbook of Solvent Extraction* and references therein.[34] Seader et al. [84] presented a textbook example in which HAc was extracted with ethyl acetate. The extract was distilled to obtain pure HAc and regenerate the solvent. The raffinate was distilled as well to recover the leaching solvent.

Low-boiling solvents can be advantageous for purification of non-volatile carboxylic acids, as the carboxylic acids cannot be recovered as the distillate, and application of high-boiling solvents involves at least one additional unit operation. A schematic view of a basic LLX-based carboxylic acid recovery process involving a low-boiling solvent is depicted in Figure 2.

*Trace amount; can be isolated by further polishing stages.

^a Carboxylic acid.

Figure 2: Basic process scheme for LLX-based carboxylic acid recovery process utilizing low-boiling solvent to be regenerated by distillation.

Some low-boiling solvents, such as ethyl acetate, can take up significant amounts of water. Distilling such a solvent together with its water content from the carboxylic acid might induce a phase split in the condenser of the distillation column that regenerates the solvent (see Figure 2). This enables separation of a major part of the water from the recycled solvent stream. When the separated water stream contains some carboxylic acid, it can be combined with the bottom product before undergoing a final distillation to dehydrate the stream.

3.3. Extraction + back-extraction

When a back-extraction is applied to regenerate the solvent, the obtained product is not a high-purity carboxylic acid stream, and at least one more separation operation is needed. When water is used for back-extraction, it typically results in a dilute aqueous product stream of the carboxylic acid. To increase the carboxylate content of the aqueous product stream significantly, an alkali solution can be used instead of water. However, the carboxylate salt of the alkali will be the product instead of the free carboxylic acid. If a pure carboxylic acid is desired, the solution has to be acidified afterwards which results in production of a salt by-product. Figure 3 shows a simplified view of a LLX-based carboxylic acid recovery process employing back-extraction for solvent regeneration. No further downstream operations are displayed in Figure 3.

*Trace amount; can be isolated by further polishing stages.

^a Carboxylic acid.

^b Alkali solution of an alkaline or alkali earth metal.

^c Alkaline salt of carboxylic acid.

Figure 3: Process scheme for LLX-based carboxylic acid recovery process utilizing low-boiling solvent to be regenerated by back-extraction with water or non-volatile alkali solution.

4. Process innovations

In the past decades, several studies have proposed innovative extraction operations to improve extraction efficiency (see section 4.1).[24, 45, 46, 76, 85-87] Most of these studies have used a solvent already known in the literature to emphasize the importance of the innovation in the operation. Some other studies intended to facilitate the solvent regeneration stage by modifying the relatively simple processes shown in Figure 1, Figure 2 and Figure 3 to significantly improve their efficiencies (see section 4.2).[41, 76, 88-92] In this section, only a selection of the innovative processes that include carboxylic acid extraction and solvent regeneration stages are discussed in more detail.[45, 76, 86, 91] In section 5.2, they are summarized in a table and compared in terms of their energy demand.

4.1. Enhancing extraction

4.1.1. Performing extraction in the presence of CO_2

The pH of the aqueous solution from which carboxylic acids are extracted is an essential parameter for extraction, and typically the optimum conditions for fermentation do not match the optimum conditions for extraction. During fermentation, the pH has to be maintained at mildly acidic to neutral values for microorganisms to survive and produce carboxylic acids at an optimal rate.[9] Since the produced carboxylic acids reduce the pH significantly, a mineral alkali (e.g. $\text{Ca}(\text{OH})_2$) is often added to neutralize them. As a result, the majority of the carboxylic acids are in their carboxylate forms, whereas their neutral acidic forms are preferred for extraction, since they are the only forms extracted by the majority of organic solvents.[23, 93-96]

As an example, during fermentative production of lactic acid (HLa), addition of CaO or $\text{Ca}(\text{OH})_2$ leads to formation of calcium lactate. Prior to extraction, the solution is acidified with H_2SO_4 to convert lactate to extractable HLa. This practice results in production of large quantities of CaSO_4 . [93] When acidification is performed using pressurized CO_2 instead of H_2SO_4 , CaSO_4 formation is eliminated, and moreover, the resulting CaCO_3 can be used to adjust the pH of the fermentation medium. In the literature, this practice has been applied on extraction of some carboxylic acids.[24, 45, 46, 85, 87, 97]

In 1983, when Urbas patented a process for enhancing HAc extraction [45], he claimed that by applying any form of CO_2 , solid or gaseous (either atmospheric or pressurized), HAc extraction from a calcium acetate solution can be facilitated. The proposed solvent was tributyl amine (TBA) which exhibits a miscibility gap with water, but upon CO_2 uptake, it forms tributyl ammonium carbonate which is miscible with water. After tributyl ammonium carbonate dissolves in water, ion

exchange generates calcium carbonate which precipitates and drives the reaction towards water-soluble tributyl ammonium acetate. Tributyl ammonium acetate is then extracted with chloroform. The obtained extract is heated to evaporate chloroform and decompose tributyl ammonium acetate into TBA and HAc. HAc is withdrawn as the final product, and TBA and chloroform are sent back to the process. The precipitated CaCO_3 can be used to adjust the pH of the fermentation medium. A simplified diagram of the process in Figure 4.

Figure 4. Simplified view of the process proposed by Urbas [45].

This process was later modified by Eggeman and Verser to avoid the impracticality of tributyl ammonium acetate decomposition and the use of a chlorinated solvent. [46] In the modified process, after obtaining the tributyl ammonium acetate solution, tributyl ammonium acetate is extracted with an alcohol and the resulting extract is subjected to esterification. Hence, the forming ester is the final product, and the distilled TBA is recycled to the extraction stage. Converting extracted carboxylic acids into esters to draw esters as the final products rather than the carboxylic acids has been examined by a few other studies as well.[98, 99]

In 1996, Baniel et al. patented a process by which HLa was separated from a sodium lactate solution in the presence of CO_2 using an amine-containing solvent.[85] After removing the CO_2 dissolved in the extract in a flash drum, the extracted HLa was recovered by back-extraction with water. The NaHCO_3 that formed in the raffinate was converted to CO_2 and Na_2CO_3 (i.e. $2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$), and the obtained Na_2CO_3 was used for adjusting the pH of the fermentation medium. This work introduced an improvement to the process they proposed earlier in 1981 which follows the concept shown in Figure 3. (see Table 1).[88]

4.1.2. Enhancing extraction with salting out

Another method to improve the extraction stage is to reduce the solubility of carboxylic acids in the aqueous solution by addition of electrolytes.[100] This facilitates the transfer of carboxylic acid molecules into the organic solvent phase,

and minimizes solvent leaching.[60] This practice is known in the literature as “salting out”.[101, 102] It should be noted that the added electrolyte must not interact with carboxylic acids in such a way that their molecular (undissociated) forms are disturbed. For instance, inorganic phosphate salts can take up carboxylic acid-originating H⁺s and thus, preventing the solvent from extracting undissociated carboxylic acids.

In 2013, De Haan et al. [86] patented a process which, based on the concept of salting out, recovers HLa from aqueous solutions. In the process they proposed, the pH of the fermentation medium which produces HLa is adjusted by addition of MgO. The resulting fermentation broth that contains magnesium lactate is acidified with HCl to transform magnesium lactate into Mg(Cl)₂ and HLa. HLa is then extracted from this solution with an appropriate solvent (e.g. C₅₊ ketones, diethyl ether, methyl-tertiary-butyl ether or a combination of them). The extracted HLa is recovered from the extract by back-extraction with water, and as the inventors claim, a preferable HLa distribution coefficient achieved during back-extraction is 20–50 % of that during forward-extraction due to the absence of Mg(Cl)₂. A part of water is then evaporated from the Mg(Cl)₂-containing raffinate, and, in the following thermal decomposition chamber, the residual aqueous Mg(Cl)₂ stream is decomposed into MgO and HCl. MgO is subsequently reused for adjusting the fermentation pH, and HCl for acidification of the fermentation broth prior to extraction. The use of MgO eliminates water-insoluble salt formation such as CaSO₄, the by-product of a conventional HLa recovery process.

4.2. Enhancing solvent regeneration by back-extraction

A major drawback of back-extraction is introduction of a significant dilution to the final product stream, thereby necessitating an extra concentration stage (e.g. precipitation or evaporation) to obtain concentrated/pure carboxylic acids. Back-extraction is often performed by contacting the extract with an alkali solution or water.[22, 23, 103] Choosing an alkali solution rather than water leads to achieving higher carboxylate concentrations in the product stream, but the carboxylates form a water-soluble salt with the cation of the alkali (see Figure 3). Such a stream needs further processing to obtain molecular carboxylic acids. Temperature and diluent swing aims at reducing the dilution of the product stream when back-extraction is performed with water. Using a volatile alkali solution for back-extraction can potentially eliminate irreversible production of carboxylate–alkali cation salts.

4.2.1. Temperature and diluent swing

To facilitate back-extraction, it is usually performed at a higher temperature than that of the extraction stage. This practice is often referred to as temperature swing back-extraction.[88, 96] Next to temperature swing, diluent swing may also be applied to improve back-extraction efficiency. Diluent swing is a result of the dependency of a composite solvent's extraction capacity on the composition of its constituents. The distribution coefficient of a composite solvent containing an amine for a carboxylic acid is dependent on the basicity of the composite solvent. For a given amine, the basicity of the composite solvent is highly influenced by the polarity of the diluent, and in addition the overall equilibrium is affected by the concentration of the amine.[44] Polar diluents (e.g. 1-octanol) often induce a higher basicity at their higher concentrations, whereas, with non-polar diluents (e.g. xylene), higher basicities are achieved at their lower concentrations.[44]a Therefore, either concentrating a non-polar diluent or diluting a polar diluent prior to back-extraction reduces the affinity of the composite solvent for the carboxylic acid. This eventually facilitates the release of the carboxylic acid from the composite solvent and enhances back-extraction.

In 1981, Baniel et al. combined diluent swing with temperature swing to boost back-extraction.[88] The solvent used by Baniel et al. was a mixture of 50 wt% xylene and 50 wt% trilauryl amine, and the extra xylene added after extraction increased its concentration to ~67 wt%. After performing back-extraction at 80 °C, compared to 25 °C at which extraction had been performed, the practically carboxylic acid free organic phase was distilled to remove the additional xylene, and the solvent was recycled to the extraction stage. A similar combined temperature swing and diluent swing back-extraction was suggested by Krzyzaniak et al. for a HAc extraction process using N,N-didodecyl pyridin-4-amine (DDAP) diluted in n-octanol as a composite solvent.[96] However, severe solvent-HLa interaction resulted in the need for a high regeneration temperature of 140 °C.

In a recent work by McMorris and Husson, the concept of diluent-swing was modified by pressurizing the back-extraction stage with a low-boiling inert hydrocarbon acting as the diluent-swing agent.[90] Employing this method might improve the overall economics of the process, as the distillation stage used to remove the additional diluent by Baniel et al. can be replaced with a simpler flash evaporation.

4.2.2. Volatile alkali back-extraction

Using a volatile alkali solution (e.g. NH_3 or trimethylamine) rather than a strong mineral alkali solution (e.g. KOH) for back-extraction enables production of molecular carboxylic acids after thermal decomposition of the alkali-carboxylic

acid complexes.[45, 91, 104] The carboxylic acid-free volatile alkali can then be sent back to the back-extraction stage. A potential drawback of this technique is experienced when the decomposition temperature of the alkali-carboxylic acid complexes is higher than the boiling point of the carboxylic acid. This results in formation of a gaseous alkali-carboxylic acid mixture with the same composition as that of the complexes. To address this issue, decomposition of the complexes is often performed in the presence of a carboxylic acid entrainer. The carboxylic acid-entrainer solution is then distilled to obtain a pure stream of the carboxylic acid and recycle the entrainer. In 1978, Mercier proposed a process in which back-extraction of HAc was aided by adding ammonia to the aqueous wash phase.[91] The ammonium acetate solution that formed in the wash phase had a higher acetate concentration than that in the original extract. The ammonium acetate solution was then subjected to decomposition in a distillation column in the presence of the same solvent used for extraction. The solvent, here acting as an entrainer, ensures that the HAc obtained from ammonium acetate is efficiently separated from NH_3 , and therefore, the following decomposition equilibrium is drawn to the right side ($\text{NH}_4\text{Ac} \rightleftharpoons \text{NH}_3 + \text{HAc}$). It should be noted that a suitable entrainer for such an operation should not interact with the entrained fragment strongly to facilitate the following stage of separating it from the entrained fragment. The ammonia stream was then drawn from the top, the water stream from the decanting tray installed in the top section, and the HAc-entrainer stream from the bottom of the column. The ammonia stream was reused for back-extraction, and HAc was recovered from the HAc-entrainer stream by distillation.

4.3. Minimizing loss of ester-based solvents caused by hydrolysis of ester

A possible drawback of using an ester for carboxylic acid extraction is hydrolysis of the ester into its parent carboxylic acid and alcohol. This results in solvent loss and introduces alcohol impurity into the product. To resolve this issue, Jang et al. [105] suggested to include a section in the extraction column packed with an esterification catalyst to convert the alcohol and a part of the extracted carboxylic acid to the ester. The extracted carboxylic acid has to be the parent carboxylic acid of the ester. This approach might reduce the solvent loss, but it introduces a serious compromise to the operational flexibility, since catalytic esterification typically requires $50 < T/^{\circ}\text{C} < 70$ while extraction is usually performed at a lower temperature.

5. Conceptual process studies on novel processes and solvents to compare their energy duties

5.1. Methodology

For all the studied processes, rates of entering and leaving streams were calculated for all unit operations by applying mass balances. In some cases, certain assumptions had to be made to enable a mass balance, as some critical parameters, such as distribution coefficients in an extraction column, were not given in the corresponding patents. Having all the stream rates determined, all the thermal operations such as heating, cooling, heat exchanging and evaporation were simulated with Aspen Plus to estimate their energy demand. For thermal operations, some key parameters, such as product purity, had to be either estimated or set as well. Various types of energy demand were considered including high quality heating duties (supplied with high pressure steam), lower quality heating duties (supplied with waste heat), cooling duty and electrical work. A summary of the assumptions made for mass balances and thermal operations is included in the *Supplementary information*.

The objective of the carboxylic acid recovery processes involving distillation-aided solvent regeneration was to obtain a product stream containing >99.8 wt% carboxylic acid. When solvent regeneration was performed by back-extraction, the carboxylic acid concentration in the product stream was dictated by the reported value in the corresponding patent. An additional distillation column was then simulated to bring the product concentration up to >99.8 wt%. To assess the applicability of the processes to recovery of fermentation-derived carboxylic acids, the concentration of the carboxylic acid in their feed streams was lowered to 1 wt%.

5.2. Assessment

This section first simulates the novel processes described previously at their reported conditions to estimate their energy demands. A rather simple process scheme involving a low boiling solvent (see Figure 2) and proposed by Seader et al. [84] is simulated for comparison as well. It should be noted that the aim of this preliminary estimation is not to compare the processes in terms of energy demands, as due to their varying initial carboxylic acid concentrations, a fair comparison cannot be drawn. In the second part of this section, the dependency of the total energy demand of the novel processes on their initial carboxylic acid concentration is assessed. In the last part of this section, the novel processes were simulated again, this time with an initial carboxylic acid concentration of 1.0 wt%, to examine their applicability to recovery of their carboxylic acid from an

aqueous stream as dilute as fermented wastewater broths. It should be noted that due to a lack of information in the reviewed patents regarding their operating conditions, the process simulations had to be performed with certain assumptions (see *Supplementary information*).

A summary of the key energy demands of the novel process when they operate at their own initial carboxylic acid concentration is presented in Table 1. A product carboxylic acid concentration of 99.8 wt% was set as the goal. However, as revealed by the simulations, not all of the processes were able to deliver a product concentration of 99.8 wt%. Therefore, for such a process, an additional distillation column was simulated to bring its product concentration to 99.8 wt%.

Table 1: Specification of novel processes; feed concentrations are taken from reference patents and product concentrations are obtained with simulations.

Inventor/author	Seader et al. [84]	Mercier [91]	Schon [76]	De Haan et al. [86]	Urbas [45]
Carboxylic acid	HAc	HAc	HAc	HLa	HAc
Feed concentration (wt%)	28	1	7.8	29	5
Product concentration (wt%)	99.8	99.8	74.9 ^a (99.8 ^b)	51.6 ^a (99.5 ^c)	99.9 ^d
Heater duty: high quality heat (MJ/kg produced carboxylic acid)	7.84	383	3.19	15	6.88
Heater duty: low quality heat (MJ/kg produced carboxylic acid)	-	-	30.9	-	-
Cooler duty (MJ/kg produced carboxylic acid)	7.42	385	40.3	17.3	6.74
Electrical work (kWh/kg produced carboxylic acid)	-	-	1.03	-	-

^a According to the specifications stated in the corresponding patent.

^b Using the patent specifications, a product concentration of 99.8 wt% could not be reached. An additional distillation column was simulated to reach a carboxylic acid concentration of 99.8 wt%.

^c Using the patent specifications, a product concentration of 99.8 wt% could not be reached. An additional distillation column was simulated to reach a carboxylic acid concentration of 99.8 wt%. The target concentration of 99.8 wt% could not be reached using an evaporation column.

^d Using the patent specifications, a product concentration of >99.9 wt% was reached. Trace amounts of other compounds in the product stream were in ppm scale.

As can be seen in Table 1, the energy demands have been divided into four categories. The heater duty is either supplied by high pressure steam (marked with high quality heat in Table 1) or waste heat (marked with quality low heat in Table 1). The values given in Table 1 were obtained with the initial carboxylic acid concentrations stated in the patents. A large difference in the initial carboxylic acid concentrations caused a large difference in the energy demands. Therefore, a valid comparison cannot be drawn. The process proposed by Schon, when simulated with the patent specifications, was not able to deliver a high purity product stream of 99.8 wt%. Therefore, an additional distillation column was

simulated to purify the product stream from a 74.9 wt% HAcr aqueous stream to a 99.8 wt% HAcr stream. The process proposed by De Haan et al. is the only one on the list that performs a non-thermal operation, i.e. back-extraction with water, to regenerate its solvent. As a result, the original product stream is an aqueous solution of HLa and water containing 51.6 wt% HLa. An additional distillation column was simulated for this process to dehydrate this stream to achieve a product HLa concentration of 99.7 wt%.

The energy demand of a carboxylic acid recovery process is highly dependent on the initial carboxylic acid concentration. The reflection of this dependency on the novel processes was examined by calculating their total energy demand at various initial carboxylic acid concentrations. The heat of combustion of the carboxylic acid of a novel process was taken as the reference point for the economics of that process. The heat of vaporization of the carboxylic acid is the lowest heater duty to supply to enable recovery of the carboxylic acid. Since the novel processes are only demonstrated with a single initial carboxylic acid concentration, the process parameters had to be kept the same as those previously used to obtain the values presented in Table 1. Figure 5 gives a simplified picture of this assessment.

As can be seen in Figure 5, the novel processes lose their economical appeal as their initial carboxylic acid concentration decreases. It should be realized that the heat of combustion of a carboxylic acid is not always a valid reference point for such a comparison. If the carboxylic acid is very valuable (e.g. an ingredient for pharmaceuticals), the operational window for the energy demand of the process can be wider. To obtain a high purity carboxylic acid stream by the novel processes, a lower-boiling fragment had to be evaporated. The lower-boiling compound in the process proposed by De Haan et al. was water (not the solvent), as the solvent was regenerated by back-extraction with water. Since the heater duties are calculated per kilogram of a carboxylic acid product, a minor reduction in the concentration of the carboxylic acid in the extract as a result of a lower initial concentration introduces large increases into the heater duties. As the initial concentration of a carboxylic acid increases, the heater duty becomes less sensitive to concentration change.

Figure 5: Heater duty of novel processes as a function of their initial carboxylic acid concentration. Carboxylic acid concentration in extract is calculated with a constant distribution factor, figure A) acetic acid, B) acrylic acid, C) lactic acid.

To evaluate and compare the applicability of the novel processes to recovery of carboxylic acids from fermentation broths, their initial carboxylic acid concentration was set to 1.0 wt%. The simulations used the parameters given in the reference patents for certain initial carboxylic acid concentrations (see *Supplementary information*). Figure 6 summarizes the obtained values for energy demands.

Figure 6: Key energy demands of processes proposed by Seader et al., Mercier, Schon, De Haan et al. and Urbas [45] with their own initial carboxylic acid concentrations as listed in Table 1 (top), and with their initial carboxylic acid concentrations set to 1.0 wt% (bottom). Heater and cooler duties are expressed as MJ/kg of carboxylic acid product, and electrical duty as kWh/kg of carboxylic acid product.

As can be seen in Figure 6, setting the initial carboxylic acid concentration to 1.0 wt% has largely increased the energy demands. All the cumulative values are much higher than the heat of combustion of their respective carboxylic acid as well, which can be an indication of impracticality of their process at such a low initial carboxylic acid concentration. While the process proposed by Mercier (with an initial concentration of 1 wt% versus (much) higher initial concentrations of the other processes) stood out previously with a large energy demand (see Figure 5), setting the initial carboxylic acid concentrations to 1.0 wt% has raised the energy demands of the processes proposed by Seader et al. and De Haan et al. to the same order of magnitude. Although the process proposed by Schon requires a large supply of energy as well (see Figure 7), the ease of utilizing waste heat can ultimately lower its heating cost significantly. Interestingly, the process proposed by Urbas has the lowest energy demand which is mainly due to its low-boiling solvent, chloroform, with a very low heat of vaporization. Unfortunately, due to environmental regulations, chloroform cannot be readily applied as an extraction solvent. However, by replacing chloroform with a more environmentally benign solvent with similar extraction capabilities and heat of evaporation, this process will be a breakthrough process. Figure 7 gives an overview of the LLX-based processes reported for recovery of carboxylic acids from aqueous solutions. It follows the same arrangement presented in this chapter.

Figure 7: Overview of processes proposed for separation of carboxylic acids by LLX and solvent regeneration.

6. Conclusions

LLX-based processes for recovery of carboxylic acids from aqueous solutions have been reviewed, and a selection of those proposing a complete process including LLX and solvent regeneration stages were assessed using process simulation. They include processes chosen from the patent literature making use of major modifications on their LLX and/or solvent regeneration stage. Based on the solvent and solvent regeneration technique, they were categorized as LLX + distillation with a high-boiling solvent, LLX + distillation with a low-boiling solvent and LLX + back-extraction. Performing solvent regeneration with distillation rather than back-extraction enables production of highly concentrated carboxylic acids at the cost of a higher energy demand. When the carboxylic acid is of high-boiling/non-boiling nature, a low-boiling solvent has to be employed to draw a high purity product stream directly or else solvent regeneration requires at least one additional unit operation e.g. back-extraction followed by distillation.

The solvents used for these processes were divided into high-boiling and low-boiling solvents, independent of their chemical structure. Innovative solvents are usually among high-boiling solvents, as the energy demand of the processes involving a high-boiling solvent is often lower due to evaporation of the carboxylic acid rather than the solvent. Switchable solvents often exhibit a dual identity, as the boiling points of switched and non-switched forms typically differ. Composite solvents form a large number of high-boiling solvents. When extraction is performed with a composite solvent containing an organic water-immiscible alkali such as trioctyl amine, back-extraction is enhanced by either lowering or increasing the content of the alkali. This can be induced by either adding extra non-polar diluent or removing a fraction of polar diluent between extraction and back-extraction stages. The use of a non-polar diluent is often more beneficial, as non-polar diluents typically exhibit a lower heat of evaporation. Back-extraction may be performed at an elevated temperature to further enhance the carboxylic acid concentration in the product stream.

The energy demand of the LLX-based processes increases rapidly with decreasing their initial acid concentration resulting in the values much higher than the heat of combustion of their respective carboxylic acid. This implies that, when applied to recovery of carboxylic acids derived by fermentation, they may not be economically attractive anymore.

The processes aiming at enhancing back-extraction with utilizing a volatile alkali such as ammonia [91] or performing salting out [86] exhibit an energy demand in the same order of magnitude as that of those using a volatile solvent such as

ethyl acetate [84] or liquefied propylene and/or propane [76]. When the solvent is gaseous at ambient conditions, waste heat can be utilized to supply the energy demand, but interestingly, its purpose is to prevent the equipment from freezing rather than to evaporate the solvent.

The energy demand of the process proposed by Urbas [45] is an order of magnitude lower than those of the aforementioned processes. Such a significant reduction in the energy demand was achieved by application of a CO₂-triggered switchable solvent. This high-boiling alkaline solvent enabled an entrainer-free decomposition of the alkali-carboxylic acid complexes. This process further reduced its energy demand by recovering the alkali-carboxylic acid complexes with a low-boiling organic solvent. Unfortunately, the low-boiling solvent was not environmentally benign. An environmentally benign alternative with similar physical and chemical properties can well make this process appealing for separation of carboxylic acids from their dilute aqueous streams.

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Appendix | Supplementary information

1. Introduction

In the article “Liquid-Liquid Extraction Processes for Recovery of Carboxylic Acids from Aqueous Solutions”, several processes have been simulated with Aspen Plus and assessed in terms of energy demand. The energy demand estimates were obtained by basing the simulation conditions on the process conditions as provided by the corresponding references and assumptions where necessary. Furthermore, a series of simulations were performed with a feed concentration of 1.0 wt% carboxylic acid, in order to estimate the energy demand of the processes when treating such dilute aqueous streams of carboxylic acids.

This *Supplementary information* describes the approaches taken for calculations, and lists the assumptions made when certain process conditions were not clearly stated by the references. Per process, a schematic view and a brief description are provided first, after which a table summarizes the specifications of the process. Another table following the first one summarizes the calculated energy demands. The following steps were taken to obtain a detailed energy demand map for each process:

1. Translation of the process description given in a reference into a flow diagram.
2. When the process was introduced in a patent, the key parameters such as distribution coefficients, carboxylic acid concentrations, solvent to feed ratios, temperatures, pressures and equilibrium reaction parameters were taken from the examples given in the patent. The key parameters of the process proposed by Seader et al. were calculated from the values given on a schematic view of the process in the corresponding reference. When an essential parameter was not available, it was estimated based on certain assumptions. The obtained parameters were then used to close the mass balance over the flow diagram.
3. After obtaining a mass balance closure, the process was simulated with Aspen Plus. Each separation unit {e.g. (extractive) distillation column, evaporation vessel and decanter} was simulated separately with the flow rates of the streams taken from the mass balance closure.
4. Each process was simulated for the second time with an inlet carboxylic acid concentration of 1.0 wt% to estimate its energy demand under these conditions.

2. Process as described by Seader et al. [1]

Figure S1: Schematic view of process as described by Seader et al. [1].

As can be seen in Figure S1, in this process, four unit operations are present: a counter-current extraction column, two distillation columns and a decanter. The specifications given by Seader et al. together with those calculated with mass balance closure are given in Table S1.

Table S1: Specifications given by Seader et al. and obtained with mass balance closure.

Unit operation	Parameter	Values given by Seader et al.	Values used for or obtained with mass balance closure
Counter-current extraction column	Solvent to feed ratio [-]	2.35	2.35
	Initial acetic acid concentration [wt%]	28	28
	Extracted acetic acid [wt%]	99.83	99.83
	Co-extracted water [wt%]	25.52	25.52
	Ethyl acetate remaining in extract phase [wt%]	97.83	97.83
Top distillation column	Acetic acid purity in bottom product [wt%]	99.8	99.8
	Recovered acetic acid [wt%]	No data	99
Decanter	Light phase composition [wt%]		
	- Acetic acid	No data	8.1 ^a
	- Water	No data	5.6 ^a
	- Ethyl acetate	No data	86.3 ^a
	Heavy phase composition [wt%]		
	- Acetic acid	No data	
	- Water	No data	
	- Ethyl acetate	No data	
Bottom distillation column	Water purity in bottom product [wt%]	No data	96.9 ^a
	Recovered water [wt%]	No data	90.8 ^a

^a Estimated with Aspen Plus using NRTL fluid package.

In the process scheme (see Figure S1), an additional stream enters the top distillation column. The flow rate of this stream was not given in the reference. Therefore, for mass balance closure, it was set to zero, thereby eliminating the stream.

Table S2 summarizes the energy demand of the individual operations. Some specifications calculated with Aspen Plus slightly deviated from the values given in Table S1.

Table S2. Selected specifications and energy demands of process proposed by Seader et al.. Simulation was performed with Aspen Plus and NRTL fluid package.

Unit operation	Parameter	Values given by Seader et al.	Values used for or obtained with mass balance closure	Values obtained with Aspen Plus
Top distillation column ^c	Acetic acid purity in bottom product [wt%]	99.8	99.8	99.1
	Recovered acetic acid [wt%]	No data	99	99
	Reboiler duty [MJ/kg] ^a			6.27
	Condenser duty [MJ/kg] ^a			5.92
	Reflux ratio [-]			0.357
	Number of trays (feed tray)			25 (11)
	Top/bottom temperature [°C]			71/117
Bottom distillation column ^{b,d}	Top/bottom pressure [bar]			1/1
	Water purity in bottom product [wt%]	No data	96.9	96.9
	Recovered water [wt%]	No data	90.8	90.7
	Heater duty of flash column [MJ/kg] ^a			1.49
	Cooler duty on top stream [MJ/kg] ^a			1.31
	Cooler duty on bottom stream [MJ/kg] ^a			0.11
	Temperature [°C]			80
	Pressure [bar]			1

^a Estimated per kg of acetic acid in the product stream.

^b Aspen Plus could not solve a *Shortcut distillation operation*, as the separation operation was too easy. A combination of a flash column and two coolers was simulated instead.

^c The heater duty is lowered by heat integration between the distillate and the feed. A minimum temperature difference of 10°C was held between the hot outlet and cold inlet streams of the heat exchanger.

^d The heater duty is lowered by heat integration between the bottom product and the feed. A minimum temperature difference of 10°C was held between the hot outlet and cold inlet streams of the heat exchanger.

3. Process proposed by Urbas [2]

In 1983, Urbas patented a process for enhancing HAc extraction with tributyl amine (TBA) as the co-solvent that in the presence of CO_2 forms water-soluble tributyl ammonium carbonate that reacts with calcium acetate to produce water-soluble tributyl ammonium acetate and calcium carbonate precipitate. Tributyl ammonium acetate is then extracted with chloroform. Chloroform is recovered by distillation, and HAc and Tributyl amine are released by thermally decomposing tributyl ammonium acetate (see Figure S2).

^a Calcium acetate

^b Tributyl amine

^c Tributyl ammonium acetate

^d Acetic acid

Figure S2: HAc extraction and solvent regeneration process proposed by Urbas [2].

The main energy demanding units are the distillation column, the decomposition vessel and the compressor pressurizing the CO₂ stream. The specifications of the processes from the reference, as well as those calculated by mass balance closure are given in Table S3.

Table S3: Specifications given by Urbas and obtained with mass balance closure.

Unit operation	Parameter	Values given by Urbas	Values used for or obtained with mass balance closure ^a
Counter-current extraction column	Solvent to feed ratio [-]	0.678	0.678
	Initial acetic acid concentration [wt%]	7.3	7.3
	Extracted tributyl ammonium acetate [wt%]	100 ^a	99.0
	Co-extracted water [wt%]	No data	1.0
	Chloroform remaining in extract phase [wt%]		
Distillation column	Chloroform purity in top product [wt%]	No data	99.9
	Recovered chloroform [wt%]	No data	99.9
Decomposition vessel	Acetic acid purity in top product [wt%]	No data	94.8
	Recovered acetic acid [wt%]	91.5	100.0
Compressor	Operation pressure [bar]	1-2	1

^a Estimated by using $E = D_{\text{acetic acid}} \cdot (S/F)$. A $D_{\text{acetic acid}}$ of 1.7, as claimed by Urbas, results in an E larger than one. Therefore, a complete extraction was assumed.

The following reactions were assumed to happen in the process:

Maintaining a close to neutral pH during fermentation

Solubilizing tributyl amine in the presence of CO₂

Formation of tributyl ammonium acetate and calcium acetate

The following assumptions have been made for mass balance closure:

1. It was assumed that an equimolar amount of CaCO₃ with respect to calcium acetate was available, and the conversion of acetic acid to calcium acetate was complete.
2. Urbas claimed a 96.0 % conversion of calcium acetate to calcium carbonate was achieved when a molar ratio of 0.93 (acetate:tributyl amine) was used. For mass balance closure, it was assumed that the conversion was complete.
3. CO₂ was introduced at 1.0 bar as an equimolar stream with respect to calcium acetate, and it fully converted to calcium carbonate.
4. It was assumed that a complete separation of calcium carbonate from the aqueous stream containing tributyl ammonium acetate was achieved using a solid-liquid separator (e.g. a membrane or cyclone).

With all the streams specified, the process was simulated with Aspen Plus to estimate the individual energy demands. In some cases, the specifications estimated with Aspen Plus were different from those determined by mass balance closure (see Table S4).

Table S4. Selected specifications and energy demands of process proposed by Urbas. Simulation was performed with Aspen Plus and NRTL fluid package.

Unit operation	Parameter	Values given by Urbas	Values used for or obtained with mass balance closure	Values obtained with Aspen Plus
Top distillation column ^c	Chloroform purity in top product [wt%]	No data	99.9	98.4
	Recovered chloroform [wt%]	No data	99.9	99.99
	Reboiler duty [MJ/kg] ^a			6.04
	Condenser duty [MJ/kg] ^a			5.72
	Reflux ratio [-]			0.79
	Number of trays (feed tray)			66 (24)
	Top/bottom temperature [°C]			31/123
	Top/bottom pressure [bar]			1/1
Decomposition vessel ^{b, c}	Cooler duty on top stream [MJ/kg] ^{a, d}			0.08
	Acetic acid purity in top product [wt%]	No data	94.8	99.99
	Recovered acetic acid [wt%]	91.5	100.0	99.99
	Reboiler duty [MJ/kg] ^a			0.84
	Condenser duty [MJ/kg] ^a			0.67
	Reflux ratio [-]			0.69
	Number of trays (feed tray)			24 (20)
	Top/bottom temperature [°C]			116/214
	Top/bottom pressure [bar]			1/1
	Cooler duty on top stream [MJ/kg] ^{a, d}			0.12
	Cooler duty on bottom stream [MJ/kg] ^{a, d}			0.14

^a Estimated per kg of acetic acid in the product stream.

^b Simulated by assuming a full conversion of tributyl ammonium acetate to acetic acid which is consequently distilled.

^c The heater duty is lowered by heat integration between the bottom product and the feed. A minimum temperature difference of 10°C was held between the hot outlet and cold inlet streams of the heat exchanger.

^d These coolers lower the temperatures of the distillate and the bottom product to 25 °C.

4. Process proposed by De Haan et al. [3]

In 2013, De Haan et al. made use of the concept of salting out to propose a process for recovery of lactic acid from aqueous solutions. Despite the common practice of using $\text{Ca}(\text{OH})_2$ to maintain an approximately neutral pH during fermentation, they devised $\text{Mg}(\text{OH})_2$ as the neutralizing agent. The resulting magnesium lactate-containing broth was acidified with HCl to enable formation of lactic acid and MgCl_2 . Lactic acid was then successfully extracted with a conventional solvent in the presence of MgCl_2 acting as the salting out agent. The extract was then exposed to back-extraction to recover lactic acid with water. The lack of a salting out agent in water facilitated back-extraction. The raffinate after a partial dehydration was subjected to thermal decomposition transforming $\text{Mg}(\text{Cl})_2$ into MgO and HCl . The neutralizing agent was produced by hydration of MgO . Using $\text{Mg}(\text{OH})_2$ rather than $\text{Ca}(\text{OH})_2$ and recycling MgCl_2 prevents formation of byproduct salts of calcium. Figure S3 shows a schematic view of the process. The patent also claims that the gaseous HCl derived after decomposition can be directly fed to the mixing vessel. Due to the presence of unknown decomposition products of lactic acid accompanying the gaseous HCl , this stream was not simulated for the process.

Figure S3: Process for recovery of HLa from fermentation broth proposed by De Haan et al. [3].

The following reactions were assumed to happen in the process:

Formation of lactate during fermentation

Acidification of broth to derive lactic acid

Thermal decomposition of hydrated MgCl_2

Hydration of MgO

The main energy demanding operations are the evaporation columns and the decomposition column. The specifications either given by the authors or calculated by mass balance closure are given in Table S5.

Table S5: Specifications given by De Haan et al. and obtained with mass balance closure.

Unit operation	Parameter	Values given by De Haan et al.	Values used for or obtained with mass balance closure ^a
First counter-current extraction column	Solvent to feed ratio [-]	1.33	1.33
	Initial lactic acid concentration [wt%]	29.0	29.0
	Initial MgCl_2 concentration [wt%]	15.3	15.3
	Extracted/co-extracted species [wt%]		
	- Lactic acid	44.0 ^a	44.0
	- Water	No data	1.0
	- HCl	No data	0.0
	- MgCl_2	No data	0.0
	- MgO	No data	0.0
Second counter-current extraction column	MIBK remaining in extract phase [wt%] ^c	No data	99.0
	Column temperature [°C]	20	20
	Solvent to feed ratio [-]	4.16	4.16
	Extracted/co-extracted species [wt%]		
	- Lactic acid	100 ^b	99.0
	- Water	No data	99.0
	- HCl	No data	0.0
	- MgCl_2	No data	0.0
	- MgO	No data	0.0
Evaporator prior to thermal decomposition	MIBK remaining in raffinate phase [wt%]	No data	100.0
	Column temperature [°C]	60	60
Evaporator dehydrating lactic acid	Water purity in top product [wt%]	No data	99.86
	Recovered water [wt%]	No data	70.0
Evaporator dehydrating lactic acid	Water purity in top product [wt%]	No data	100.0
	Recovered water [wt%]	No data	99.8

^a The reported $D_{\text{lactic acid}}$ of 0.33 at a S/F of 1 was correlated with the reported S/F of 1.33 to obtain 44 wt% extraction.

^b The reported $D_{\text{lactic acid}}$ of 0.33 at a S/F of 1 was correlated with the reported S/F of 4.16 to obtain >100 wt% extraction. Therefore, complete extraction was assumed.

^c Methyl isobutyl ketone (MIBK) was chosen from the suggested selection as the solvent.

The binary interaction parameters of the salts with the organic compounds could not be estimated with the NRTL model. Therefore, the salts were not considered for simulation of the process. A summary of the energy demands of the process estimated by Aspen Plus is given in Table S6.

Table S6: Selected specifications and energy demands of process proposed by De Haan et al... Simulation was performed with Aspen Plus and NRTL fluid package.

Unit operation	Parameter	Values given by De Haan et al.	Values used for or obtained with mass balance closure	Values obtained with Aspen Plus
Evaporator prior to thermal decomposition ^c	Water purity in top product [wt%]	No data	100.0	98.8
	Recovered water [wt%]	No data	70.0	69.4
	Heater duty of flash column [MJ/kg] ^a			13.2 ^a
	Cooler duty on top stream [MJ/kg] ^a			11.4 ^a
	Temperature [°C]			80
Thermal decomposition vessel ^b	Pressure [bar]			0.33
	Cooler duty [MJ/kg] ^d			27.9 ^a
	Heater duty [MJ/kg]			13.8 ^a
	Cooler duty [MJ/kg]			0.03 ^a
Heat integration between extraction columns	Heater duty [MJ/kg]			0.18 ^a
	Water purity in top product [wt%]	No data	100.0	97.2
	Recovered water [wt%]	No data	99.8	95.2
	Heater duty of flash column [MJ/kg]			4.18 ^a
	Cooler duty on top stream [MJ/kg] ^c			3.55 ^a
	Cooler duty on bottom stream [MJ/kg] ^c			0.16 ^a
	Temperature [°C]			85
	Pressure [bar]			0.05
Evaporator dehydrating lactic acid ^c	Water purity in top product [wt%]	No data	100.0	97.2
	Recovered water [wt%]	No data	99.8	95.2
	Heater duty of flash column [MJ/kg]			4.18 ^a
	Cooler duty on top stream [MJ/kg] ^c			3.55 ^a
Evaporator dehydrating lactic acid ^c	Cooler duty on bottom stream [MJ/kg] ^c			0.16 ^a
	Temperature [°C]			85
	Pressure [bar]			0.05

^a Estimated per kg of lactic acid in the product.
^b Simulated by assuming a total conversion of MgCl_2 to MgO and that volatile byproducts are evaporated in a flash vessel.
^c The heater duty is lowered by heat integration between the top product and the feed. A minimum temperature difference of 10°C was held between the hot outlet and cold inlet streams of the heat exchanger.
^d Used to cool the distillate down to 20 °C.
^e Estimated using external coolers to cool the stream down to 20 °C.

5. Process proposed by Schon et al. [4]

Schon et al. proposed a process using liquefied propylene and/or propane as the solvent to extract acrylic acid from aqueous solutions. This method replaces the distillation column needed for solvent regeneration with a few flash drums operating at low temperatures. This enables the use of waste heat a major part of which is supplied to prevent the equipment from freezing. With the use of a more volatile solvent than acrylic acid, non-volatile acrylic acid self-polymerization inhibitors can be added to acrylic acid. Furthermore, since propylene and/or propane are used to produce acrylic acid, their liquefied forms are usually available at the production plant. This eliminates the need for storing and handling of an extra chemical. A schematic view of this process is shown in Figure S4.

Figure S4: Acrylic acid extraction and solvent regeneration process proposed by Schon et al. [4]

The stream marked as *product* was estimated to have a composition of 90.9 wt% HAcr, 0.4 wt% water and 8.7 wt% propylene confirming the claim stated in the reference. It was assumed that no acrylic acid was flashed during solvent regeneration. Table S7 summarizes the specifications of the processes given by Schon et al. and calculated with mass balance closure.

Table S7: Specifications given by Schon et al. and obtained with mass balance closure.

Unit operation	Parameter	Values given by Schon et al.	Values used for or obtained with mass balance closure
First counter-current extraction column	Solvent to feed ratio [-]	6.08	6.08
	Initial acrylic acid concentration [wt%]	7.80	7.80
	Extracted/co-extracted species [wt%]		
	- Acrylic acid	91.0	91.0
	- Water	No data	4.0
	Propylene remaining in extract phase [wt%]	No data	98.0
	Column temperature [°C]	ambient	25
	Column pressure [bar]	16.2	16.2
Flash column (16.18/10 bar) ^a	Recovered propylene [wt%]	90.0	90.0
	Co-recovered water [wt%]	No data	82.0
	Column temperature [°C]	40	40
Flash column (10/2 bar) ^a	Recovered propylene [wt%]	No data	90.0
	Co-recovered water [wt%]	No data	82.0
	Column temperature [°C]	Above freezing	25
Flash column on raffinate (16.18/1 bar) ^a	Recovered propylene [wt%]	No data	93.0
	Co-recovered water [wt%]	No data	82.0
	Column temperature [°C]	Above freezing	25
Flash column on product (2/1 bar) ^a	Recovered propylene [wt%]	No data	93.0
	Co-recovered water [wt%]	No data	82.0
	Column temperature [°C]	Above freezing	25
Compressor 1	Inlet/outlet pressure [bar]	No data/16.2	10/16.2
Compressor 2	Inlet/outlet pressure [bar]	1/2	1/2

^a Inlet and outlet pressures are given respectively.

The energy demands of the individual unit operations of the process are given in Table S8. Some specifications were estimated by Aspen Plus.

Table S8: Selected specifications and energy demands of process proposed by Schon et al.. Simulation was performed with Aspen Plus and NRTL fluid package.

Unit operation	Parameter	Values given by Schon et al.	Values used for or obtained with mass balance closure	Values obtained with Aspen Plus
Flash column (16.18/10 bar) ^b	Recovered propylene [wt%]	90.0	90.0	99.7
	Co-recovered water [wt%]	No data	82.0	39.6
	Inlet/outlet temperature [°C]	Ambient/40	25/40	25/40
	Duty [MJ/kg]			27.9 ^a
Flash column (10/2 bar) ^b	Recovered propylene [wt%]	No data	90.0	84.9
	Co-recovered water [wt%]	No data	82.0	0.32
	Inlet/outlet temperature [°C]	No data	40/25	40/25
	Duty [MJ/kg]			0.01 ^a
Flash column on raffinate (16.18/1 bar) ^b	Recovered propylene [wt%]	No data	90.0	99.3
	Co-recovered water [wt%]	No data	82.0	0.19
	Inlet/outlet temperature [°C]	Above freezing	25/25	25/25
	Duty [MJ/kg]			0.07 ^a
Flash column on product (2/1 bar) ^b	Recovered propylene [wt%]	No data	93.0	54.3
	Co-recovered water [wt%]	No data	82.0	0.06
	Inlet/outlet temperature [°C]	Above freezing	25/25	25/25
	Duty [MJ/kg]			0.58 ^a
Compressor 1	Inlet/outlet pressure [bar]	No data/16.2	10/16.2	10/16.2
	Inlet/outlet temperature [°C]			40/66
	Compressor duty [MJ/kg]			3.26 ^a
	Cooler duty [MJ/kg] ^c			31.27 ^a
Compressor 2	Inlet/outlet pressure [bar]	1/2	1/2	1/2
	Inlet/outlet temperature [°C]			25/63
	Compressor duty [MJ/kg]			0.10 ^a
	Cooler duty [MJ/kg] ^c			0.12 ^a

^a Estimated per kg of acrylic acid in the feed.

^b Inlet and outlet pressures are given respectively.

^c Used to lower the temperature to 25°C.

6. Process proposed by Mercier [5]

In 1978, Mercier proposed a process by which HAc can be recovered from dilute aqueous HAc solutions. According to the patent, HAc was counter-currently extracted from an aqueous solution with a mixture of an alcohol (25 wt%) and the acetate ester of the alcohol (75 wt%). The extracted HAc was then back-extracted from the extract with an aqueous ammonia solution to form an aqueous ammonium acetate solution. The HAc concentration in the alkali solution exceeded that in the extract. The regenerated solvent was sent back to the extraction stage. The ammonium acetate solution was subjected to decomposition in a distillation column in the presence of the same solvent used for extraction, here serving as the entrainer. Three streams were drawn from the distillation column: an ammonia stream from the top, a water stream from the decanting tray installed in the top section of the column, and a HAc-entrainer stream from the bottom. Ammonia was reused in the back-extraction stage, and HAc was recovered from the HAc-entrainer solution by distillation. Figure S5 shows a schematic view of this process.

Figure S5: Acetic acid extraction and solvent regeneration process proposed by Mercier [5].

Merciér suggested a recycle of half the back-extract stream to the back-extraction column. The decomposition column was assumed to achieve a full conversion of ammonium acetate to acetic acid and ammonia. Table S9 gives a list of the specifications of the process either given in the reference or calculated with mass balance closure.

Table S9: Specifications given by Merciér and obtained with mass balance closure.

Unit operation	Parameter	Values given by Merciér	Values used for or obtained with mass balance closure
Counter-current extraction column	Solvent to feed ratio [-]	1.6	1.6
	Initial acetic acid concentration [wt%]	1.0	1.0
	Extracted/co-extracted species [wt%]		
	- Acetic acid	95	95
	- Water	7.5	7.5
	- Butanol	98	98
	- Butyl acetate	98	98
	- NH_4^+	No data	100
	- NH_3	No data	100
	- Ammonium acetate	No data	100
Counter-current back-extraction column	Column temperature [°C]	No data	25
	Column pressure [bar]	No data	25
	Solvent to feed ratio [-]	0.07	0.07
	Extracted/co-extracted species [wt%]		
	- Acetic acid	n.a. ^a	n.a. ^a
	- Water	52	52
	- Butanol	No data	0
	- Butyl acetate	No data	0
	- NH_4^+	No data	0
	- NH_3	No data	0
Decomposition column	- Ammonium acetate	98.5	98.5
	Column temperature [°C]	No data	25
	Column pressure [bar]	No data	25
Distillation column 1	Recovered NH_3 [wt%]	No data	99.5
	Co-recovered water in decanter [wt%]	No data	99.0
	NH_3 purity [wt%]	No data	100.0
Distillation column 2	Water purity in bottom product [wt%]	No data	99.9
	Recovered water [wt%]	No data	99.9
Distillation column 3	Recovered butanol [wt%]	No data	70.0
	Recovered butyl acetate [wt%]	No data	100.0
Distillation column 3	Acetic acid purity in bottom product [wt%]	No data	99.9
	Recovered acetic acid [wt%]	No data	99.9

^a No acetic acid remains when a full conversion is achieved.

The energy intensive sections of the process are the decomposition column and the distillation columns. A detailed list of their energy demands is given in Table S10.

Table S10: Selected specifications and energy demands of process proposed by Mercier. Simulation was performed with Aspen Plus and NRTL fluid package.

Unit operation	Parameter	Values given by Mercier	Values used for or obtained with mass balance closure	Values obtained with Aspen Plus
Decomposition column ^b	NH ₃ purity [wt%]	No data	100.0	
	NH ₃ recovered [wt%]	No data	99.5	
	Water recovered in decanter [wt%]	No data	99.0	
	Heater duty [MJ/kg] ^a			
Distillation column 1 ^b	Water purity in bottom product [wt%]	No data	99.9	
	Recovered water [wt%]	No data	99.9	
	Reboiler duty [MJ/kg] ^a			
	Condenser duty [MJ/kg] ^a			
	Reflux ratio [-]			
	Number of trays (feed tray)			
	Top/bottom temperature [°C]			
	Top/bottom pressure [bar]			
Distillation column 2 ^c	Cooler duty on top stream [MJ/kg] ^a			
	Recovered butanol [wt%]	No data	70.0	51.7
	Recovered butyl acetate [wt%]	No data	100.0	99.0
	Reboiler duty [MJ/kg] ^a			48.5
	Condenser duty [MJ/kg] ^a			43.5
	Reflux ratio [-]			13.9
	Number of trays (feed tray)			25 (19)
	Top/bottom temperature [°C]			86.8/99.5
	Top/bottom pressure [bar]			1/1
	Cooler duty on top stream [MJ/kg] ^a			0.54
Distillation column 3 ^d	Cooler duty on bottom stream [MJ/kg] ^a			4.18
	Acetic acid purity in bottom product [wt%]	No data	99.9	95.6
	Recovered acetic acid [wt%]	No data	99.9	99.0
	Reboiler duty [MJ/kg] ^a			305
	Condenser duty [MJ/kg] ^a			306
	Reflux ratio [-]			12.27
	Number of trays (feed tray)			189 (83)
	Top/bottom temperature [°C]			105/117
	Top/bottom pressure [bar]			1/1
	Cooler duty on bottom stream [MJ/kg] ^a			0.12

^a Estimated per kg of acetic acid in the feed.

^b Could not be simulated.

^c The heater duty is lowered by heat integration between the bottom stream and the feed. A minimum temperature difference of 10°C was held between the hot outlet and cold inlet streams of the heat exchanger.

^d No heat exchange was possible between the top/bottom stream and the feed.

7. References

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- [5] J. Mercier, “Recovery of acetic acid from dilute aqueous solutions thereof”, US Patent 4100189, 1978.

V
F
A

A large, stylized white silhouette of a microscope is positioned on the right side of the page. It features a large eyepiece at the top, a central vertical tube, and a large, curved base. A series of vertical white lines of varying heights are positioned to the right of the 'VFA' text, resembling a barcode or a series of vertical bars.

Extraction of
volatile fatty acids
from fermented
wastewater:
mechanisms and
interference of salts

CHAPTER

Abstract

Valorization of wastewater streams can be done by fermentation to produce volatile fatty acids (VFAs) which are applied as platform chemicals for synthesis of value-added chemicals. Since VFA concentration in fermented wastewater is very low (~ 1 wt%) and fermented wastewater contains considerable amounts of dissolved salts, recovery of VFAs from fermented wastewater is challenging. To study the potential of some ionic liquids compared to traditional solvents for extraction of VFAs from fermented wastewater, a detailed study on the effects of various salt-originating ions on VFA extraction was performed. Ion exchange and intermolecular interactions (e.g. hydrogen bonding) were found to be responsible for extraction of VFAs. The presence of salts (e.g. KCl) resulted in extraction of acidic forms of salt-originating anions (e.g. $\text{H}^+ + \text{Cl}^-$). 20 wt% trioctylamine (TOA) in *n*-octanol (representing conventional solvents) and $[\text{P}_{666,14}][\text{Phos}]$ (an ionic liquid) were found to be the most promising VFA-extracting solvents. Their maximum VFA loadings while being in equilibrium with an artificial fermented wastewater were determined by performing cross-current extractions. $[\text{P}_{666,14}][\text{Phos}]$ achieved a higher maximum VFA loading which enables it to deliver a much more concentrated VFA stream at a lower solvent to feed ratio (S/F).

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Nomenclature

MCFAs:	Medium chain fatty acids
VFAs:	Volatile fatty acids
HLa:	Lactic acid
HAc:	Acetic acid
HPr:	Propionic acid
HBu:	Butyric acid
Ac ⁻ :	Acetate
TOA:	Trioctylamine
[P _{66,14}][Cl]:	Trihexyl(tetradecyl)phosphonium chloride
[P _{66,14}][Br]:	Trihexyl(tetradecyl)phosphonium bromide
[P _{66,14}][Phos]:	Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate
[P _{66,14}][N(CN) ₂]:	Trihexyl(tetradecyl)phosphonium dicyanamide

1. Introduction

Due to rising concerns on depletion of easily accessible petroleum resources over the next decades, production of bio-based chemicals is gaining interest. Several major routes have been proposed to produce bio-based chemicals among which fermentation has gained the interest of many researchers, and much attempt has been made to improve the efficiency of fermentation-based processes.[1] Production of various groups of chemicals through fermentation has been reported in the literature. Many studies have focused on production of carboxylic acids through fermentation, as carboxylic acids are major platform chemicals for synthesis of value-added chemicals.[2-4] Volatile fatty acids (VFAs) are versatile carboxylic acids utilized in production of bio-plastic and bio-energy.[1, 5, 6] However, synthesis of value-added chemicals starting with production and purification of VFAs in an economically viable process is not straightforward. An important obstacle is the low concentration of VFAs in fermentation broths, which makes separation and purification of VFAs challenging.

Several separation techniques have been proposed to recover VFAs from aqueous solutions such as straight distillation, extractive distillation, membrane filtration and crystallization.[7-12] However, due to the low concentration of VFAs in fermented wastewater, any separation technique attempting to recover VFAs by removing the water content of fermented wastewater is not economical. Therefore, affinity separation techniques with affinity for VFAs are considered as the only practical techniques to recover VFAs from fermented wastewaters. Preferentially, the separating agents used for affinity separation target the VFA molecules while minimizing water removal. Liquid-liquid extraction is one of the most applied affinity separation techniques, and with a proper choice of solvent, it can enable effective recovery of VFAs from dilute solutions in an energy efficient manner.[13] Traditional solvents used for extraction of organic acids from aqueous solutions include alcohols, ketones, ethers, aliphatic hydrocarbons, organophosphates, and aliphatic amines.[7, 14-17] In the recent extraction literature, ionic liquids have been reported for extraction of VFAs, and some are shown to be superior to conventional solvents in terms of extraction efficiency from idealized aqueous solutions containing only acids and water.[18-22]

Fermented wastewater contains less VFA compared to a fermentation broth purposely made for VFA recovery, as the carbon content of wastewater prior to fermentation is much lower. Furthermore, fermented wastewaters are not ideal aqueous solutions and typically contain significant amounts of various dissolved salts. Na^+ , K^+ , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, Cl^- , and SO_4^{2-} are the most common ions originating from the dissolved salts present in fermented wastewater (see Table 1 for typical

composition of fermented wastewater). Due to the low concentration of VFAs and the presence of salt-originating ions, the typical pH of fermented wastewater ranges from 4 to 6. How the presence of these ions affects extraction of VFAs using ionic liquids and the traditional solvent trioctylamine (TOA) in *n*-octanol was the main research question investigated here.

Table 1: Typical composition of fermented wastewater.

Component	Chemical formula	Concentration [g/L]	pK _a
Acetate	CH ₃ COOH	2.5–10	4.76
Propionate	CH ₃ CH ₂ COOH	2.5–10	4.88
Butyrate	CH ₃ (CH ₂) ₂ COOH	2.5–10	4.82
Lactate	CH ₃ CH(OH)COOH	2.5–10	3.86
Sodium	Na ⁺	1–5	
Potassium	K ⁺	1–5	
Chloride	Cl ⁻	1–10	
Phosphate	H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	1–10	
Sulphate	SO ₄ ²⁻	1–10	
Sulphide	S ²⁻	0.3	
Magnesium	Mg ²⁺	0.3	
Calcium	Ca ²⁺	0.3	
Ammonium	NH ₄ ⁺	0.1	
Trace elements (e.g. cobalt, nickel and iron)	Co, Fe, Ni (ionic forms)	10 ⁻⁴	
Inert COD (e.g. humic acid and fulvic acid)		1	
Microbes			

For this study, an artificial fermented wastewater resembling an actual fermented wastewater was prepared according to the composition shown in Table 1. Next to extraction studies with this artificial fermented wastewater, several simpler model solutions were also prepared to examine the effects of salt-originating ions on extraction of VFAs. The study with the artificial fermented wastewater included multi-stage cross-current extraction to investigate the accumulation of VFAs in the studied solvents.

2. Experimental and analysis

2.1. Chemicals

Acetic acid (HAc, >99.7%), lactic acid (HLa, Ph.Eur.), propionic acid (HPr, >99.5%), butyric acid (HBu, >99%), nitric acid (1 M), *n*-octanol (>99%), trioctylamine (TOA, 98%), potassium chloride (>99%), anhydrous sodium phosphate dibasic (>99%), and anhydrous sodium sulfate (>99%) were purchased from Sigma-Aldrich. Hydrochloric acid (1 M) and potassium hydroxide (1 M) were supplied by Merck. [P_{666,14}][Cl] (Cyphos® IL101, >95%), [P_{666,14}][Br] (Cyphos® IL102, >95%), [P_{666,14}][Phos] (Cyphos® IL104, >95%), and [P_{666,14}][N(CN)₂] (Cyphos® IL105, >95%) were purchased from io-li-tec.

2.2. Artificial fermented wastewaters and model solutions

The composition of the aqueous solutions used for this study is shown in Table 2. Solution 3 is considered as an artificial fermented wastewater resembling an actual fermented wastewater. Solutions 1–2f are simpler model solutions prepared to study the effects of dissolved salts and pH on extraction of VFAs.

Table 2: Composition of applied model aqueous solutions.

Solution	Concentration [mol/L]									pH
	HAc	HPr	HBu	HLa	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	HCl	HNO ₃	
1	0.17 (1 wt%)									2.8
1a	0.17				0.05					2.9
1b	0.17					0.05				3
1c	0.17						0.1			4.6
2	0.17						0.2			6
2a	0.17						0.2	0.01		5.9
2b	0.17						0.2	0.1		4.8
2c	0.17						0.2	1		0.4
2d	0.17						0.2		0.01	5.9
2e	0.17						0.2		0.1	4.8
2f	0.17						0.2		1	0.4
3	0.04 (0.25 wt%)	0.03 (0.25 wt%)	0.03 (0.25 wt%)	0.03 (0.25 wt%)	0.05	0.05	0.1			5

2.3. Solvents

The solvents used in this study include TOA–*n*-octanol solutions and several phosphonium ionic liquids, and are listed in Table 3.

Table 3: Solvents used in this study and their water uptake as reported in the literature.

Solvent	Water uptake	
	[wt% of solvent phase after extraction]	
<i>n</i> -Octanol	4.9	[23]
10 – 50 wt% TOA in <i>n</i> -octanol	n.a.*	
[P _{666,14}][Cl]	13.4 – 14.4	[24] – [20]
[P _{666,14}][Br]	6.3	[24]
[P _{666,14}][Phos]	14.4 – 16.0	[20] – [25]
[P _{666,14}][N(CN) ₂]	3.3	[20]

* Not available

2.4. Experimental procedures

2.4.1. Single-stage liquid-liquid extraction

Single-stage liquid-liquid extraction experiments were performed at the volumetric solvent to feed ratio (S/F) of 3/5 using 3 mL of a solvent (see Table 3) and 5 mL of an aqueous model solution (see Table 2) at room temperature (20±1 °C). The S/F of 3/5 was chosen to follow a certain experimental procedure described elsewhere.[23] To reach equilibrium, the liquid mixtures were magnetically stirred (>500 rpm) for 1 h. The time to reach equilibrium was experimentally validated to be less than 1 h for all feed–solvent pairs. After 1 h of stirring, phases were separated by a centrifuge (8000 rpm for 5 minutes). The phases were then sampled for analysis.

2.4.2. Multi-stage cross-current liquid-liquid extraction

Multi-stage cross-current liquid-liquid extraction experiments were carried out with solution 3 to monitor the accumulation of VFAs in the solvents in the presence of dissolved salts. After every extraction stage which was carried out in an identical way to the procedure described for single-stage extraction, the solvent phase was separated from the raffinate phase, and without any further treatment, it was contacted with fresh solution 3. Subsequent extraction stages were performed until the raffinate composition did not change anymore. The VFA loading of the VFA-saturated solvents was measured after washing the solvent phases with KOH (1 M) and analyzing the alkaline phase with HPLC.

2.5. Analysis

The concentrations of HAc, HLa, HPr, HBu, $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$, [Phos] $^-$ ($[\text{C}_{16}\text{H}_{34}\text{O}_2\text{P}]^-$), and the summation of Cl^- and SO_4^{2-} concentrations were measured with HPLC [Agilent Hi-Plex H column (300×7.7 mm) and refractive index detector on a Agilent 1200 series HPLC system]. Individual Cl^- and SO_4^{2-} concentrations and $[\text{N}(\text{CN})_2]^-$ and Br^- concentrations were quantified with IC (Metrosep A Supp 4 - 250/4.0 column and Metrohm 732 IC detector on a Metrohm 733 IC Separation Center). The water content was measured with Karl-Fischer titration (Metrohm 787 KF Titrano). Na^+ and K^+ concentrations were measured with a flame photometer (BWB Flame Photometer XP). The pH was measured with a Metrohm pH probe (6.0234.100) connected to a Metrohm 780 pH meter.

3. Results and discussion

3.1. Single-stage HAc extraction from idealized solutions containing only water and acid

Various solvents have been reported for extraction of carboxylic acids from idealized aqueous solutions of only acid in water.[17, 21, 24] In this study, validation of the applied experimental methods was done with an idealized aqueous solution containing 1 wt% HAc (solution 1 in Table 2). TOA was applied diluted in *n*-octanol in the range of 0–50 wt%, and the phosphonium ionic liquids were used in their pure forms. The HAc distribution coefficients and water uptakes obtained after these experiments (with a single volumetric S/F ratio of 3/5) are summarized in Table 4.

Table 4: Distribution coefficients and water uptakes for HAc extraction from solution 1 ($pH_{initial} = 2.8$, volumetric S/F = 3/5, $T = 20 \pm 1$ °C).

Solvent	DHAc [wt%/wt%]	Water uptake [wt% of solvent phase after extraction]
n-Octanol	0.6	4.8
10 wt% TOA in n-octanol	4.3	4.5
20 wt% TOA in n-octanol	8.8	3.7
30 wt% TOA in n-octanol	11.5	3.2
40 wt% TOA in n-octanol	9.9	2.5
50 wt% TOA in n-octanol	8.2	2.1
[P _{666,14}][Cl]	3.7	13.6
[P _{666,14}][Br]	2.2	6.6
[P _{666,14}][Phos]	17	14.1
[P _{666,14}][N(CN) ₂]	1.8	3.9

Table 4 shows that the HAc distribution coefficient obtained with pure *n*-octanol is 0.6 which is perfectly in line with the values reported previously.[13, 25] Table 4 also shows that the HAc distribution coefficients of TOA–*n*-octanol solutions follow a trend in which the highest values are obtained for the TOA concentration range of 20–40 wt%. This trend was reported previously for extraction of HLa with TOA–*n*-octanol solutions [15–17], and it was attributed to the stabilizing effect induced by *n*-octanol molecules on HLa–TOA complexes via hydrogen bonding. [17] By comparing the values presented in Table 4, it can be clearly seen that, at the low HAc concentration applied, [P_{666,14}][Phos] has a significantly higher HAc distribution coefficient than the other solvents. This is in line with the observation by Marták and Schlosser where it was shown that the HLa distribution coefficient of [P_{666,14}][Phos] strongly increases with decreasing raffinate concentration.[20] To validate this trend, several HAc extraction experiments were performed with varying the initial HAc concentration in the aqueous phase while using the same volumetric S/F used for the rest of this study (3/5). The results are displayed in Figure 1.

Figure 1: HAc distribution coefficient as a function of HAc equilibrium concentration in raffinate phase (volumetric $S/F = 3/5$, $T = 20 \pm 1^\circ\text{C}$).

The water uptake of $[\text{P}_{666,14}][\text{Phos}]$ was remarkably high, but in line with the observations by others.[20, 26] With the results of the idealized HAc solution being well in line with the values reported in the literature, the effects of salt-originating ions on extraction of VFAs can be discussed next.

3.2. Effects of dissolved salts on extraction of HAc

Each of the salts commonly present in fermented wastewater was separately added to a simple aqueous solution containing only HAc to prepare solutions 1a, 1b and 1c (see Table 2). The effects of the salts on extraction of HAc were studied by comparison with HAc extraction from solution 1, and in addition, the distribution of each salt-originating ion was studied. The obtained results for the anions are summarized in Table 5a, and the cation distributions are presented in Table 5b as well as water distribution. For the species Ac^- , SO_4^{2-} and HPO_4^{2-} , the reported values in Table 5a are the summation of all occurring forms (e.g. HAc and acetate anion in the case of Ac^-). Measuring the total aqueous concentrations and the water distribution over the phases enabled determination of the total amounts in the aqueous raffinates and in the extract phases. The values presented in Tables 5a and 5b were obtained from extraction systems composed of 10 g of solution 1, 1a, 1b or 1c and a solvent at a volumetric S/F of $3/5$.

Table 5a: Total initial and final amounts of salt-originating anions for extractions from solutions 1a ($HAc + KCl$, $pH_{initial} = 2.9$), 1b ($HAc + Na_2SO_4$, $pH_{initial} = 3.0$) and 1c ($HAc + Na_2HPO_4$, $pH_{initial} = 4.6$) at volumetric S/F of 3/5 and 20 ± 1 °C. The reported values for Ac^- , SO_4^{2-} and HPO_4^{2-} are the summation of all occurring forms.

Exp. No.	Initial mass in aqueous phase [g]				Final mass in aqueous phase [g]				Initial mass in solvent phase [g]				D _{HAc} [wt%/wt%]		
	Ac ⁻	Cl ⁻	SO ₄ ²⁻	HPO ₄ ²⁻	Br ⁻	Ac ⁻	Cl ⁻	SO ₄ ²⁻	HPO ₄ ²⁻	Br ⁻	Ac ⁻	Cl ⁻		SO ₄ ²⁻	HPO ₄ ²⁻
20 wt% TOA in <i>n</i> -octanol															
1	Solution 1	0.106				0.018					0.088				8.8
2	Solution 1a	0.099	0.018			0.034	0.002				0.065	0.016			3.5
3	Solution 1b	0.098		0.044		0.046		0.015			0.052		0.029		2.1
4	Solution 1c	0.106		0.095		0.062		0.088			0.044		0.006		1.3
[P _{663,14}][Cl]															
5	Solution 1	0.106				0.031	0.025			0.348	0.075	0.324			3.7
6	Solution 1a	0.099	0.017			0.03	0.042			0.351	0.069	0.326			3.5
7	Solution 1b	0.103	0.046			0.033	0.048	0.013		0.344	0.07	0.296	0.033		3.5
8	Solution 1c	0.108		0.096		0.035	0.041	0.088		0.344	0.073	0.303	0.009		3.4
[P _{663,14}][Br]															
9	Solution 1	0.108				0.049		0.029		0.724	0.059			0.696	2.2
10	Solution 1a	0.098	0.017			0.046	0.009	0.049		0.717	0.052	0.008		0.668	2
11	Solution 1b	0.102	0.046			0.048		0.039	0.063	0.723	0.054		0.007	0.66	2.1
12	Solution 1c	0.108		0.096		0.063		0.095	0.051	0.717	0.046		0.001	0.666	1.4
[P _{663,14}][Phos] ^a															
13	Solution 1	0.108				0.009					0.099				17
14	Solution 1a	0.1	0.018			0.032	0.001				0.068	0.017			3.3
15	Solution 1b	0.1	0.044			0.037		0.018			0.063		0.025		2.6
16	Solution 1c	0.107		0.095		0.061		0.086			0.046		0.009		1.2
[P _{663,14}][N(CN) ₂] ^b															
17	Solution 1	0.106				0.053					0.053				1.8
18	Solution 1a	0.099	0.018			0.049	0.014				0.05	0.004			1.7
19	Solution 1b	0.099	0.044			0.049		0.043			0.05		0.001		1.7
20	Solution 1c	0.107		0.095		0.078		0.094			0.03		0.001		0.7

^a $[P_{663,14}][Phos]$ has been reported to be very hydrophobic [28], and therefore, its leaching into aqueous phase is negligible. This was confirmed by analysis of the raffinates with HPLC.

^b Analysis of the raffinates with IC showed no measurable leaching of $[N(CN)_2]$.

Table 5b: Initial and final amounts of salt-originating cations and water for extractions from solutions 1a (HAc + KCl, $pH_{initial} = 2.8$), 1b (HAc + Na_2SO_4 , $pH_{initial} = 3.0$) and 1c (HAc + Na_2HPO_4 , $pH_{initial} = 4.8$) at volumetric S/F of 3/5 and 20 ± 1 °C.

Exp. No.		Initial mass in aqueous phase [g]			Final mass in aqueous phase [g]			Initial mass in solvent phase [g]			Final mass in solvent phase [g]		
		K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water	K ⁺	Na ⁺	Water
20 wt% TOA in <i>n</i> -octanol													
1	Solution 1			9.974			9.775						0.199
2	Solution 1a	0.019		9.993	0.019		9.797						0.196
3	Solution 1b		0.021	9.978		0.021	9.782						0.195
4	Solution 1c		0.045	9.929		0.047	9.733						0.196
[P _{666,14}][Cl]													
5	Solution 1			9.924			9.122						0.803
6	Solution 1a	0.019		9.934	0.019		9.125						0.809
7	Solution 1b		0.022	10.39		0.022	9.598						0.793
8	Solution 1c		0.046	10.08		0.047	9.282						0.793
[P _{666,14}][Br]													
9	Solution 1			10.13			9.771						0.361
10	Solution 1a	0.019		9.904	0.019		9.547						0.358
11	Solution 1b		0.022	10.36		0.022	10.002						0.36
12	Solution 1c		0.046	10.12		0.049	9.757						0.358
[P _{666,14}][Phos]													
13	Solution 1			10.12			9.289						0.834
14	Solution 1a	0.02		10.06	0.019		9.225						0.837
15	Solution 1b		0.021	9.987		0.022	9.153						0.834
16	Solution 1c		0.046	9.988		0.048	9.152						0.835
[P _{666,14}][N(CN) ₂]													
17	Solution 1			9.974			9.761						0.213
18	Solution 1a	0.019		9.954	0.019		9.725						0.228
19	Solution 1b		0.021	10.01		0.022	9.783						0.224
20	Solution 1c		0.045	9.948		0.047	9.745						0.204

As can be seen in the first section of Table 5a, for all of the extraction experiments with 20 wt% TOA in *n*-octanol where Cl⁻, SO₄²⁻ or HPO₄²⁻ was present, a reduced distribution of Ac⁻ was observed. Although the initial pH of solution 1a was almost the same as that of solution 1 (see Table 2), almost all the Cl⁻, initially present in solution 1a, was co-extracted along with Ac⁻. Since no cation was extracted by 20 wt% TOA in *n*-octanol (see Table 5b), Cl⁻ has to be extracted along with H⁺ to maintain the charge neutrality in the solvent phase. Based on the extraction mechanisms proposed for similar cases in the literature [27, 28], and the fact that Cl⁻ and H⁺ do not form molecular HCl in aqueous phase, TOA most likely forms complexes with H⁺ at the interface between the aqueous and organic phases which is then followed by extraction of Cl⁻ as the counter-ion forming [TOAH][Cl] in the solvent phase. This extraction mechanism is favored for extraction of strong acids (HCl here), whereas weak acids (HAc here) may distribute over the phases in their undissociated forms.[29] The same phenomenon was observed when 20 wt% TOA in *n*-octanol was used to extract HAc from solutions 1b and 1c. Here, the net extracted species were H₂SO₄ and H₃PO₄. In the case of solution 1c, the

higher pH caused by the presence of HPO_4^{2-} resulted in the lack of H^+ needed for extraction of HAc and H_3PO_4 .

Table 5a shows that, when $[\text{P}_{666,14}][\text{Cl}]$ was used as the solvent, next to extraction of Ac^- , some SO_4^{2-} and HPO_4^{2-} (to a lower extent) was also extracted. This in combination with the significant leaching of Cl^- from $[\text{P}_{666,14}][\text{Cl}]$ phase into aqueous phase (7–14 % of the initial Cl^- content in $[\text{P}_{666,14}][\text{Cl}]$, depending on the model solution used) suggests that ion exchange was one of the extraction mechanisms. Similar to Cl^- , Br^- also significantly leached from $[\text{P}_{666,14}][\text{Br}]$ phase into the aqueous phases resulting in a Br^- content loss of 4–9 % from the solvent phase, depending on the model solution used. The Cl^- and Br^- leaching from the $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$ phases indicates that one of the HAc extraction mechanisms used by these two ionic liquids is ion exchange through which Cl^- or Br^- are replaced with Ac^- . The ion exchange mechanism in these cases is an irreversible interaction, as without replacing leached Cl^- and Br^- , recovery of extracted Ac^- from $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$ phases is impossible. To further support the presence of ion exchange mechanism in the case of $[\text{P}_{666,14}][\text{Cl}]$ and $[\text{P}_{666,14}][\text{Br}]$, the pH of all the obtained raffinates was also measured. The measured values are presented in Table 6 and compared with the pH of their associated model solutions.

Table 6: Equilibrium pH of obtained raffinates after extraction compared with that of their associated model solutions.

Exp. No.		Initial pH of model solution	Equilibrium pH of raffinate
20 wt% TOA in <i>n</i> -octanol			
1	Solution 1	2.8	3.5
2	Solution 1a	2.9	5
3	Solution 1b	3	5.3
4	Solution 1c	4.6	5.7
$[\text{P}_{666,14}][\text{Cl}]$			
5	Solution 1	2.8	1.3
6	Solution 1a	2.9	1.3
7	Solution 1b	3	1.9
8	Solution 1c	4.6	4.4
$[\text{P}_{666,14}][\text{Br}]$			
9	Solution 1	2.8	1.6
10	Solution 1a	2.9	1.4
11	Solution 1b	3	2
12	Solution 1c	4.6	4.7
$[\text{P}_{666,14}][\text{Phos}]$			
13	Solution 1	2.8	4.5
14	Solution 1a	2.9	5.6
15	Solution 1b	3	5.6
16	Solution 1c	4.6	6.2
$[\text{P}_{666,14}][\text{N}(\text{CN})_2]$			
17	Solution 1	2.8	3.6
18	Solution 1a	2.9	3.9
19	Solution 1b	3	3.9
20	Solution 1c	4.6	5

As can be seen in Table 6, the pH of the raffinates obtained after extraction with $[P_{666,14}][Cl]$ or $[P_{666,14}][Br]$ is lower than that of their associated model solutions. This is due to the replacement of Ac^- with Cl^- or Br^- in the aqueous phases as a result of ion exchange mechanism. Since HCl and HBr completely dissociate in an aqueous phase contrary to the weak acid HAc , the removal of Ac^- has resulted in an increased H^+ concentration. Ion exchange was responsible for 55 % or 35 % of the removal of Ac^- from solution 1 using $[P_{666,14}][Cl]$ or $[P_{666,14}][Br]$ respectively. The rest was due to extraction of molecular HAc . Extraction of molecular HAc into these ionic liquids was promoted by hydrogen bonding between the proton of HAc and a hydrogen bond donating atom (Cl^- , Br^- and/or oxygen of exchanged Ac^-). The lower water uptake of $[P_{666,14}][Br]$ compared to that of $[P_{666,14}][Cl]$ shows its weaker tendency towards hydrogen bonding which may explain the slightly lower HAc extraction capacity of $[P_{666,14}][Br]$. The significant hydrophilicity of $[Cl]^-$ and $[Br]^-$ makes $[P_{666,14}][Cl]$ and $[P_{666,14}][Br]$ too instable, as was shown by their significant leaching. Therefore, these ionic liquids are not promising solvents for extraction of VFAs from aqueous solutions.

Table 5a shows that $[P_{666,14}][Phos]$ extracted significant amounts of Ac^- , Cl^- , SO_4^{2-} and HPO_4^{2-} . It was also observed that $[Phos]^-$ was highly stable in the $[P_{666,14}][Phos]$ phases. Furthermore, $[P_{666,14}][Phos]$ did not extract any Na^+ or K^+ (see Table 5b). These imply that, in terms of extraction mechanism, $[P_{666,14}][Phos]$ is similar to 20 wt% TOA in *n*-octanol, i.e. mineral acids are extracted via interfacial protonation of the extractant followed by extraction of their anions to maintain charge balance. In this case, the anion of $[P_{666,14}][Phos]$ is protonated, and due to the hydrophobic character of $[Phos]^-$, it remains in the ionic liquid phase in protonated form as well.

$[P_{666,14}][N(CN)_2]$ seems not to be affected by any of the salt-originating anions (see Table 5a), as it did not extract any considerable amount of any of them while keeping a constant extraction capacity for HAc when it was exposed to solutions 1, 1a and 1b. It did not extract any Na^+ or K^+ either (see Table 5b). The reduction in its HAc extraction capacity while being exposed to solution 1c was due to the higher pH of solution 1c which reduced the amount of molecular HAc (extracted species) in the aqueous phase. Based on this observation, it may be concluded that interfacial protonation of Ac^- did not take place, and extraction of HAc was mainly through hydrogen bonding of the molecular form of the acid.

Contrary to $[P_{666,14}][Cl]$ and $[P_{666,14}][Br]$, $[P_{666,14}][Phos]$ and $[P_{666,14}][N(CN)_2]$ were found to be highly stable, and no measurable leaching of $[Phos]^-$ or $[N(CN)_2]^-$ was detected in the aqueous phases.

From the results presented in Tables 5a and 5b, it can be concluded that multiple phenomena such as co-extraction of mineral acids, ion exchange, and extraction through intermolecular interactions (e.g. hydrogen bonding) affect HAc distribution. However, the role of pH in the observed changes in HAc distribution was not clear enough based on the experiments described in this section. pH is often a very important factor in liquid-liquid extraction and therefore, to clarify its effect on HAc extraction, additional experiments (next subsection) were carried out.

3.3. Effect of pH on extraction of HAc

The effect of pH was studied by adding strong acids to solution 2. The obtained solutions were named solutions 2a, 2b, 2c, 2d, 2e and 2f (see Table 2). Figure 2 shows the HAc distribution coefficients obtained after the extraction experiments performed with $[P_{666,14}][Phos]$ and $[P_{666,14}][N(CN)_2]$.

Figure 2: HAc distribution coefficient of $[P_{666,14}][Phos]$ and $[P_{666,14}][N(CN)_2]$ using solutions 2a, 2b, 2c, 2d, 2e and 2f (volumetric S/F = 3/5, $T = 20 \pm 1^\circ C$).

As can be seen in Figure 2, decreasing the pH of the aqueous solution has resulted in increase in the HAc distribution coefficient of both of the solvents. This confirms the nature of the extraction mechanism described in the previous section, proceeding through hydrogen bonding of molecular HAc and not ion exchange of acetate anion. By lowering pH, the dissociation equilibrium of HAc in the aqueous phase shifts to HAc being the predominant form present, and therefore, the ongoing equilibria series (dissociation, partitioning and organic phase complexation) shifts to a higher HAc distribution. This was previously observed when amines and fatty acids were used as solvents.[13, 30] Compared to the HAc distribution observed for $[P_{666,14}][Phos]$ using solution 1 (see Figure 1), the maximum HAc distribution obtained for $[P_{666,14}][Phos]$ in the presence of strong acids, as seen in Figure 2, is much lower. When a strong acid is present, $[P_{666,14}][Phos]$ co-extracts the anion of the strong acid (here Cl^- or NO_3^-) together with H^+ in significant amounts which results in a significantly reduced solvent capacity for HAc.

3.4. Liquid-liquid extraction – multi-stage

From the previous subsections, it was concluded that the salts present in fermented wastewater may significantly reduce the HAc distribution of the solvent. However, since all the results presented so far were obtained from single-stage extraction experiments, they do not elucidate any maximum solvent capacity obtained when the solvent is in equilibrium with fermented wastewater. In order to determine the maximum VFA loading of the solvents $[P_{666,14}][Phos]$ and 20 wt% TOA in *n*-octanol (benchmark solvent in many studies and second best in HAc extraction after $[P_{666,14}][Phos]$) when they are in equilibrium with the artificial fermented wastewater (solution 3), two series of cross-current extraction experiments were carried out according to the method described in section 2.4.2. Figures 3a and 3b show the gradual increase in the VFA content of the solvents with increasing the number of extraction stages. The points in the Figures 3a and 3b correspond to the VFA loadings determined by calculating the amount of VFA extracted based on the change in the aqueous phase concentration after every extraction stage, whereas the dashed lines correspond to the maximum VFA loadings determined by washing the solvent phases with KOH (1 M) which allowed a complete recovery of extracted VFAs from the solvents. As can be seen in Figures 3a and 3b, “KOH-wash” lines are in good agreement with the maximum loadings determined by analysis of raffinates presented by the points.

As can be seen in Figures 3a and 3b, both of the solvents show the same order in VFA extraction efficiency: $\text{HLa} < \text{HAc} < \text{HPr} < \text{HBu}$. This trend is logical, as with similar pK_a s and increasing the number of carbons, the growing hydrophobic domain in acid leads to a better extraction. HLa is a C_3 -acid, but due to its additional $-\text{OH}$ functionality and lower pK_a , it was the most challenging VFA to extract.

Figure 3a: Multiple extraction stages using solution 3 and $[P_{666,14}][\text{Phos}]$. Points correspond to VFA loadings determined by analysis of aqueous raffinates. Dashed lines correspond to maximum concentrations obtained from base wash of solvent phase at the end of cross current extraction series.

Figure 3b: Multiple extraction stages using solution 3 and 20 wt% TOA in *n*-octanol. Points correspond to VFA loadings determined by analysis of aqueous raffinates. Dashed lines correspond to maximum concentrations obtained from base wash of solvent phase at the end of cross current extraction series.

Table 7 shows the VFA loadings and water contents of the solvents in equilibrium with solution 3. The VFA loading values correspond to the KOH-wash lines presented in Figures 3a and 3b. Table 7 also shows the VFA and water content of the recovered VFA–water streams from the solvents assuming a complete recovery of VFAs from the solvents is possible with no addition of any extra water or chemical. This assumption is not so unrealistic, as in the literature, it has been reported that under deep vacuum and high temperatures, extracted organic acids can be recovered from extracting solvents.[31] Such a method for recovery of extracted VFAs is advantageous over any form of back-extraction, as the resulting VFA concentrations will be much higher in the obtained stream, as compared to those achieved by back-extraction. Furthermore, the VFAs will not be contaminated by salts, as would be the case in a back-extraction using an alkaline solution.

Table 7: Maximum VFA loadings in solvents in equilibrium with solution 3 ($C_{HLA} = C_{HAc} = C_{HPr} = C_{HBu} = 0.25$ wt%, $pH = 5.0$).

	[P _{666,14}][Phos]		20 wt% TOA in <i>n</i> -octanol	
	Loading in solvent phase [wt%]	Concentration in recovered stream [wt%]	Loading in solvent phase [wt%]	Concentration in recovered stream [wt%]
HLA	0.25	1.6	0.17	2.2
HAc	0.6	3.7	0.26	3.3
HPr	2.49	15.4	0.89	11.2
HBu	6.82	42.2	2.65	33.5
Water	5.99	37.1	3.95	50

As can be seen in Table 7, the water content of [P_{666,14}][Phos] has decreased with increasing its VFA loading. This phenomenon has been previously observed and reported by Schlosser et al..[20, 32] Table 7 shows that if the assumption made above holds, starting with a combined VFA concentration of 1 wt% in solution 3, a final combined VFA concentration of up to ~65 wt% can be obtained. It must be noted that since [P_{666,14}][Phos] has higher VFA loadings than 20 wt% TOA in *n*-octanol does, it will deliver the recovered stream at a lower S/F.

4. Conclusions

In fermented wastewater, significant amounts of dissolved salts accompany VFAs. This makes fermented wastewater a complex aqueous solution containing many ions. In this study, the effects of these ions on extraction of VFAs from fermented wastewater was studied using several simpler aqueous model solutions each containing HAc and a single salt. It was observed that the cations originating from these salts (Na^+ and K^+) are not extracted at all. On the other hand, the anions were co-extracted which resulted in significant reduction in the VFA extraction capacity of the solvents. Also, some salts increased the pH of the aqueous solutions, thereby reducing VFA distribution. $[\text{P}_{666,14}][\text{Phos}]$ was found to be the solvent with the highest extraction capacity for VFAs. Through multi-stage cross-current extraction, $[\text{P}_{666,14}][\text{Phos}]$ achieved a maximum combined VFA loading of up to 10 wt% in equilibrium with solution 3, the solution resembling an actual fermented wastewater (containing 0.25 wt% of each VFA).

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CO₂-enhanced
extraction of
acetic acid
from fermented
wastewater

CHAPTER

4

Abstract

The industrial process of recovering fermentation-based volatile fatty acids (VFAs) utilizes H_2SO_4 to acidify the fermentation broth containing VFA-salts {e.g. $\text{Ca}(\text{CH}_3\text{COO})_2$ } to enable formation of molecular VFAs. Molecular VFAs are then recovered by liquid-liquid extraction. However, acidification with H_2SO_4 results in production of large quantities of salts (e.g. CaSO_4). Using CO_2 rather than mineral acids for acidification of fermentation broth is an environmentally benign alternative which eliminates salt formation. In this study, CO_2 was applied in pressures up to 40 bar to enhance the efficiency of extraction of acetic acid (HAc) from fermented wastewater. HAc extraction at atmospheric conditions was also investigated to obtain benchmarks. The ionic liquid $[\text{P}_{666,14}][\text{Phos}]$ and trioctylamine (TOA) dissolved in *n*-octanol were applied as solvents to extract HAc from fermented wastewater model solutions containing HAc (1 wt%) and various salts resulting in pH ranging from 2.8 to 6. A more pronounced increase in extractability of HAc, expressed as HAc distribution ($D = [\text{HAc}]_{\text{solvent}}/[\text{HAc}]_{\text{aqueous}}$), was observed for $[\text{P}_{666,14}][\text{Phos}]$ with increasing CO_2 pressure. A mathematical model taking into account carbonic acid equilibria and dissociation of HAc and salts showed that the measured influence of CO_2 cannot be explained by the effect of CO_2 on aqueous phase pH. Thus, it may be concluded that the pressurized CO_2 has altered the fluid properties of the solvents and made them more accessible for HAc. This suggests that applying pressurized CO_2 may enhance extraction efficiency of processes other than those involving extraction of volatile fatty acids.

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Nomenclature

MCFAs: Medium chain fatty acids

VFAs: Volatile fatty acids

HAc: Acetic acid

TOA: Trioctylamine

[P_{66,14}][Phos]: Trihexyl(tetradecyl)phosphonium bis-2,4,4 (trimethylpentyl) phosphinate

1. Introduction

Rising concerns on depletion of easily recoverable petroleum resources over the next decades together with rising awareness of the need for more sustainable processes in industry has resulted in significant attention for production of bio-based chemicals in both academia and industry. Several strategies to obtain bio-based chemicals have been proposed including thermochemical routes such as pyrolysis[1-3] and gasification followed by gas-to-liquid techniques [4-6], and fermentative routes.[7]

Various approaches for fermentative routes have been examined in the literature. Steinbusch et al. developed a method to produce medium chain fatty acids (MCFAs) from residual biomass streams via fermentation.[8] Fermentative production of MCFAs from municipal solid waste has also been reported.[9] Another fermentative route is production of volatile fatty acids (VFAs) from waste streams.[10, 11] Bio-based VFAs have been used as platform chemicals to produce plastics.[12] They are also utilized in bio-energy.[13] The advantage of VFA platform is its versatility in downstream conversions.[7] However, producing chemicals from waste through VFAs in an economically viable operation is not straightforward. An important limitation for commercializing VFA production from wastewater is the low VFA concentration in fermented wastewater (see Table 1 for typical composition of fermented wastewater), which is mainly due to the limited carbon content of wastewater before undergoing fermentation. Therefore, effective separation methods must be developed to recover VFAs from dilute fermented wastewater.

Table 1: Typical composition of fermented wastewater

Component	Chemical formula	Concentration [g/L]	pK _a
Acetate	CH ₃ COOH	2.5–10	4.76
Propionate	CH ₃ CH ₂ COOH	2.5–10	4.88
Butyrate	CH ₃ (CH ₂) ₂ COOH	2.5–10	4.82
Lactate	CH ₃ CH(OH)COOH	2.5–10	3.86
Sodium	Na ⁺	1–5	
Potassium	K ⁺	1–5	
Chloride	Cl ⁻	1–10	
Phosphate	H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	1–10	
Sulphate	SO ₄ ²⁻	1–10	
Sulphide	S ²⁻	0.3	
Magnesium	Mg ²⁺	0.3	
Calcium	Ca ²⁺	0.3	
Ammonium	NH ₄ ⁺	0.1	
Trace elements (cations)	Co, Fe, Ni	10 ⁻⁴	
Inert COD		1	
Microbes			

Separation of VFAs from aqueous solutions can be performed using various methods. Most commercialized processes use distillation.[14] However, due to the low concentration of VFAs in fermented wastewater, the amount of water to evaporate is extremely large and therefore, distillation is not economical. Other separation methods reported for VFA recovery include azeotropic or extractive distillation[15] membrane filtration[16, 17] and crystallization[18, 19]. Affinity separation techniques make use of physical and/or chemical interactions to form intermolecular complexes with VFA molecules. Adsorption and liquid-liquid extraction are the most common affinity separation techniques. They are considered as suitable techniques to separate VFAs from dilute solutions in an energy efficient manner.[20]

Through liquid-liquid extraction, VFA molecules are transferred into an extracting solvent due to the affinity between them and the solvent. With increasing affinity strength, the distribution of VFAs (defined as the ratio of VFAs concentration in the extract phase to that in the raffinate phase) increases. Since a further recovery step is needed to retrieve extracted VFAs from the solvent and regenerate the solvent, extremely high affinities must be avoided to make solvent regeneration feasible. Next to affinity for VFAs, affinity for water and other accompanying compounds is also an important factor, and preferentially, the solvent must have a high affinity for VFAs, but a limited affinity for water and other species accompanying VFAs. Very hydrophobic solvents limit water co-extraction, but on the other hand, they often show limited VFA distribution. In the literature, many different solvents are proposed to extract VFAs from aqueous solutions including alcohols, ketones, ethers, aliphatic hydrocarbons, organophosphates, and aliphatic amines.[14, 21-24] Furthermore, in recent years, ionic liquids have gained interest for extraction of carboxylic acids, as they are considered as “green” solvents.[25-29] Contrary to non-ionic solvents, for some ionic liquids, VFA distribution is reported to continuously increase with decreasing VFA concentration in raffinate.[27, 28] This behaviour is particularly interesting for this study, as the VFA concentration in fermented wastewater is low due to the limited carbon content of the feedstock.

Another challenge for extraction of VFAs from fermented wastewater streams is the presence of salts (see Table 1) which results in a pH of 4.5–6. Due to the low concentration of VFAs and relatively high pH, VFAs are present predominantly in their dissociated form. Since the reported solvents (e.g. tertiary amines) extract carboxylic acids in their molecular form [23, 30], extraction of VFAs from fermented wastewater is challenging.

Production of large quantities of salts through the industrial process of recovering volatile fatty acids from fermentation broth poses environmental problems. [31, 32] The alternative technique reported in the literature to avoid salt production utilizes CO_2 rather than H_2SO_4 to reversibly acidify fermentation broth. [33–36] Urbas demonstrated that the concentration of molecular HAc in an aqueous solution can be increased by applying high pressure or atmospheric CO_2 which results in enhanced extraction of HAc.[33] This technique was later improved by Eggeman and Verser.[34] Reversible acidification with CO_2 was also used to facilitate recovery of lactic acid by Baniel et al..[35] Recently, Peterson and Daugulis showed that sparging CO_2 through a butyric acid containing fermentation broth increases the amount of recovered butyric acid.[36]

In this study, reversible acidification with pressurized CO_2 was combined with the use of an ionic liquid ($[\text{P}_{666,14}][\text{Phos}]$) as solvent to enhance extraction of VFAs from fermented wastewater in which VFA concentration is much lower than that in a typical VFA-containing fermentation broth. In order to compare the performance of $[\text{P}_{666,14}][\text{Phos}]$ with that of conventional molecular solvents, 20 wt% TOA in *n*-octanol solution was also applied for extraction of HAc from fermented wastewater model solutions. These systems were chosen based on the literature. 20 wt% TOA in *n*-octanol has been the best traditional solvent for extraction of carboxylic acids [23, 30], and recently the use of $[\text{P}_{666,14}][\text{Phos}]$ has been shown to be very promising due to high distributions obtained at very low carboxylic acid concentrations in raffinate.[27] The applied CO_2 pressure was up to 40 bar. Since the fermented wastewater model solutions prepared for this study are not previously examined in the literature, HAc extraction at atmospheric conditions was also studied.

2. Experimental and analysis

2.1. Chemicals

Acetic acid (HAc, >99.7%), *n*-octanol (>99%), trioctylamine (TOA, 98%), potassium chloride (>99%), anhydrous sodium phosphate dibasic (>99%), and anhydrous sodium sulphate (>99%) were purchased from Sigma-Aldrich. Potassium hydroxide (1 M) was supplied by Merck, and [P_{666,14}][Phos] (Cyphos® IL104, >95%) was purchased from io-li-tec. Fermented wastewater model solutions were prepared by adding the desired amounts of HAc and salts to demi water (see Table 2).

2.2. Experimental equipment

The setup used to perform liquid-liquid extraction under high CO₂ pressures consisted of an autoclave (Büchi, V = 1 L, P_{max} = 60 bar) coupled to a CO₂ supply vessel (Swagelok, V = 1 L, P_{max} = 120 bar). The CO₂ supply vessel was connected to a CO₂ cylinder (via Valve 1 in Figure 1) to allow refilling the vessel. Figure 1 shows a schematic view of the setup. The autoclave was kept at the operating temperature (20±0.1 °C) using a heating/cooling jacket.

2.3. Single stage liquid-liquid extraction at atmospheric pressure

Atmospheric pressure liquid-liquid extraction experiments were performed using 5 mL of a fermented wastewater model solution (see Table 2) and 3 mL of a solvent. The volumetric solvent to feed ratio (S/F) of 3:5 was chosen to keep the obtained results comparable with those obtained from high pressure experiments, as the location of the autoclave sampling ports were adjusted to the liquid heights associated with 500 mL of a feed and 300 mL of a solvent. The liquid mixtures were magnetically stirred at 500 rpm or more at room temperature (20±1 °C) for 1 h, as it was experimentally verified that the time needed to reach equilibrium is less than 1 h for every pair of feed and solvent.

After 1 h of stirring, the mixtures were centrifuged at 8000 rpm for 5 minutes. After centrifugation, samples were taken from both of the phases for analysis.

Table 2: Composition of fermented wastewater model solutions

Model solution	Concentration [mol/L]				pK _a
	HAc	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	
pH 2.8 solution	0.17 (1 wt%)				2.8
pH 4.8 solution	0.17 (1 wt%)	0.05	0.05	0.1	4.8
pH 6.0 solution	0.17 (1 wt%)			0.2	6.0

Figure 1: High pressure liquid-liquid extraction setup

2.4. Multistage cross-current liquid-liquid extraction at atmospheric pressure

Atmospheric multistage cross-current liquid-liquid extraction experiments were carried out to monitor the accumulation of HAc in $[P_{666,14}][Phos]$ and in 20 wt% TOA in *n*-octanol with increasing the number of extraction stages. The volumetric solvent to feed (pH 4.8 solution) ratio was 3:5. After every extraction stage (following the same procedure described in the previous section), the solvent phase was separated from the raffinate phase, and without further treatment, it was exposed to fresh feed in another extraction stage. After every extraction stage, the HAc content of the obtained raffinate phase was measured. Additional extraction stages were performed until the HAc concentration in the raffinate phase did not change anymore. The final concentration of HAc in the solvent phase was measured via washing the solvent phase with KOH (1 M) followed by analysis of the alkaline phase with HPLC.

2.5. Single-stage liquid-liquid extraction at high pressure

In each high pressure liquid-liquid extraction experiment, 500 mL of a fermented wastewater model solution and 300 mL of a solvent was loaded into the autoclave. The autoclave was then sealed and any residual air was removed from inside the autoclave using a vacuum pump. A leak test was performed with CO₂ at the intended pressure of experiment (up to 40 bar) for 5 min. If no leak was detected, stirring started while the autoclave was already at the intended pressure and 20±0.1 °C. The stirring speed for every experiment was 620 rpm, and during the experiments, CO₂ pressure was controlled and kept constant by continuously supplying CO₂ from the vessel. After 1 h, (enough for reaching equilibrium, validated experimentally), stirring was stopped to let the liquid phases settle for 30 minutes. To avoid disturbing equilibrium, the autoclave was kept pressurized while taking samples from both phases.

2.6. Analysis

The concentrations of HAc, HPO₄²⁻ in aqueous phases were measured with HPLC [Agilent 1200 series HPLC system equipped with Agilent Hi-plex H column (300×7.7 mm) and Agilent 1200 series refractive index detector]. Cl⁻ and SO₄²⁻ concentrations were quantified with IC (Metrosep A Supp 4 - 250/4.0 column and Metrohm 732 IC detector coupled to Metrohm 733 IC Separation Center). The water contents of solvent phases were measured with Karl-Fischer titration (Metrohm 787 KF Titrano). Na⁺ and K⁺ concentrations were measured with a flame photometer (BWB Flame Photometer XP).

3. Results and discussion

3.1. Liquid-liquid extraction at atmospheric pressure

HAc extraction at atmospheric pressure was studied (see Table 3) and used as benchmark for HAc extraction under high CO₂ pressure. Because in many previous studies ideal model solutions containing only a VFA and water were used, a model solution containing only HAc (1 wt%) and water (pH = 2.8) was also examined in this study for comparison.

As can be seen in Table 3, all the HAc distribution coefficients significantly decreased when the pH of fermented wastewater model solution increased from 2.8 to 4.8 or 6.0. For 20 wt% TOA in *n*-octanol, this trend matches the previously suggested extraction mechanism by which carboxylic acids are extracted only in their molecular form.[23, 30] Due to the increase in pH, less HAc was available in molecular form, and as a result, HAc distribution dropped significantly for pH 4.8 and 6.0 solutions compared to pH 2.8 solution. The decrease in the HAc distribution coefficient of [P_{666,14}][Phos] suggests that it also extracts HAc in its molecular form. In a set of additional experiments, presented in the *Supporting information*, measuring the concentrations of both the cations Na⁺ and K⁺ and the anions present in the aqueous solutions before and after extraction revealed that the cations are not extracted by [P_{666,14}][Phos] which confirms that [P_{666,14}][Phos] indeed extracts HAc in its molecular form.

Comparing the HAc distribution coefficients obtained for [P_{666,14}][Phos] with those obtained for 20 wt% TOA in *n*-octanol, it can be seen that although the HAc distribution coefficient of [P_{666,14}][Phos] was twice that of 20 wt% TOA in *n*-octanol for pH 2.8 solution, it significantly decreased for pH 4.8 and pH 6.0 solutions resulting in values similar to those of 20 wt% TOA in *n*-octanol.

In order to identify the major phenomenon responsible for this significant decrease, the experiments in the *Supporting information* were executed and the concentrations of the anions present in the extraction systems (Cl⁻, SO₄²⁻ and HPO₄²⁻) were also measured using HPLC and IC. It was observed that Cl⁻, SO₄²⁻ and HPO₄²⁻ were extracted by both of the solvents, but not their counter ions Na⁺ and K⁺. Thus, HCl, H₂SO₄ and H₃PO₄ were the extracted species with distributions in the order HCl > H₂SO₄ > H₃PO₄.

Table 3: *HAc distribution coefficients and water co-extraction. Volumetric $S/F = 3/5$, $T = 20 \pm 1$ °C.*

Solvent	pH 2.8 solution			pH 4.8 solution			pH 6.0 solution		
	[HAc] _{raff} [wt%]	D _{HAc} [wt%/wt%]	Water co-extraction [wt%]	[HAc] _{raff} [wt%]	D _{HAc} [wt%/wt%]	Water co-extraction [wt%]	[HAc] _{raff} [wt%]	D _{HAc} [wt%/wt%]	Water co-extraction [wt%]
20 wt% TOA in <i>n</i> -octanol [P _{666,14}][Phos]	0.18	8.9	3.7	0.73	0.8	3.7	0.84	0.3	3.3
	0.09	17.5	14.1	0.81	0.6	14.9	0.80	0.5	15.7

As a result, the pH of the aqueous phase increased significantly resulting in much lower HAc distributions. Co-extraction of HCl, H₂SO₄ and H₃PO₄ was much more remarkable for [P_{666,14}][Phos] than 20 wt% TOA in *n*-octanol which led to a stronger decrease in HAc distribution for pH 4.8 and pH 6.0 solutions.

Both [P_{666,14}][Phos] and 20 wt% TOA in *n*-octanol have been previously studied for extraction of carboxylic acids from aqueous solutions similar to pH 2.8 solution. Extraction of lactic acid by [P_{666,14}][Phos] resulted in distribution coefficients up to 40.[27, 37] Using 20 wt% TOA in *n*-octanol, lactic acid distribution coefficients up to 30 were obtained.[24] Therefore, although HAc distribution is in the same order of magnitude, its value is lower which may be due to the higher pK_a of HAc (4.76 vs 3.86 for lactic acid).

The final VFA loading of a solvent after a single extraction stage is always lower than that when the loaded solvent leaves a counter-current extraction process, and to study the highest HAc loading achievable with the pH 4.8 model solution, cross-current extraction was continued until no more HAc extraction was observed. At this point, the solvents were in equilibrium with the fresh pH 4.8 model solution. Figure 2 shows the gradual increase in the HAc content of the solvents with increasing the number of extraction stages. The HAc loading of every extraction stage is the summation of extra loading achieved after the current stage and the loading existed in the solvent from previous extraction stages. The total HAc loadings of the solvents after they reached equilibrium with fresh pH 4.8 solution were experimentally determined by washing the solvent phases with KOH (1 M) and analysis of the alkali phases. The obtained values are presented with “KOH-wash loading” lines in Figure 2. They are well in agreement with the final accumulative loadings obtained by analysis of the raffinate phases after extraction.

As can be seen in Figure 2, HAc loadings as high as 4.5 wt% in [P_{666,14}][Phos] can be achieved in cross-current extraction with the pH 4.8 solution, while the maximum loading achieved in 20 wt% TOA in *n*-octanol was only 1.7 wt%. Based on the maximum loading of the solvents, a mass-balance for a counter-current extraction column was performed at minimum S/F. At these conditions, the pH 4.8 solution is in equilibrium with the loaded solvents. The calculated composition of the streams leaving the columns is depicted in Figure 3.

The water content of each HAc-saturated solvent was also measured, and the values in equilibrium with the feed are also included in Figure 3. The water content of [P_{666,14}][Phos] decreases as its HAc content increases, which was previously observed by Schlosser et al.[27, 38] This suggests that (a part of) the co-extracted water by is interacting with [P_{666,14}][Phos] in a competitive way with HAc. The

Figure 2: HAc loading in solvent phase during cross current extraction using pH 4.8 solution. Volumetric $S/F = 3/5$, $T = 20 \pm 1$ °C, $[P_{666,14}][Phos]$ (top), 20 wt% TOA in n-octanol.

calculation of the $(S/F)_{\min}$ is based on mass balance and assuming 90 wt% removal of the initial HAc content of pH 4.8 solution through the columns. Since the $(S/F)_{\min}$ needed to use $[P_{666,14}][Phos]$ in the counter-current column described above is rather low, it may be practical to impregnate $[P_{666,14}][Phos]$ in solid particles. [39] Considering the ratio of the extracted HAc to the co-extracted water in the solvents, as shown in Figure 3, it can be concluded that $[P_{666,14}][Phos]$ is superior to 20 wt% TOA in n-octanol in terms of extraction capacity and selectivity. Starting with a solution containing 1 wt% HAc and obtaining a ratio of 4.4 wt% HAc to 8.4 wt% water (34 % HAc) in the solvent implies that when both water and HAc are fully recovered from the ionic liquid, a 34 times more concentrated solution can be obtained. Although 34 times more concentrated, there is still a large amount of water and the HAc concentration in the solvent is not very high. A method that may improve this is to use pressurized CO_2 .

Figure 3: Counter-current extraction columns at minimum S/F for the pH 4.8 solution: 20 wt% in n-octanol (a), $[P_{66,14}][Phos]$ (b)

3.2. Liquid-liquid extraction at high pressure

The high pressure extraction experiments were performed using the apparatus depicted in Figure 1 at 10, 20, 30 and 40 bar of CO₂ pressure. The obtained HAc distribution coefficients are presented in Figure 4. The data points at 0 bar of CO₂ pressure represent the distribution coefficients obtained at atmospheric conditions (see Table 3).

Figure 4 shows that the HAc distribution of both solvents significantly increases with increasing CO₂ pressure, which was expected as result of acidification with pressurized CO₂ on extractability of VFAs. The expected increase as result of shifting the dissociation equilibrium of HAc with decreasing pH due to increasing CO₂ pressure was calculated. Since considerable amounts of ions are present in both of the solutions, the calculations were performed including a Debye-Hückel approximation for ion activity coefficients in electrolytes.[20, 40] Since it was shown that only molecular HAc is extracted by the solvents, the effect of acidification with pressurized CO₂ on HAc distribution can be expressed using equation 1:

$$D_{\text{calculated}} = D_0 \frac{\left(\frac{[\text{HAc}]}{[\text{HAc}] + [\text{Ac}^-]} \right)_P}{\left(\frac{[\text{HAc}]}{[\text{HAc}] + [\text{Ac}^-]} \right)_{P_0}} \quad (1)$$

D₀ is the distribution coefficient experimentally obtained at atmospheric conditions (see Table 3), and [HAc] and [Ac⁻] are the calculated concentrations of molecular HAc and acetate anion respectively.

As can be seen in Figure 4, independent of the initial pH of the aqueous solution, the HAc distribution of [P_{666,14}][Phos] and 20 wt% TOA in *n*-octanol increased from ~0.5 to ~4 and ~1.5 respectively. The increase in HAc distribution was more substantial for [P_{666,14}][Phos]. Due to the higher [Ac⁻]/[HAc] in the pH 6.0 solution than in the pH 4.8 solution, a more pronounced increase in HAc distribution due to acidification of aqueous phase was expected for the pH 6.0 solution. The expected increase is shown by the model lines, and by comparing the calculated distributions with the experimental values, it can be concluded that the influence of CO₂ on the equilibria in the aqueous phases is not the major phenomenon governing HAc distribution under high CO₂ pressure. Pressurized CO₂ has likely altered the fluid properties of the solvents and made them more accessible for HAc fragments, and this effect is more pronounced for the ionic liquid than the molecular solvent. Supporting this statement, in the literature, CO₂ solubility in [P_{666,14}][Phos] is reported to be significant, mole fraction of 0.587 at 40 bar and 60 °C [41], and it is expected to be even higher at 25 °C. This will

Figure 4: HAc distribution coefficient as a function of CO_2 pressure. pH 4.8 solution (a), pH 6.0 solution (b), volumetric $S/F = 3/5$, $T = 20 \pm 0.1$ °C.

significantly affect physical properties of $[P_{666,14}][Phos]$. To confirm that the effect is of physical nature, and the ionic liquid has not changed chemically, a ^{31}P -NMR study was performed. The full results of this study are presented in the *Supporting information* from which it can be concluded that sparging CO_2 through $[P_{666,14}][Phos]$ does not chemically change the ionic liquid. Adding water to $[P_{666,14}][Phos]$ changes the chemical shift of the anion which is attributed to aggregates of water. [42] However, both in the samples without water and in those with water, sparging CO_2 does not affect the chemical shift of $[P_{666,14}][Phos]$ significantly. This finding suggests that using pressurized CO_2 may also be beneficial for other extraction systems in which acidification of an aqueous phase is not intended.

Since it is known that amines can react with CO_2 [43], and the ammonium carbonate might leach to the aqueous phase more easy than the neutral tertiary amine, the aqueous phase was analysed after sparging biphasic samples of water and 20 wt% TOA in *n*-octanol. Although the conductivity with 0.122 mS/cm was about five times higher than sparged water (0.0235 mS/cm), it is still orders of magnitude lower than regular electrolyte solutions, and in the ion chromatograph, no peak was observed, indicating a maximum concentration in the order of ppm's of any leachate.

The solvent loadings obtained after single extraction stages under high CO_2 pressure are comparable to those obtained at atmospheric conditions after multiple extraction stages. This implies that applying pressurized CO_2 to the counter-current extraction columns depicted in Figure 3 can significantly improve the efficiency of HAc removal from fermented wastewater.

4. Conclusions

In this study, high pressure CO_2 was utilized to enhance extraction of HAc from fermented wastewater model solutions with pH ranging from 2.8 to 6. $[\text{P}_{666,14}][\text{Phos}]$ and 20 wt% TOA in *n*-octanol were used as solvents. The obtained results showed that with increasing CO_2 pressure the HAc distribution of the solvents increases significantly, and the increase in HAc distribution was more substantial for $[\text{P}_{666,14}][\text{Phos}]$ than for 20 wt% TOA in *n*-octanol. The difference between the experimentally obtained HAc distribution coefficients and those obtained by simulating the aqueous phases under CO_2 pressure implies that acidification of aqueous phase is not likely the only consequence of pressurizing the extraction system with CO_2 . The change in the physical properties of the solvents caused by pressurized CO_2 has likely made them more accessible for HAc molecules. This suggests that applying pressurized CO_2 to other extraction systems in which acidification of aqueous phase is not intended may also be beneficial.

5. References

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Appendix | Supporting information

1. Atmospheric extraction data

The data reported in the Table S2 is obtained from a single-stage extraction system consisting of approximately 10 g of an aqueous solution and approximately 5 g of a solvent to achieve a volumetric S/F of 3/5 which is used for all the experiments reported in this article. The aqueous phases were prepared based on the most simple fermented wastewater model solution used in this article, pH 2.8 solution, to better understand the ongoing phenomenon associated with every single dissolved salt present in an actual fermented wastewater. The initial composition of the aqueous solutions is brought in the following Table S1:

Table S1: Initial composition of aqueous solutions prepared to study effects of salt-originated ions and pH on extraction of acetic acid

Solution	Concentration [mol/L]				pH
	HAc	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	
1	0.17 (1 wt%)				2.8
1a	0.17	0.05			2.8
1b	0.17		0.05		3.0
1c	0.17			0.1	4.8

Table S3 compares the water uptake of the solvents after a single-stage extraction with pH 4.8 solution with the water uptakes of the acetic acid-water-saturated solvents after multi-stage cross-current extraction with pH 4.8 solution.

Table S3: Water uptake of solvents

Solvent	wt% water after single	wt% water after cross-current
	extraction	extraction
[P _{666,14}][Phos]	15.7	8.4
20 wt% TOA in <i>n</i> -octanol	3.7	3.7

Table S2: Initial and final distribution of salt-originated ions and water in aqueous and solvent phases using aqueous solutions presented in Table S1

	M _{aq,i} ^a [g]					M _{org,i} ^b [g]					M _{org,f} ^c [g]				
	Ac ⁻	Cl ⁻	SO ₄ ²⁻	HPO ₄ ²⁻	Na ⁺	K ⁺	Water	Ac ⁻	Cl ⁻	SO ₄ ²⁻	HPO ₄ ²⁻	Na ⁺	K ⁺	Water	
20 wt% TOA in <i>n</i> -octanol															
Solution 1	0.106						9.974	0.018						9.775	0.199
Solution 1a	0.099	0.018				0.019	9.993	0.034	0.002				0.019	9.797	0.196
Solution 1b	0.098		0.044		0.021		9.978	0.046		0.015		0.021		9.782	0.195
Solution 1c	0.106			0.095	0.045		9.929	0.062			0.088	0.047		9.733	0.196
[P _{661d}][Phos]															
Solution 1	0.108						10.122	0.009						9.289	0.834
Solution 1a	0.1	0.018				0.02	10.062	0.032	0.001				0.019	9.225	0.837
Solution 1b	0.1		0.044		0.021		9.987	0.037		0.018		0.022		9.153	0.834
Solution 1c	0.107			0.095	0.046		9.988	0.061			0.086	0.048		9.152	0.835

^a. Initial mass in aqueous phase

^b. Final mass in aqueous phase

^c. Final mass in solvent phase

2. Extraction under CO₂ pressure

To get more insights in the interaction between [P_{666,14}][Phos] and CO₂, the ionic liquid was studied by ³¹P-NMR.

Figure S1: ³¹P-NMR spectra of [P_{666,14}][Phos] (IL104) under various conditions, and of Cyanex 272 which is the commercially available molecular form of the anion [Phos]⁻, thus H[Phos].

The bottom spectrum of dry IL104 in the absence of CO₂ shows two main peaks: the phosphorus in the anion at 25.6 ppm and the phosphorus in the cation at 33.0. The smaller signals belong to some impurities, as IL104 is sold as 95% pure. Going upwards through the spectra, the second spectrum is obtained for an IL104 sample that was sparged with CO₂. The spectrum shows a slightly broadened anion spectrum, but no significant change. The third spectrum belongs to wet IL104, but without CO₂. The spectrum shows a significant change as compared with those of dry IL104 and CO₂-sparged dry IL104. The anion peak is now at 37.4 ppm. Sparging wet IL104 with CO₂ does not significantly change its spectrum, although there is a very small change in the chemical shift to 37.7 ppm. The significant change in the chemical shift of the anion is due to the changed environment, as it is known from the work by Blahusiak and Schlosser that aggregates of water are formed in IL104. To confirm that it is not the molecular form of the anion, diisooctyl phosphinic acid (Cyanex 272 in the figure, the commercial name) that is causing this signal, this species was also analyzed by ³¹P-NMR and presented as the top spectrum, showing a peak at 51.7 ppm.

Carboxylic acid
recovery from
phosphonium
phosphinate ionic
liquid

CHAPTER

5

Abstract

Production of volatile fatty acids (VFAs) by fermentation is a potential sustainable alternative for conventional petrochemical routes to VFAs. Due to the limited VFA content of fermentation broths, a robust and economical VFA-separating technology has to be devised. Liquid-liquid extraction of VFAs with the ionic liquid (IL) $[P_{666,14}][Phos]$ enables a good VFA extractability. For an extraction process to be practical, it is essential to regenerate the solvent and recover the extracted compound. In this study, the chemistry of acetic acid (HAc) solutions with $[P_{666,14}][Phos]$ was studied with 1H -NMR, ^{31}P -NMR, FT-IR and isothermal titration calorimetry (ITC) to gain insight into their intermolecular interactions and support our studies on the use of several procedures to recover HAc, selected as model VFA, from the IL. Evaporation at an elevated temperature under vacuum, possibly assisted by nitrogen stripping, in situ esterification and back-extraction with volatile bases were investigated for recovery of HAc from the IL. Evaporative regeneration of the IL, assisted with nitrogen as the stripping gas, could remove HAc from the IL down to a HAc/IL molar ratio of approximately 1. The remaining molar equivalent of HAc interacts tightly with the phosphinate anion of the IL through partial proton transfer and strong hydrogen bonding. Back-extraction of HAc from the IL with an aqueous solution of trimethylamine (TMA) and subsequent thermal decomposition of HAc-TMA complexes could successfully regenerate the IL. Provided that thermal decomposition of HAc-TMA complexes is performed in the presence of an entrainer to capture the liberated HAc, this regeneration procedure is capable of producing high purity VFAs without generating large streams of byproducts.[1, 2]

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Nomenclature

VFAs:	Volatile fatty acids
HAc:	Acetic acid
IL:	Ionic liquid
TOA:	Trioctylamine
TMA:	Trimethylamine
[P _{66,14}][Phos]:	Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate
HexD:	Hexadecane
DoD:	Dodecane

1. Introduction

Volatile fatty acids (VFAs) are important chemicals for daily life with applications ranging from precursors for polymers to food and feed preservers.[3-5] Currently, they are mainly produced through petrochemical routes with a total volume of about 10^7 ton/a.[5] Fermentation is a well-known approach to produce VFAs from renewable resources.[5, 6] Next to glucose, anaerobic fermentation can run on wastewater and transform its carbon content into value-added VFAs, a true circular economy example.[7, 8] However, the limited carbon content of wastewater results in low VFA concentrations in the fermentation broth and eventually causes serious separation challenges. Since VFAs exhibit higher boiling points than that of water, it is not economically feasible to obtain them in high purities by distillation techniques starting with such low VFA concentrations. Therefore, economically more appealing separation techniques have to be considered. Affinity separation techniques such as liquid-liquid extraction (LLX) can selectively recover VFAs from their dilute aqueous solutions.[9, 10] A solvent for such a LLX process must be selective for VFAs to minimize the energy demand of further purification. Furthermore, it is essential that the solvent is regenerated after extraction to release the extracted VFAs and be reused.

Conventional solvents for carboxylic acid extraction include alcohols, ethers, ketones, esters and composite solvents thereof, often containing organophosphates and aliphatic amines to improve their extraction performance.[9, 11-15] When used for extraction of carboxylic acids from aqueous streams as dilute as fermented wastewater, they often exhibit only a moderate extraction capacity and/or selectivity, and may be hindered by a significant solvent loss. In an attempt to address these limitations, ionic liquids (ILs) have been recently proposed for extraction of carboxylic acids.[16-21] A potential advantage of ILs is their low volatility which might facilitate their regeneration.[22, 23] Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl)phosphinate ($[P_{666,14}][Phos]$) has been particularly reported to exhibit a high carboxylic acid extraction capacity and hydrophobicity.[16, 18, 24] Unlike the molecular extraction solvents based on aliphatic amines, $[P_{666,14}][Phos]$ maintains a high extraction performance at low carboxylic acid concentrations [16, 24, 25], ideal for processing dilute streams such as fermented wastewater.

Unfortunately, most studies report solely on extraction with an IL and do not cover subsequent regeneration of the IL. The number of studies proposing a practical regeneration method for $[P_{666,14}][Phos]$ that yields molecular carboxylic acids rather than their carboxylate salts is even more limited. Back-extraction of extracted carboxylic acids from $[P_{666,14}][Phos]$ with a strong base (e.g. NaOH)

is so successful that it has been the standard method for determination of the carboxylic acid content of the IL.[17, 20, 24, 26] However, the product is an aqueous carboxylate salt of the alkali metal rather than a highly concentrated molecular carboxylic acid stream that is desired for further industrial processing. Blahušiak et al. have proposed molecular distillation as a regeneration strategy for $[P_{666,14}][Phos]$ that can deliver a molecular VFA stream.[26, 27] Although elegant and proven effective at higher VFA contents of the IL, the required deep vacuum may hinder scale-up and it remains questionable whether this procedure can yield a $[P_{666,14}][Phos]$ phase that is essentially free of VFAs or not. The non-volatile nature of $[P_{666,14}][Phos]$ will largely determine the evaporation temperature of its mixtures with VFAs at lower VFA contents. As a result, a significant increase in the temperature of the IL even at low pressures that will eventually degrade the IL renders deep recovery of VFAs cumbersome. An incomplete removal of VFAs from $[P_{666,14}][Phos]$ may not limit the extraction process when they are extracted from concentrated aqueous solutions. However, when $[P_{666,14}][Phos]$ is to extract VFAs from diluted aqueous solutions such as fermented wastewater, deep regeneration is essential for an effective extraction.

In this study, several strategies that have previously been investigated for recovery of carboxylic acids from conventional solvents[1, 2, 28-31] have been studied for regeneration of $[P_{666,14}][Phos]$, using acetic acid (HAc) as the model VFA. $[P_{666,14}][Phos]$ -HAc solutions with various HAc contents were characterized with 1H -NMR, ^{31}P -NMR, FT-IR and isothermal titration calorimetry (ITC) to gain insight into the nature of the (strong) $[P_{666,14}][Phos]$ -HAc interactions. The studied regeneration strategies include evaporation of HAc from a $[P_{666,14}][Phos]$ -HAc solution under vacuum and assisted with a stripping N_2 stream to reduce the activity of HAc in the gas phase. The effect of hexadecane, serving as a diluent, on evaporative regeneration of $[P_{666,14}][Phos]$ was investigated as well. The presence of an inert diluent next to a reactive solvent has been shown to weaken the solvent-carboxylic acid interactions, thus facilitating solvent regeneration.[28, 32] Esterification of HAc within the IL phase was examined in a reactive distillation apparatus as well in an attempt to recover less IL-interacting acetate esters from the IL instead of HAc. Reactive back-extraction of HAc from the IL with aqueous solutions of the volatile bases NH_3 and trimethylamine (TMA) was the other studied regeneration strategy. Applying this strategy on an IL is a novelty that was inspired by the patent literature proposing that carboxylic acids, especially non-volatile ones, can be recovered from various media with a volatile base solution.[1, 30, 31, 33] The complexes of volatile bases with carboxylic acids can be thermally decomposed to release the carboxylic acids and volatile bases.[1, 2, 30, 31] This eliminates formation of large byproduct streams of salts.

2. Experimental

2.1. Chemicals

Acetic acid (HAc, $\geq 99.7\%$), ammonium acetate (NH_4Ac , $\geq 99\%$), ammonium hydroxide (NH_4OH , 28.0–30.0%), methyl acetate (MeAc, $\geq 99.8\%$), dodecane (DoD, $\geq 99\%$) and hexadecane (HexD, $\geq 99\%$) were purchased from Sigma-Aldrich. Methanol (MeOH, $\geq 99.9\%$) and potassium hydroxide (KOH, 1 M) were supplied by Merck. $[\text{P}_{666,14}][\text{Phos}]$ (Cyphos® IL104, $\geq 95\%$) was purchased from io-li-tec. Cyanex 272 ($\text{H}[\text{Phos}]$) was kindly provided by CYTEC Industries France SARL.

2.2. Acid loading and characterization of acid-loaded IL phases

The IL-HAc solutions were prepared by adding various amounts of HAc to a fixed amount of the IL to achieve the desired HAc:IL molar ratios (Z , defined in Equation 1). To prepare the IL-HAc-HexD and IL-HAc-DoD solutions, various amounts of HAc were added to a fixed amount of a IL-HexD or IL-DoD solution with a IL:HexD or IL:DoD mass ratio of 70:30.

$$Z = \frac{\text{mol HAc}}{\text{mol IL}} \quad (1)$$

For the ^{31}P -NMR and FT-IR studies, a set of IL-HAc solutions with $0.25 < Z < 40$ was prepared. Pure $\text{H}[\text{Phos}]$ was included as the reference point for the protonated anion ($[\text{Phos}]^-$) of the IL.

ITC was performed on a IL-HexD solution (70 wt% IL) by a TA Instruments TAM III Microcalorimeter operated with a measurement principle based on dynamic correction. The titration syringe was filled with 300 μL HAc. The 4 mL sample vial contained about 2.7 mL of the IL-HexD solution. A certain amount of water with an equal heat capacity to that of the IL-HexD solution was transferred into the reference cell. The stirrer speed was set at 80 rpm and the temperature at 25 $^\circ\text{C}$. HAc was injected into the IL-HexD solution with an injection volume of 10 μL for the first 26 injections and 20 μL for the following injections. The injection interval was 85 minutes to ensure that the signal was back at the baseline level before the following injection.

2.3. Experimental procedures

2.3.1. Regeneration by vacuum evaporation of HAc

Typically, about 20 g of either a binary IL-HAc solution or a ternary IL-HAc-HexD solution was transferred into a glass flask equipped with a magnetic stirrer and a thermometer, and connected to a vacuum pump (vacuubrand PC 3001 VARIO^{pro}). The experiments were started by heating the solution to the temperature set point of 130 °C. After 130 °C was reached, the vacuum pump was turned on to reduce the pressure to 40 mbar. A N₂ stream at a flow rate of about 0.2 L/min was let into the flask while maintaining the reduced pressure at 40 mbar. Any contact between the N₂ line and the IL-HAc or IL-HAc-HexD solution was avoided to prevent formation of aerosols that were potentially harmful to the vacuum pump. A schematic representation of the experimental apparatus is shown in Figure 1.

Figure 1: Schematic representation of evaporation apparatus.

After operating the apparatus at the set temperature and pressure for 1 h, the pressure was first brought back to ambient pressure, and then the heater was turned off to let the residue cool down to room temperature. A sample was then taken from the residue, and it was brought in contact with 1 M KOH solution at a KOH solution:residue mass ratio of 10:1, sufficient to extract all the remaining HAc into the base phase. The base phase was then neutralized with H₂SO₄ and analyzed with IC to quantify the unevaporated HAc and assess the efficiency of regeneration.

2.3.2. Reactive regeneration by esterification

Two IL-HAc solutions with $Z = 6.7$ and 1.7 were prepared and about 25 g of each was separately transferred into a glass flask equipped with a magnetic stirrer and a thermometer. The catalyst Amberlyst 15 wet was then added at the fresh catalyst:HAc mass ratio of about 20:80 to the solution with $Z = 6.7$ and about 50:50 to the solution with $Z = 1.7$. The mixtures were then heated to 50 °C at ambient pressure while being stirred. At 50 °C, MeOH was added to the solution with $Z = 6.7$ at a MeOH:HAc molar ratio of 1:1 and to the solution with $Z = 1.7$ at a MeOH:HAc molar ratio of 1.85:1. Several samples were taken from the liquids over time and analyzed for their water content with a Karl Fischer titrator to calculate the conversion. The esterification equilibrium reaction is given in Equation 2. Figure 2 shows a schematic view of the experimental setup.

Figure 2: Experimental apparatus for esterification of HAc with MeOH in IL.

2.3.3. Reactive back-extraction with aqueous NH_3 or TMA solutions

Regeneration of the IL by back-extracting HAc with an aqueous volatile base solution was examined by multi-stage cross-current extraction experiments. An IL-HAc solution with a HAc content of 4.4 wt% was used as the feed and a 1 M aqueous NH_3 or TMA solution was used as the back-extracting solvent. The mass-based solvent to feed ratio was 1:1. The two phases were contacted for 1 h (sufficient to reach equilibrium) at room temperature. Afterwards, the base phase (back-extract) was separated from the IL phase (raffinate), sampled and, without any further treatment, contacted with the same fresh IL-HAc solution at the same solvent to feed ratio. Subsequent back-extraction stages were carried out until the composition of the base phase did not change anymore, implying that it was in equilibrium with the IL-HAc solution. HAc and NH_3 /TMA concentrations in the base phases were determined by ion chromatography (IC). The NH_3 /TMA amounts that leached into the IL phases were calculated based on the difference between their initial and final amounts.

2.3.4. Thermal decomposition of acetic acid-volatile alkali pairs

Two aqueous solutions were prepared by either dissolving ammonium acetate (NH_4Ac) in water at a salt:water mass ratio of 50:50, or by adding HAc to a 25 wt% aqueous TMA solution to reach a HAc:TMA molar ratio of 1:1. Approximately 20 g of a HAc-containing aqueous solution of a volatile base was loaded into a three-neck flask. The flask, equipped with a thermocouple and stirring magnet, was placed on a heater/stirrers. A N_2 stream was let into the liquid to facilitate evaporation of HAc and the volatile base. The temperature set point was 150 °C, higher than the boiling points of all the species. The liquid loss over time was monitored visually. After either fully evaporating/decomposing the contents of the flask or obtaining a visually unchanging residue, the flask was cooled down to room temperature and weighed to determine the mass loss. A sample was then taken from the residue to be analyzed with IC. A schematic view of the experimental apparatus is shown in Figure 3.

Figure 3: Experimental apparatus for NH_3 or TMA removal from aqueous NH_4Ac or TMA-HAc solution.

2.4. Analysis

HAc concentrations were determined with IC (using a Grom Resin H⁺ IEX column, 8 μ m, 250 $\times$ 8 mm, 1 mM H₂SO₄ solution as mobile phase, a column temperature of 45 $^{\circ}$ C, and a flow rate of 0.6 mL/min, on a Metrohm 850 Professional IC). NH₄⁺ concentrations were measured with IC as well (Metrosep C6 - 150/4.0 column, 1.7 mM HNO₃ + 1.7 mM dipicolinic acid solution as mobile phase, column temperature of 20 $\pm$ 1 $^{\circ}$ C, flow rate of 1.0 mL/min, Metrohm 850 Professional IC). The water contents of the IL phases were quantified with Karl-Fischer titration (Metrohm 787 KF Titrano).

³¹P{¹H}-NMR and ¹H-NMR spectra were recorded on an Agilent 400-MR 400 MHz NMR spectrometer. The chemical shifts in the ³¹P{¹H}-NMR were referenced to an external standard of 85% H₃PO₄. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Thermo Nicolet iS5 FT-IR Spectrometer equipped with a diamond ATR crystal iD5 accessory. All the measurements were conducted under ambient conditions in air. For each spectrum, 24 scans were recorded with a resolution of 4.0 cm⁻¹.

3. Results and discussion

3.1. Characterization of HAc-loaded IL phases

It has been known for over ten years that IL phases are micro-structured [34], and that such micro-structuring may affect their properties. Blahušíak and Schlosser showed that reversed micelles can form in $[P_{666,14}][Phos]$ phases.[35] Giant vesicles[36] and bicontinuous phases with continuous hydrophilic and hydrophobic domains[37] have been reported as well. Kashin et al. showed that even with an IL miscible in all ranges with water, at the microscopic level, the system organizes itself as hydrophilic and hydrophobic domains.[38] In line with these observations, aggregate formation with carboxylic acids thus micro-structuring is expected for $[P_{666,14}][Phos]$ as well, as suggested by Marták et al.[39, 40] To understand the effects of micro-structuring and intermolecular interactions in a HAc-containing $[P_{666,14}][Phos]$ phase on the behavior and recoverability of HAc, IL-HAc mixtures of varying Z were studied with FT-IR, $^{31}P\{^1H\}$ -NMR and 1H -NMR. The degree of proton transfer and hydrogen bonding between HAc and the $[Phos]^-$ anion was monitored throughout these studies. The ^{31}P -NMR and 1H -NMR spectra of the IL-HAc solutions with $0 < Z < 40$ are shown in Figure 4.

At $Z = 0$, the ^{31}P -NMR spectrum shows the two expected peaks at 26.7 ppm and 34.3 ppm for the anion and cation of the IL respectively. Minor amounts of organophosphorus impurities were detected in the IL as well.[41] Upon addition of HAc to the IL, a considerable shift is seen for the anion signal with a concomitant change in peak shape, whereas the cation peak remains unchanged. Cholico-Gonzalez et al. previously studied the interaction of the conjugate acid of $[Phos]^-$ ($H[Phos]$ or Cyanex 272) with the IL trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL101), and similarly observed an upfield shift for the $H[Phos]$ ^{31}P -NMR signal upon dilution with IL-101.[42] They attributed this shift to partial deprotonation of $H[Phos]$. Similarly, the gradual downfield shift observed here for $[Phos]^-$ upon increasing Z can be attributed to an increasing degree of protonation of $[Phos]^-$ by HAc, with larger amounts of HAc shifting the equilibrium further towards $H[Phos]$. With the equilibrium being dynamic and the proton exchange fast on the NMR timescale, a weighted average chemical shift was thus observed. If it was to be assumed that the weighted average chemical shift is only due to protonation of the anion $[Phos]^-$ and deprotonation of HAc, with respect to the chemical shift of pure $H[Phos]$, full protonation of the anion $[Phos]^-$ would occur between $10 < Z < 20$.

Figure 4: a) ^{31}P -NMR spectra obtained for IL-HAc solutions at various Z values; b) ^1H -NMR spectra for the same solutions. The inset shows the evolution of the signal shape.

In addition to the gradual shift of the anion-associated signal, the broad signal, which is initially observed at low Z s, sharpens and splits upon increasing Z , and, at $Z = 10$, it exhibits the same peak shape observed for pure H[Phos]. Given that the ^{31}P spectra are ^1H -decoupled, the origin of this doublet for H[Phos] and the IL-HAc with $Z = 10$ is unclear, with literature examples indeed reporting singlet signals for dialkyl phosphinates instead.[42, 43] Notably, addition of more HAc caused the signal to broaden again and shift beyond the H[Phos] position, as can be seen in the spectra recorded for $Z \geq 20$. A similar shift was observed when 20 equivalents of HAc were added to pure H[Phos], suggesting, in both cases, an additional strong interaction of HAc with H[Phos] that is capable of shifting the signal as well. Strong hydrogen bonding and possibly formation of clusters is expected in the IL-HAc solutions.[44] Formation of clusters can explain the shoulder that appears in the ^1H -NMR spectrum at $Z \geq 20$. It seems that, at these high loadings, the protons that are present in different types of clusters and have a slightly different chemical shift exchange relatively slowly between different clusters.

The infrared spectra of IL-HAc solutions with various Zs are shown in Figure 5 with peak assignments listed in Table 1. The spectrum of the neat IL showed three strong C–H stretching bands between 2960 and 2860 cm^{-1} . The strong band at 1168 cm^{-1} is assigned to the asymmetric stretching vibration of the $\text{R}_2(\text{O})\text{P}=\text{O}$ group of the IL anion [45, 46], with the doublet at 1050 cm^{-1} and 1025 cm^{-1} corresponding to its symmetric stretching vibrations.[46, 47] The spectrum of pure H[Phos] shows the bands that are characteristic of the $\text{R}_2(\text{HO})\text{P}=\text{O}$ group, i.e. a broad P–OH deformation at 1683 cm^{-1} , P=O stretching at 1166 cm^{-1} and stretching of the P–O group at 954 cm^{-1} . The IR spectrum of pure HAc shows the strongest band at 1702 cm^{-1} , corresponding to C=O asymmetric stretching. The band at 932 cm^{-1} is associated with the dimer’s out-of-plane OH deformation.[46]

Table 1: List of infrared bands associated with $[\text{P}_{666,14}][\text{Phos}]$, HAc and H[Phos]

Assignment	Frequency (cm^{-1})	Assignment	Frequency (cm^{-1})	Assignment	Frequency (cm^{-1})
$[\text{P}_{666,14}][\text{Phos}]$		HAc		H[Phos] (Cyanex 272)	
C–H str	2953 (s)	O–H	3000-2500 (m,w)	C–H str	2948 (s)
C–H str	2925 (s)	C=O str _(asym)	1702 (s)	C–H str	2898 (s)
C–H str	2861 (s)	C–O str coupled with OH def _(in-plane)	1407 (s) & 1288 (s)	C–H str	2869 (m)
CH_2/CH_3 bend	1465 (s)	C–O str	1230 (s)	O–H str	2589 (w)
PO_2 str _(asym)	1168 (s)	OH...O def _(out-of-plane)	930 (s)	O–H str	2245 (w)
PO_2 str _(sym)	1050 (s) & 1025 (s)			OH def	1683 (w, br)
C–C skeletal	806 (s)			CH_2/CH_3 bend	1471 (m)
C–H and P–C str	720 (s)			P=O str	1166 (s)
				P–O str	954 (s)
				C–C skeletal	812 (s)
				C–H and P–C str	730 (s)

Figure 5: FT-IR spectra of IL-HAc solutions with varying Z . Bands in A, B and C regions are indicative of the strength of hydrogen bonding in IL-HAc solutions.

[Phos]⁻ protonation leads to a decrease in the intensity of the symmetric (1050 cm⁻¹ & 1025 cm⁻¹) and asymmetric (1168 cm⁻¹) stretching vibrations of the R₂(O) P=O group. This decline is accompanied with an increase in the intensity of the P–O and P=O stretching vibrations at 968 cm⁻¹ and 1090 cm⁻¹ bands respectively. The latter is shifted considerably to lower wavenumbers compared to the pure compound. This is attributed to the ability of the phosphoryl group, a strong proton acceptor [48], to form strong hydrogen bonds with HAc. Such a hydrogen bonding decreases the double-bond character of the phosphoryl group, thereby lowering the frequency and broadening the band.[49]

Indicative of the strength of the hydrogen bonding in the IL-HAc solutions are the broad characteristic bands in the ranges of 2800-2400 cm⁻¹, 2400-1900 cm⁻¹ and 1900-1600 cm⁻¹, namely A, B and C bands.[50] The A and B bands arise from Fermi resonance interactions with the OH in plane deformations, while the C band originates from interactions with the OH torsion mode.[50] Appearance of the C band around 1910 cm⁻¹ at Z > 1 indicates that hydrogen bonds are very strong, significantly stronger than those between carboxylic acid dimers.[50] The presence of such hydrogen bonds also influences the out-of-plane OH deformation vibrations of HAc. Fischmeister found a linear positive relationship between the strength of a hydrogen bond and out of plane OH deformation frequency.[51] In line with this, the spectra shown in Figure 5 revealed a noticeable shift of this vibration from 930 cm⁻¹ band to 950 cm⁻¹.

Upon addition of HAc, already at Z = 0.25, a small band that is assigned to the asymmetric COO⁻ stretching vibration of carboxylates appeared at 1583 cm⁻¹. [46, 47, 49] This confirms the interpretation of the NMR results that, next to the strong hydrogen bonds, deprotonation of HAc occurs as well. It should be noted that the system is not aqueous, and using aqueous phase pK_a values should be done with caution for such a system.[52] Nevertheless, a set of protonation/deprotonation calculations on the basis of the difference in the pK_a values of phosphinic acid and HAc may help understand the observations in the NMR and FT-IR spectra. The extent of protonation may thus be estimated from the difference in the pK_a of the two acids. However, different pK_a values of 6.4[53, 54] and 3.32[55, 56] have been reported for H[Phos] in the literature. Moreover, depending on the medium, a pK_a value reported for H[Phos] can vary from around 3 (in water) to 5.4 (in a 75% (v:v) ethanol–water solution).[56] Therefore, a pK_a value between the two extremes mentioned in literature is expected, i.e. 3.32 < pK_a < 6.4. It is worth noting that, since the composition of the system changes with increasing Z from 0 to 40, the physicochemical nature of the system changes as well suggesting that the pK_a values may not remain constant.

Calculations based on a pK_a of 6.4 for H[Phos] and 4.8 for HAc (see *Supplementary information*) show quick protonation of [Phos] $^-$, according to Equation 3. With the corresponding equilibrium constant of 39.8, the protonation is almost quantitative for $Z > 3$, and some free acetate is indeed expected at $Z = 0.25$ which is in line with the observed asymmetric COO^- stretching vibration.

However, assuming a pK_a of 3.32 for H[Phos] suggests that, even at $Z = 40$, full protonation is not reached. Increasing Z from 0.25 to 1 caused a decline in the carboxylate band until finally at $Z > 1$ no carboxylate peak can be observed anymore, as the spectra are dominated by the vibration of the excess HAc. Excess HAc at $Z = 1$ together with the visible carboxylate signals at $Z = 0.25$ indicate that the [Phos] $^-$ is partially protonated, and the effective pK_a may indeed be between the extremes 3.32 and 6.4.

In conclusion, the NMR and IR data show that both partial protonation and strong hydrogen bonding contribute to the tight HAc-IL interactions, as shown in Figure 6. A similar interaction was previously proposed [39], but it did not consider protonation of the anion [Phos] $^-$.

Figure 6. Intermolecular interactions between [Phos] $^-$ and HAc.

To study the effect of dilution with an apolar co-solvent on the HAc-IL interactions, the FT-IR and ^{31}P -NMR spectra were also recorded for several IL-HAc-DoD solutions with various Z s. The spectra, given in Figure 7, are very similar to those given in Figures 4 and 5 for the undiluted mixtures. For instance, the ^{31}P chemical shifts for [Phos] $^-$, indicative of the equilibrium shown in Figure 6, are at 39.4 ppm and 39.3 ppm for undiluted and diluted solutions with $Z = 2.5$ respectively. Overall, the IR and NMR spectra suggest that the ionic and hydrogen bonding HAc-IL interactions stay unchanged upon dilution with dodecane.

Figure 7: FT-IR (a) and ^{31}P -NMR (b) spectra obtained for IL-HAc-DoD solutions with varying Z .

Thermodynamics of the HAc-IL interactions were studied with ITC and measuring the energy released upon HAc addition to a IL-HexD mixture over time. The injections were stopped when the energy released was not significant anymore implying that no further change in complexation between HAc and IL was taking place. The obtained values over the injection intervals are shown in Figure 8.

Figure 8: Energy released from regulated injections of HAc into 70 wt% IL IL-HexD solution using ITC. $T=25\text{ }^{\circ}\text{C}$.

Figure 8 shows that, when Z was approaching 5, the energy release was not significant anymore. This suggests that above an average loading of five HAc molecules per one IL ion pair, the heat of interaction originating from formation of the IL-HAc complexes is not noteworthy anymore. It should be noted that the obtained value of 5 for Z is dependent on the IL concentration and the complexation equilibrium constant. Previously, an overall complexation stoichiometry of $Z = 8$ was found for the IL-butyric acid solutions, and complexes with a stoichiometry of up to $Z = 11$ were applied in a model to predict the distribution of butyric acid in the IL-butyric acid solutions.[39] Achieving a higher loading with butyric acid than HAc may be due to the larger hydrophobic hydrocarbon tail of butyric acid. The shape of the curve in Figure 8 suggests that, at the higher HAc loadings, there was a much smaller heat effect than at the initial stoichiometric IL-HAc pairs. This indicates that solvation at higher loadings does not affect the chemistry of the system as strongly as it does at lower loadings.

3.2. Regeneration by VFA evaporation under vacuum

Evaporation of HAc from the IL-HAc and IL-HAc-HexD solutions at an elevated temperature, under vacuum and in the presence of a stripping gas was studied to investigate the practicality of regenerating the IL with a simple strategy in the absence and presence of an inert diluent.[28, 32] The obtained results are depicted in Figure 9.

Figure 9: Regeneration of the IL by evaporation at 130 °C and 40 mbar in the presence (black symbols) or absence (red symbols) of a stripping nitrogen stream. Displayed is the final loading versus the initial loading of HAc in the IL-HAc and IL-HAc-HexD solutions. Open symbols: IL-HAc-HexD solutions, closed symbols: IL-HAc solutions, dashed line: $Z_{initial} = Z_{final}$.

As can be seen in Figure 9, for any initial HAc loading of $Z > 1$, evaporation lowered the HAc loading in the solutions down to $Z = 1$, but not any lower. Repeating the same experiments without the stripping nitrogen stream showed no further reduction in Z than 2.5. Blahušiak et al showed that under extremely reduced pressures as low as 5 mbar at prolonged evaporation times, the initial Z of an IL-butyric acid solution can be lowered down to 0.1.[26] These observations indicate that the activity of a VFA in the IL is very low, likely due to formation of aggregates with higher Z values.[39] Since, in our experiments even under reduced pressure and in the presence of a stripping gas, the first equivalent of HAc could not be removed, it seems that there is a very strong affinity between $[Phos]^+$ and the first HAc equivalent. The lowest Z that could be obtained in the systems diluted with HexD was approximately 1 as well. This suggests that, in these systems as

well as in the systems containing the IL and HAc only, higher order complexes that formed at $Z > 1$ due to hydrogen bonding and proton transfer are reduced to 1:1 complexes in which HAc or Ac^- tightly binds to H[Phos] or $[\text{Phos}]^-$. The strong hydrogen bonds observed with FT-IR support this hypothesis. Since the Z of the saturated IL after LLX when it is in equilibrium with an artificial fermented wastewater is below or at best around one [20, 24], unfortunately, regeneration of the IL by VFA evaporation under vacuum is not a feasible practice. The presence of such a strong interaction between the IL and HAc suggests that the physical removal of HAc from the IL phase is not practical. Therefore, the IL phase has to be exposed to chemical regeneration.

3.2. Reactive regeneration by esterification

Solvent regeneration by in situ conversion of the carboxyl group of an extracted organic acid to a chemical functionality for which the solvent has a significantly lower affinity has been reported in the literature.[11, 29, 57] Since $[\text{P}_{666,14}][\text{Phos}]$ is expected to have a much lower affinity for methyl acetate than for HAc, an attempt was made to esterify HAc to methyl acetate. Two esterification experiments were performed with two different IL-HAc solutions, one with $Z = 6.7$ and the other with $Z = 1.7$. The conversion in time is displayed in Figure 10 for these experiments.

Figure 10: Esterification of HAc in IL-HAc solutions with MeOH. a) $Z_{\text{initial}} = 6.7$, molar $\text{MeOH:HAc} = 1:1$, b) $Z_{\text{initial}} = 1.7$, molar $\text{MeOH:HAc} = 1.85:1$.

As can be seen in Figure 10a, when Z was 6.7, an equilibrium conversion of around 0.50 was achieved. An equilibrium conversion of around 0.65 was previously observed for esterification of pure HAc with MeOH at 50 °C when the HAc:MeOH molar ratio was 1:1.[58] Thus, the conversion in the presence of the IL is in line with the reported value in the literature on esterification of HAc in the absence of the IL. When the initial amount of the IL was increased, resulting in a lower Z of 1.7 (see Figure 10b), no conversion was observed at all. This phenomenon was most likely a result of the limited reactivity of HAc in the IL phase induced by formation of IL:HAc complexes. The presence of this phenomenon implies that no

esterification is possible at HAc loadings achievable when HAc is extracted from dilute aqueous solutions such as artificial fermented wastewater.[24] Therefore, it is concluded that in situ esterification of HAc is not practical for regeneration of the IL, and that another chemical regeneration strategy that induces a chemical interaction with HAc more favorable than the interaction of HAc with the IL has to be devised.

3.3. Regeneration by reactive back-extraction with a volatile base

Aqueous solutions of volatile bases have been used to recover carboxylic acids from adsorbents and conventional solvents.[1, 30, 31] This practice was modified to regenerate an IL in this study. The HAc content of the IL was back-extracted with aqueous solutions of the volatile bases NH_3 and TMA. The molar loading of HAc in the basic aqueous solutions at equilibrium with the 4.4 wt% IL-HAc solution was determined by multistage cross-current back-extraction experiments. The obtained results are depicted in Figure 11.

Figure 11: Cross-current back-extraction of HAc from 4.4 wt% IL-HAc solution with aqueous NH_3 or TMA solution. Closed symbols represent NH_3 solution and open symbols represent TMA solution. Error bars are calculated based on a 2% error in analysis.

Figure 11 shows that, for both volatile bases, a back-extraction stoichiometry of approximately unity was achieved after two cross-current extraction stages. Previously, King et al. reported that approximately 2 mol TMA was needed to completely recover 1 mol succinic acid (a dicarboxylic acid) from an adsorbent, pointing to a chemistry similar to that of carboxylic acids and strong bases.[31] The major difference is the fact that a volatile base is capable of preserving the proton of a carboxylic acid. Approximately 10 wt% of the initial NH_3 and 2 wt%

of the initial TMA leached into the HAc-free IL phase after back-extraction. This suggests that, to prevent losses of the volatile bases, the HAc-free IL has to undergo stripping before it is sent back to the primary extraction stage. The obtained molar ratio of 1:1 can be used to determine the required flow rate of a concentrated NH_3 or TMA solution for back-extraction. The amount of the volatile base that leaches into IL has to be accounted for as well. The volatile base-HAc complexes that form after back-extraction have to be thermally decomposed to free volatile base and HAc to recycle the volatile base and present HAc as the product.[1, 2]

To reach high HAc concentrations after thermal decomposition of the TMA-HAc complexes, the initial TMA concentration should be as high as possible. When a saturated TMA solution (40 wt% TMA in water) is used for back-extraction, calculations show that HAc concentrations of up to 46.9 wt% can be achieved in the back-extract (see *Supplementary information*). Thermal treatment of the back-extract and a complete removal of TMA transforms the back-extract into a 90 wt% HAc/10 wt% water stream. These concentrations are calculated assuming that a 4.4 wt% HAc-IL stream containing 8.4 wt% water is obtained after extraction of HAc from fermented wastewater with only 1 wt% HAc [24], and the HAc-free IL stream has a water content of 14.4 wt%.[40] An average TMA loss of 1.75 wt% (on initial TMA content basis) was considered. The calculated compositions of all the streams are listed in Table 2.

Table 2: Calculated concentrations for back-extraction of a 4.4 wt% HAc-IL solution with a saturated aqueous TMA solution of 40 wt%.

Species	Concentration [wt%]				
	Saturated TMA solution before back-extraction	HAc-IL solution to undergo back-extraction	TMA solution after back-extraction	HAc-free IL solution after back-extraction	Final product stream after TMA removal
TMA	40.0	0.0	47.9	0.1	0.0
Water	60.0	8.4	5.2	14.4	10.0
HAc	0.0	4.4	46.9	0.0	90.0
IL	0.0	87.2	0.0	85.5	0.0

Table 2 shows that an impressive purification step for HAc from 1 wt%[24] to 90 wt% is possible by LLX with $[\text{P}_{66,14}][\text{Phos}]$, back-extraction with TMA and thermal decomposition of the TMA-HAc complexes. A similar analysis could be carried out using NH_3 as the volatile base.

3.4 Thermal decomposition of volatile base–HAc complexes

To complete this regeneration procedure, molecular HAc has to be recovered from the aqueous HAc-volatile base complexes obtained after back-extraction. Thermal decomposition of carboxylic acid-volatile base complexes has been previously examined in the literature.[1, 2, 30, 31] An incomplete decomposition of the complexes that is reflected in formation of a residue either liquid with a high viscosity or solid is a potential difficulty. It is worthwhile to mention that, for a non-volatile carboxylic acid, a residue will form despite a complete decomposition. Such a residue has to be analyzed to determine the efficiency of decomposition. Decomposition of NH_3 -HAc and TMA-HAc complexes was assessed with the method described in section 2.3.4. The first stage in each decomposition experiment was a significant mass loss at 100 ± 1 °C which was associated with evaporation of water. After evaporation of water from the solutions at 100 ± 1 °C, two relatively viscous liquids were obtained. The viscous liquids maintained a relatively stable mass until 140 °C. From 140 °C to 150 °C, the temperature rise was obviously slower and the viscous liquids continuously lost mass. At 150 °C, all the viscous liquids had disappeared, indicating that a complete decomposition was achieved. The decomposition temperature range was thus 140–150 °C. A decomposition temperature above the boiling points of TMA and HAc comes with the drawback of formation of a gaseous mixture of HAc and TMA that needs to be purified. To address this issue equally faced in a NH_4Ac decomposition case, Mercier and Kobler et al. proposed the use of an entrainer that captures HAc while having no interaction with NH_3 . [1, 2] The disadvantage of using an entrainer is the need for an extra distillation column to separate HAc from the entrainer. Nevertheless, as these downstream operations are much smaller in volume than the primary extraction, regeneration of the IL with a TMA solution presents an effective solution enabling the use of ionic liquids for extraction of carboxylic acids from dilute aqueous solutions such as fermented wastewater. To further boost the performance of the process, extraction of VFAs may be carried out under pressurized CO_2 . [24] Figure 12 presents a schematic view of this process. The presented scheme only includes the main operations.

As can be seen in the simplified scheme of the process shown in Figure 12, the regenerated IL stream is directly sent back to the first extraction column. However, in practice, this is not feasible, as the leaching TMA into the regenerated IL stream has to be recovered first in a stripping column. The analysis of the extract phases obtained after the cross-current back-extraction experiments suggested that approximately 1.75 wt% of the initial TMA would be lost into the IL stream through the back-extraction column.

Figure 12: Scheme of LLX-based process for recovery of VFAs from fermented wastewater using $[P_{606,114}][Phos]$ as extraction solvent and TMA as back-extraction solvent.

It has been known that the IL co-extracts mineral acids (e.g. HCl and H₂SO₄) together with VFAs from fermented wastewater.[20, 24] Exposing a mineral acid and VFA-containing stream of the IL to back-extraction with a TMA solution will result in formation of TMA-mineral acid complexes next to TMA-VFA complexes in the extract phase. The upside of this phenomenon is the fact that the IL regains its entire extraction capacity. The downside is that it raises TMA losses. TMA-mineral acid complexes cannot be decomposed at temperatures that are sufficiently high for decomposition of TMA-VFA complexes. Therefore, they can be removed from the distillation column in which TMA-VFA complexes are decomposed (see Figure 12) as a side byproduct stream without interfering with decomposition of TMA-VFAs complexes. The raffinate stream leaving the first extraction column has to be further treated as well to recover the leaching IL during extraction. Although the leaching amount is very small [40], extensive operation of the process over time makes it significant, and if not recovered, it can definitely impose financial and environmental risks. The following is a few critical concluding remarks:

- When the IL extracts VFAs from fermented wastewater, butyric acid (HBu) accounts for the majority of the VFA loading of the IL.[20] It is known that ammonium butyrate turns into butyramide at about 185 °C.[59] Based on the results of this work, it can be estimated that decomposition of ammonium butyrate requires a temperature of about 200 °C. The very high possibility of formation of butyramide at such a temperature makes ammonia the unfavorable candidate for regeneration of the IL. Contrary to ammonia, TMA is a tertiary amine and thus immune to such a reaction. Therefore, it is the best candidate for regeneration of VFA-containing [P_{666,14}][Phos].
- A limited carboxylic acid concentration in an aqueous feed results in a limited carboxylic acid loading of the IL when it is in equilibrium with the feed. Since such a limited carboxylic acid loading cannot be (fully) recovered from the IL by stripping, the working capacity of the IL will be much lower than its actual capacity. The aforementioned regeneration approach is capable of completely resolving this issue, as, by adjusting the initial TMA concentration or flow rate, the carboxylic acid loading of the IL can be lowered to any desired value. A major advantage of this capability is that the unit operations and other equipment will process smaller volumes, and therefore, waste-derived carboxylic acids will be available with a lower capital cost.

4. Conclusions

Regeneration of acetic acid (HAc)-containing $[P_{666,14}][Phos]$ phases was studied in an attempt to enable a practical and sustainable liquid-liquid extraction (LLX) process for dilute aqueous HAc streams. Evaporative regeneration at 130 °C and 40 mbar was not capable of lowering the HAc:IL molar ratio down to below 1:1. Extensive analysis with NMR and FT-IR suggested that (partial) deprotonation of HAc and a very strong hydrogen bonding prevent HAc from evaporating below a HAc:IL molar ratio of 1:1. Reactive recovery of HAc by esterifying it with methanol inside the IL phase was not capable of regenerating the IL with a low HAc content either. However, back-extraction of HAc from the IL phase with an aqueous solution of trimethylamine (TMA) did prove successful. Thermal decomposition of the HAc-TMA complexes that formed after back-extraction took place at a temperature higher than the boiling points of HAc and TMA. The presence of an entrainer during thermal decomposition of the HAc-TMA complexes enables separation of liberated HAc and TMA molecules. Separation of the entrainer from HAc in a distillation column can provide a high purity product stream of HAc.

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Appendix | Supplementary information

In this section, the calculations performed on protonation of the phosphinate anion of the IL ([Phos]⁻) by acetic acid (HAc) together with all the assumptions that have been made are described first. Afterwards, the calculation performed on back-extraction of HAc from the IL with a concentrated TMA solution are described.

Protonation of [Phos]⁻ by HAc

The equilibrium reaction between [Phos]⁻ and HAc is given in Chapter 5 Equation 5. Upon addition of HAc to the IL, a part of [Phos]⁻ will be protonated. To estimate the possible extent of this protonation, a set of calculations based on the reported pK_a values for aqueous solutions of HAc (pK_a = 4.8) and H[Phos] [pK_a = 3.32 (aqueous phase) or pK_a = 6.4 (organic phase)] was performed. For each of the two pK_a values reported for H[Phos], a separate set of calculations was performed. For the calculations, the following assumptions have been made:

1. No excess mixing volume, i.e. the total volume is the sum of the pure components' volumes, determined using their densities and molar weights.
2. Ideal solution behavior, i.e. all the activity coefficients are set to unity by default.

It is realized that the applied aqueous phase-derived pK_as may not represent the actual situation in a non-aqueous solution.

Table S1. Information on [P_{66,14}][Phos] and HAc

Species	Density (kg/m ³)	Molar weight (g/mol)	pK _a
HAc	1050	60.05	4.8
[P _{66,14}][Phos]	895	773.27	3.32/6.4 (for H[Phos])

As Z (mol HAc / mol [P_{66,14}][Phos]) varied from 0 to 40 in the experiments described in chapter 5, the calculations were carried out for 1 mol [P_{66,14}][Phos] and 0.25 up to 40 mol HAc. The volume per Z was the summation of the volume of one mol [P_{66,14}][Phos] and the volume of the added HAc. The total concentrations of [Phos]⁻ and Ac⁻ were calculated using their added molar amounts divided by the total volume of both the species. Therefore, for Equation 5, Equation S1 should hold:

$$K = \frac{K_A(\text{HAc})}{K_A([\text{P}_{66,14}][\text{Phos}])} = \frac{[\text{R}_2\text{POOH}][\text{CH}_3\text{COO}^-]}{[\text{R}_2\text{POO}^-][\text{CH}_3\text{COOH}]} \quad (\text{S1})$$

Using MS Excel, for each value of Z from 0.25 to 40, the concentration of $[\text{Phos}]^-$ and with that the corresponding concentrations of $\text{H}[\text{Phos}]$ (component mass balance), Ac^- (charge balance) and HAc (component mass balance) were found by solving for the equilibrium constant.

For $\text{p}K_a(\text{H}[\text{Phos}]) = 6.4$, the fraction of $[\text{Phos}]^-$ that is not protonated is displayed in Figure S1, and the concentrations of all four species participating in the equilibrium are given in Figure S2.

Figure S1: Fraction of non-protonated $[\text{Phos}]^-$ as a function of Z for $\text{p}K_a(\text{H}[\text{Phos}]) = 6.4$

Figure S2: Molar concentrations as functions of Z for $\text{p}K_a(\text{H}[\text{Phos}]) = 6.4$

For $pK_a(H[\text{Phos}]) = 3.32$, the fraction of $[\text{Phos}]^-$ that is not protonated is displayed in Figure S3, and the concentrations of all four species participating in the equilibrium is given in Figure S4.

Figure S3: Fraction of non-protonated $[\text{Phos}]^-$ as a function of Z for $pK_a(H[\text{Phos}]) = 3.32$

Figure S4: Molar concentrations as functions of Z for $pK_a(H[\text{Phos}]) = 3.32$

Back-extraction of HAc from $[P_{666,14}][Phos]$ with a concentrated TMA solution

A schematic view of the back-extraction column in which HAc is back-extracted from the IL is depicted in Figure S5.

Figure S5: Schematic view of the column in which HAc is back-extracted from IL with an aqueous TMA solution.

Table S2 summarizes the set values for the inlet streams and the calculated values for the outlet streams. The calculated values were obtained by applying a mass balance on the inlet and outlet streams. According to Figure 11 in chapter 5, a HAc:TMA molar ratio of 0.96:1 can be achieved in the outlet TMA stream. It was assumed that:

- The IL inlet stream has a flow rate of 100 kg/h.
- 99 wt% of the HAc that was initially a part of the IL inlet stream is back-extracted into the TMA outlet stream.
- The amount of TMA leaching into the IL outlet stream is 1.75 wt% of the initial TMA in the TMA inlet solution.

According to the specifications of the TMA outlet stream presented in Table S2, if TMA is removed from the stream, the remaining HAc-water stream will have a composition of about 90 wt% HAc/10 wt%.

Table S2. Specifications of the inlet and outlet streams of the back-extraction column depicted in Figure S5.

IL inlet stream			
	Concentration [wt%]	Stream flow rate [kg/h]	Flow rate in stream [kg/h]
HAc	4.4	100	4.4
Water	8.4		8.4
IL	87.2		87.2
IL outlet stream			
HAc	0.04	102.01	0.0
Water	14.40		14.7
IL	85.48		87.2
TMA	0.08		0.1
TMA inlet stream			
TMA	40.0	11.335	4.534
Water	60.0		6.801
HAc	0.0		0
TMA outlet stream			
TMA	47.80	9.323	4.456
Water	5.48		0.511
HAc	46.72		4.356

Solvent selection
approach for
liquid-liquid
extraction with
an ionic liquid

CHAPTER

6

Nomenclature

LLX:	Liquid-liquid extraction
BE:	Back-extraction
Phys. reg.:	Physical regeneration
VFA:	Volatile fatty acids
HAc:	Acetic acid
IL:	Ionic liquid
TMA:	Trimethylamine
AS:	Anti-solvent

Symbols

D:	Distribution coefficient
D_f :	Distribution coefficient at feed concentration
ΔG_{mix} :	Gibbs free energy of mixing
ΔH_{mix} :	Enthalpy of mixing
ΔH^v :	Enthalpy of vaporization
ΔS_{mix} :	Entropy of mixing
W_{sep} :	Minimum separation work
Q_{reb} :	Reboiler duty
T:	Temperature
P:	Pressure
P^* :	Saturated pressure
R:	Universal gas constant
η_c :	Carnot efficiency
η_f :	Internal efficiency
x:	Molar fraction in liquid phase
y:	Molar fraction in gas phase
γ :	Activity coefficient

1. Introduction

Separation typically uses 30–80 % of the energy spent on production of chemicals. [1, 2] Depending on the composition of the stream to be subjected to separation, a direct separation practice involving a single unit operation (e.g. distillation or crystallization) or an indirect separation practice involving multiple unit operations (e.g. liquid-liquid extraction or adsorption followed by one or more regeneration steps) is employed. For instance, for separations of acetic acid from aqueous streams, the boundary concentration above which distillation is applied is about 50 wt%, whereas liquid-liquid extraction (LLX) is typically applied for dilute streams.[3] The decision to choose either distillation or LLX as the separation technology is often made after extensive process calculations. Nevertheless, a pre-screening of the technologies can be carried out using a theoretical framework that is based on distillation efficiency as a function of feed composition. By considering a distillation column as a heat engine, its maximum achievable efficiency can be expressed as that of a Carnot engine operating between the reboiler as the heat source and the condenser as the heat sink. Furthermore, the actual efficiency of the unit operation can be expressed as the product of its internal efficiency and the Carnot efficiency. The internal efficiency of a distillation column is feed composition dependent. For ideal binary distillations, it was shown that, as the concentration of the compound of interest in the feed stream decreases, the efficiency of the distillation column decreases as well.[4]

This theoretical conclusion implies that when separation of volatile fatty acids (VFAs) from fermented waste streams is concerned, their limited VFA content (~1 wt%) makes distillation by definition highly inefficient and impractical. For separation cases of a similar nature, LLX can be applicable, if there is an affinity between the solvent and the compound of interest. After extraction (1st step), the solvent containing extracted VFAs, i.e. the extract, has to undergo solvent regeneration (2nd step) to unload them and be reused. Figure 1 gives a schematic view of a multi-step process separating VFAs from fermented waste streams by LLX.

Figure 1: A schematic view of a multi-step process for separation of VFAs from fermented waste streams.

The solvent has to exhibit a reasonable capacity and a high selectivity for VFAs to maximize the efficiency of solvent regeneration. In the recent literature, the ionic liquid (IL) $[P_{666,14}][Phos]$ has been reported to be capable of extracting carboxylic acids with a high capacity and selectivity.[5-9] However, the focus of these studies has been mainly on extraction, leaving solvent regeneration unexplored. Chapter 5 of this thesis describes our investigations on several solvent regeneration techniques for regeneration of this IL. The investigated techniques have previously been reported for regeneration of conventional solvents and adsorbents.[10-14] The observations revealed that a straightforward physical solvent regeneration by stripping with an inert gas under reduced pressure was not capable of fully regenerating the IL. This shows that the statement often made in the literature considering the negligible vapor pressure of an IL an advantage for regenerating it[15, 16] might be valid only when the IL can be regenerated at all. In situ conversion of extracted VFAs to their esters with an added alcohol failed as well, pointing to the strong interaction of the IL with VFAs. Back-extraction (BE) of extracted VFAs from the IL with aqueous alkali solutions was the only method capable of fully regenerating the IL. In order to obtain molecular VFAs, application of the volatile alkali trimethylamine (TMA) was attempted, followed by thermal decomposition of the TMA-VFA complexes. BE with a volatile alkali solution is a rather harsh method and success is not guaranteed a priori, since facile thermal decomposition of the TMA-VFA complex is a prerequisite for this method to be practical. The summary of the regeneration techniques described above clearly suggests that regeneration of ILs is, in contrary to what might be the perception of many researchers, not necessarily easy. Realizing this, any study on using ILs as solvents in separation processes should consider their regeneration as well, and preferably by a practical and quick method.

The aim of this chapter is to suggest an approach to quickly assess the practicality of utilizing ILs in a separation process that follows the schematic view depicted in Figure 1. The suggested approach is in fact applicable to any LLX solvent. The insights gained from regeneration of $[P_{666,14}][Phos]$ in chapter 5 as well as evaluation of the experimental procedures described in chapters 3 to 5 were the basic considerations for this chapter. Since the aim of this thesis has been separation of VFAs from aqueous streams while keeping their molecular forms intact, the examined regeneration techniques could not deliver a product stream of dissociated VFAs. This imposed extra restrictions on selection of regeneration techniques which may well be unnecessary for other solvent-solute systems. Supporting the practical considerations to be given in this chapter is a mathematical model predicting the practicality of an intended solvent regeneration technique. It should be noted that the following approach is limited to separations where regeneration of an IL is aimed for, and is not applicable to processes intending to capture and store an extracted compound in an IL without regenerating it.

2. Theory

Regeneration of a solvent can be either physical or chemical. Physical regeneration is often more preferable, as chemical regeneration is usually energy intensive and complex. The latter is a result of introducing at least one extra chemical to the process hence, an additional operation to reverse the chemical reaction and recover the introduced chemical. Distillation of a solvent–solute mixture or back-extracting the solute from a solvent–solute mixture with a physical (non-reactive) solvent are examples of physical regeneration. A common chemical regeneration practice is BE of the solute from a solvent–solute mixture with a chemical (reactive) solvent. In order to visualize various separation routes, a conceptual Gibbs energy diagram may be constructed (see Figure 2). The minimum amount of energy needed to separate two fractions is the amount just sufficient to reverse their mixing, and therefore, it is equal to the reverse of their Gibbs energy of mixing ($-\Delta G_{\text{mix}}$). Figure 2 compares distillation, a single-operation separation, with multi-operation LLX in terms of energy gain/loss to supply $-\Delta G_{\text{mix}}$. The energy gain/loss pattern of LLX + BE is included in Figure 2 as well.

Figure 2: Conceptual Gibbs energy diagram for separations. Included are direct separation by distillation and indirect separations by LLX followed by either distillation (physical regeneration, *Phys. reg.*) or BE (physical/chemical regeneration, *BE*) and physical regeneration.

Since LLX proceeds spontaneously, its ΔG should be negative. As can be seen in Figure 2, for LLX + *Phys. reg.* and LLX + BE + *Phys. reg.* routes, the Gibbs energy after extraction is lower than before, and solvent regeneration requires additional energy to separate the extracted fraction from the solvent. The additional energy has to be invested through a thermal separation operation such as distillation or crystallization. The Invest energy vectors of LLX + *Phys. reg.* and LLX + BE + *Phys. reg.* routes can then be the vector sum of the Invest energy and Lose energy vectors of distillation in Figure 2.

Figure 2 suggests that the use of a LLX solvent that introduces a $\Delta G \ll 0$, expressible as a Lose energy vector with a large magnitude, may lead to an impractical solvent regeneration. The distribution coefficient (D) obtained with a LLX experiment, expressed as the ratio of the mole fraction of the solute in the extract phase to that in the raffinate phase, can be a qualitative indication of the experienced ΔG . The D obtained when the extract is in equilibrium with the feed, referred to as D_p , is of particular importance, as it describes the performance of the counter-current LLX column to be designed for the intended separation.

A $D_f \gg 1$ implies that $\Delta G_{\text{mix}}(\text{extract}) \ll \Delta G_{\text{mix}}(\text{feed})$ and, as a result, solvent regeneration may be complicated. It should be noted that despite the fact that LLX forces G to move in an undesirable direction with respect to the additional energy needed to complete the separation (Invest energy vector of LLX + Phys. reg. in Figure 2), it can be beneficial, as the resulting additional energy requirement can be lower than that of a physical separation procedure applied directly on the feed {Invest energy vector of distillation (Phys. reg.) in Figure 2}.

When a distillation column is to supply the energy required to complete LLX + Phys. reg. and LLX + BE + Phys. reg. routes (their Invest energy vectors in Figure 2), noted as W_{sep} , its reboiler duty (Q_{reb}) can be expressed as a function of W_{sep} , i.e. $-\Delta G_{\text{mix}}[4]$. Such a distillation column is analogous to a heat engine operating between the temperature of a heating fluid in the reboiler (e.g. steam, T_H) and that of a cooling fluid in the condenser (e.g. cooling water, T_C). A Carnot engine operating between the same temperatures will naturally demonstrate the highest efficiency that can be achieved with a heat engine. Therefore, considering that no practical distillation column can be operated under perfectly reversible conditions, the aforementioned distillation column can be considered as a lower efficiency variation of such an ideal heat engine. A schematic view of a distillation column operating as a heat engine is given in Figure 3.

As can be seen in Figure 3, higher quality heat at a higher temperature, reflected in a higher exergy, is gained from the heat source in the reboiler (Q_{reb}). After supplying the W_{sep} required to separate the compound of interest from a LLX or BE solvent and losing exergy, lower quality heat at a lower temperature is transferred to the heat sink in the condenser. Equation 1 expresses Q_{reb} as a function of W_{sep} .

$$Q_{\text{reb}} = \frac{W_{\text{sep}}}{\eta_c \eta_i} = \frac{-\Delta G_{\text{mix}}}{\eta_c \eta_i} \quad (1)$$

η_c is the Carnot efficiency of an ideal distillation column operating between the same temperatures (see Equation 3) and η_i is the internal efficiency of the non-ideal distillation column that is to be provide W_{sep} .

$$\eta_c = 1 - \frac{T_c}{T_H} \quad (2)$$

According to Equation 1, experiencing a ΔG_{mix} with a larger absolute value after LLX does not necessarily suggest that a higher reboiler duty is expected for distillation of the back-extract, as the product of η_c and η_i can well be larger than that of distillation of the feed which eventually lowers the reboiler duty. Blahušiak et al. showed that, for an ideal binary mixture, the internal efficiency (η_i) is a

Figure 3: Schematic view of a distillation column operating as a heat engine between a heat source and a heat sink to supply the energy required to complete the LLX + Phys. reg. and LLX + BE + Phys. reg. routes.

function of the relative volatility and composition of the mixture.[4] However, for a non-ideal binary mixture, developing such a correlation is not straightforward.

A solute–IL mixture is a non-ideal mixture. The boiling point of a binary mixture is dependent on the boiling points of its constituents. An IL often decomposes before boiling, and therefore, when an IL is one of the constituents, the mixture cannot be distilled to a high purity of the IL. The impracticality of this practice will express itself as a drastic increase in the temperature of the reboiler stage that will eventually decompose the IL. To eliminate the possibility of decomposing the IL, evaporation of the volatile solute under reduced pressure in a flash vessel is arguably the most practical approach for physical regeneration of an IL. Application of a stripping gas may facilitate evaporation of the volatile solute.

The correlation between the partial pressure of species A (volatile) and its mole fraction in an IL phase is given in Equation 3. Since an IL has a negligible vapor pressure, if no stripping gas is used, all the vapor above it is made of compound A only, hence $y_A = 1$. The activity coefficient of species A (γ_A) is the property that reflects the non-ideality of the IL-species A mixture.

$$P y_A = P_A^* x_A \gamma_A \xrightarrow{y_A=1} P = P_A^* x_A \gamma_A \quad (3)$$

When an IL containing species A is to be physically regenerated in a flash vessel, equation 3 can be written for the reboiler of this flash vessel to obtain Equation 4. Subscript R stands for reboiler.

$$P_R = P_{A,R}^* x_{A,R} \gamma_{A,R} \quad (4)$$

In the condenser, the vapor and liquid are purely composed of compound A (see Figure 4). Equation 5 can then be written for the condenser. Subscript C stands for condenser.

$$P_C y_{A,C} = P_{A,C}^* x_{A,C} \gamma_{A,C} \xrightarrow{y_{A,C} x_{A,C} \gamma_{A,C} = 1} P_C = P_{A,C}^* \quad (5)$$

Figure 4: Schematic view of a flash vessel regenerating an IL.

The pressure inside a common flash vessel is uniform. This implies that $P_R = P_C = P_{A,C}^*$. Therefore, at a given condenser temperature, can be determined with a known correlation for $P_{A,C}^* = f(T_C)$ (e.g. Antoine equation). Using Equation 4, with a known P_R and $\gamma_{A,R}$ and a desired $x_{A,R}$, $P_{A,R}^*$ and consequently the reboiler temperature (T_R , $T_R = f^{-1}(P_{A,R}^*)$) can be calculated.

Regeneration of the IL $[P_{666,14}][Phos]$ after it extracted acetic acid (HAc) is an interesting example to examine with the mathematical model described above. At a reasonably set condenser temperature of 20 °C and various activity coefficients (ranging from 0.1 to 2), $x_{HAc,R}$ can be obtained as a function of T_R . The results are depicted in Figure 5. It should be noted that, in real non-ideal systems, activity coefficient is of course not constant with a varying composition, and that this example only aims at visualizing the effect of activity coefficient on practicality/impracticality of regenerating an IL in a flash vessel.

Figure 5: Required reboiler temperature to recover HAc from $[P_{666,14}][Phos]$ in a flash vessel as a function of intended recovered fraction, activity coefficient of HAc in $[P_{666,14}][Phos]$ and condenser temperature.

As can be seen in Figure 5, to achieve a deep HAc removal, the reboiler has to operate at significantly high temperatures as high as about 400 °C. Any IL starts to degrade at a certain temperature [17, 18], and therefore, a reboiler temperature of higher than that immediately renders such a thermal regeneration operation impractical. Degradation of $[P_{666,14}][Phos]$ starts at about 250 °C.[19] One should note that:

- The extent of solute removal from an IL is dependent on the intended working capacity of the IL, i.e. difference in the solute loading of the IL before and after regeneration. When the solute is extracted from a dilute stream (see Figure 1), the final loading of the solute in the IL will be limited. To maximize the working capacity of the IL in such a process, the solute removal has to be as deep as possible.
- When the molecular form of the solute has a tendency for distortion in an IL phase, the final loading of the solute in the IL after extraction has to be as high as possible to achieve a reasonable working capacity for the IL. Dissociation of HAc in the $[P_{666,14}][Phos]$ phase, as observed in chapter 5, is an interesting example of such a situation. Since the final loading of HAc in $[P_{666,14}][Phos]$ after extraction was not high enough due to the limited HAc content of fermented wastewater, physical regeneration of the IL by evaporation/stripping was not capable of delivering any working capacity.

The aforementioned theoretical section can be generalized to any LLX-based separation process utilizing any solvent type. In this work, the insights gained from the theoretical section are used to support the approach proposed for selection of an IL for a LLX-based separation process. Studying regeneration of the selected IL is of special importance in this approach.

3. Proposed approach

The current section provides a three-step approach for selection of an IL for a LLX-based separation process. The first two steps assist with screening a selection of ILs and narrowing it down to a few potential ILs, solely based on their extraction capabilities. Step 2 aims at minimizing the experimental work that is needed to assess the extraction performance of the ILs selected after completing step 1. The ILs that remain on the list after completing step 2 will then be subjected to an experimental procedure in step 3 to determine the practicality of regenerating them physically.

3.1. Step 1. Solvent pre-screening (simulation and literature)

Many individual ILs and IL families have already been investigated, and their characteristics and potential applications are reported in the literature.[9, 20-23] Software packages such as COSMO-RS (COnductor-like Screening MOdel for Real Solvents) and ICAS (Integrated Computer Aided System) can assist with selection of a group of potentially promising ILs from the literature.[24-27] These software packages can predict the extraction performance of an IL by simulating the molecular interactions between the IL and the compound of interest.[27, 28] It should be noted that the predicted extraction performance, often expressed as a distribution coefficient, provides a ballpark figure that may well be inaccurate when compared to the actual extraction performance observed experimentally in step 2.[29, 30] Another tool to predict the extraction capability of an IL is the Abraham model.[31, 32] This model can estimate the distribution coefficient of the compound of interest in an IL by the linear free energy relationship.[33] The literature survey may include conventional separation methodology of the compound of interest, molecular interactions, etc. The IL to be chosen has to meet a certain list of requirements for any solvent two of which are a reasonable extraction capacity and a high selectivity. According to Figure 2, a very high extraction capacity, expressible as a large reduction in Gibbs energy, can potentially lead to a challenging solvent regeneration. Based on the insights gained with the literature survey, one may intend to synthesize or customize an IL. Synthesis methodologies of some ILs have been reported in the literature as well.[34]

3.2. Step 2. Experimental solvent screening

To experimentally validate the extraction performance of the ILs selected by pre-screening, an extraction isotherm can be constructed for each. To start with, a mother solution containing all the solutes that are found in the feed each with a concentration of x times that in the feed ($x > 2$) can be prepared.[35] The mother solution is then diluted twice and x times to obtain two additional solutions the second one of which will be the feed. These three solutions will serve as the starting solutions for constructing the isotherms. The reason for including all the species in construction of the isotherms is the fact that the presence of certain impurities in the feed can affect the extraction behavior of an IL so significantly that excluding them will lead to incorrect conclusions.[8, 9, 36] If n ILs have made the cut to be examined experimentally, n sets of starting solutions ($3n$ solutions in total) have to be prepared. The starting solutions are then exposed to the ILs at the same solvent to feed ratio. After equilibrium is reached by stirring the mixtures overnight, the equilibrium concentrations in the raffinate phases have to be determined. The isotherms can then be constructed by plotting the equilibrium concentrations in the raffinate phases on x-axis, and those in the extract phases (obtainable by mass balance) on y-axis. The interpolated extract concentration at the concentration of the feed is the value to consider for comparing the ILs. This value is an estimation of the highest extract concentration that can be obtained in a counter-current LLX column when the extract is in equilibrium with the actual feed. The multi-component isotherms will give a clear picture of the extraction performance of the IL. However, the extract concentrations at the feed concentrations often tend to deviate from those obtainable in a counter-current LLX column due to competitive extraction.[36] A set of extremely high extract to raffinate concentration ratios, i.e. distribution coefficients, on an isotherm is an indication of a potentially impractical physical regeneration to be experienced in step 3. As soon as extraction capability of the chosen ILs is experimentally verified, they should undergo the regeneration test devised in step 3.

3.3. Step 3. Experimental evaluation of solvent regeneration

To utilize an IL in a practical LLX-based separation process, it has to be regenerated after extracting the compound of interest. One should have a certain level of confidence in deep regeneration of the ILs chosen by following steps 1 and 2, particularly when the expected final loading of the compound of interest in them is limited. The number of studies reported on regeneration of ILs is limited which implies that for a chosen IL and the compound of interest, if no regeneration study is reported, it has to be investigated experimentally. The IL solutions to be used for regeneration experiments can be prepared by simply adding a certain amount of the compound of interest to the ILs to obtain their expected final loadings after extraction. The vapor pressure of the compound of interest above a solution of it with an IL is a measure of the activity coefficient experienced by the compound of interest in that solution. The vapor pressure of a compound in a solution is a function of temperature and the composition of the solution. After the solutions of the ILs with the compound of interest are prepared, the vapor pressure of the compound of interest above them will be a function of temperature. An apparatus similar to that depicted in Figure 6 can assist with measuring the vapor pressure of the compound of interest above these solutions.

After an IL solution with the compound of interest is loaded into the three-neck flask, the air that occupies the volume above the liquid can be first removed with a vacuum pump. Due to the possibility of evaporating minor amounts of the compound of interest while the air is being removed, before increasing

Figure 6: Apparatus for measuring vapor pressure of HAc above an IL-HAc solution.

the temperature of the solution to the desired value, a sample can be taken from the liquid to determine the actual initial composition. After the desired temperature is reached, the pressure indicator will indicate the vapor pressure of the compound of interest above the solution. A sample can then be taken from the solution to determine its composition. Using Equation 3, with known P (pressure indicator value), $P_A^*\{f(T), A \text{ refers to the compound of interest}\}$ and x_A (determined composition), the activity coefficient of the compound of interest in the solution (γ_A) can be calculated. According to Figure 5, a low activity coefficient will eventually render physical regeneration of the IL impractical. However, facing impractical physical regeneration of an IL does not necessarily suggest that regeneration of the IL is impossible. What it does suggest is that the IL has to be subjected to chemical regeneration. Chemical regeneration techniques are very diverse and often tailored to a certain pair of a compound of interest and a solvent. If designed and tuned properly, they can be very effective and compete with physical regeneration procedures. Novel and elaborate chemical regeneration techniques are often proposed in the patent literature almost always for conventional solvents. Most of these techniques can be modified to work on an IL, and simplified to be practical in a laboratory.

3.4. Concluding remarks

A simple rule of thumb states that as a solvent becomes better and better in extraction, its regeneration becomes harder and harder (see Figure 2). Therefore, an ideal solvent is just strong enough to maintain a reasonable extraction capacity and not so strong that it compromises its regeneration capability. ILs are no exception, and in fact, a large number of them cannot be properly regenerated which implies that they can never make their way to a realistic separation process. The concluding note can then be the practicality of regenerating an IL has to be studied immediately after a set of simple experiments (see step 2) revealed its potential for extraction. The three-step procedure proposed in this work can be applied to any solvent selection case to ensure that the chosen solvent(s) can be utilized in a practical LLX-based separation process. The decision tree depicted in Figure 7 can assist with the regeneration study.

Figure 7: Decision tree to assist with finding a suitable regeneration procedure for a solvent to obtain a high-purity stream of the compound of interest.

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The background is a solid green color. It features several large, white, curved shapes that resemble stylized letters or organic forms. A white line with black dots runs diagonally across the upper half. Three white arrows with black outlines point in different directions: one towards the top left, one towards the top right, and one towards the bottom right. The number '7' is partially visible on the right side, rendered in white.

Recovery of
volatile fatty acids
from fermented
wastewater by
adsorption

CHAPTER

Abstract

Separation of volatile fatty acids (VFAs) from fermented wastewater is challenging, due to low VFA concentrations in mineral rich streams. As a result, separation capacity and selectivity with traditional solvents and adsorbents are both compromised. In this study, using a complex artificial model solution mimicking real fermented wastewaters, it is shown that a simple and robust adsorption-based separation technique can retain a remarkable capacity and selectivity for VFAs. Four types of polystyrene-divinylbenzene-based resins (primary, secondary and tertiary amine-functionalized, and non-functionalized) were examined as the adsorbents. The presence of chloride, sulphate and phosphate salts resulted in co-adsorption of their acidic forms HCl , H_2SO_4 and H_3PO_4 on amine functionalized adsorbents, and severely reduced the VFA capacity. With the non-functionalized adsorbent, almost no mineral acid co-adsorption was observed. This together with a high total VFA capacity of up to 76 g/kg in equilibrium with the model solution containing a total VFA concentration of 1 wt% resulted in a very high selectivity for the VFAs. Nitrogen-stripping with various temperature profiles was applied to regenerate the adsorbent, and study the potential for fractionation of the VFAs during regeneration. Butyric acid (HBu) was obtained in mole fractions of up to 0.8 using a stepwise increase in the stripping temperature from 25 °C via 120 °C to 200 °C. During four successive adsorption-regeneration cycles, no reduction in the adsorption capacity was observed.

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Nomenclature

VFA:	Volatile fatty acid
HAc:	Acetic acid
HPr:	Propionic acid
HBu:	Butyric acid
HLa:	Lactic acid
PSDVB:	Polystyrene-divinylbenzene
T, temp:	Temperature

1. Introduction

Volatile fatty acids (VFAs) are widely used chemicals, and among other applications, they serve as precursors to fuels and high-value chemical products such as polymers.[1-4] The major fraction of the global VFA demand is met by the VFAs produced through petrochemical routes.[2] However, petroleum-based routes are considered unsustainable, and therefore, recent research and development has aimed at cradle to cradle technologies such as biological production of VFAs from waste streams.[5-9] Using wastewater as fermentation feed produces broths with a much lower VFA content compared to glucose-fed fermentation broths, due to the limited carbon content of wastewater. To achieve an economical production of bio-based VFAs, implementation of a robust VFA recovery technique is inevitable. Furthermore, the presence of various ions in fermented wastewater in significant amounts must be considered when designing a downstream separation process. Na^+ , K^+ , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, Cl^- , and SO_4^{2-} are the most common ions found in fermented wastewater (see Table 1 for typical composition of fermented wastewater). Depending on the wastewater's origin and fermentation approach, the concentration of species may vary within the given ranges.

Table 1: Typical composition of fermented wastewater

Component	Chemical formula	Concentration [g/L]	pK _a
Acetate	CH_3COOH	2.5–10	4.76
Propionate	$\text{CH}_3\text{CH}_2\text{COOH}$	2.5–10	4.88
Butyrate	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	2.5–10	4.82
Lactate	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	2.5–10	3.86
Sodium	Na^+	1–5	
Potassium	K^+	1–5	
Chloride	Cl^-	1–10	
Phosphate	$\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$	1–10	
Sulphate	SO_4^{2-}	1–10	
Sulphide	S^{2-}	0.3	
Magnesium	Mg^{2+}	0.3	
Calcium	Ca^{2+}	0.3	
Ammonium	NH_4^+	0.1	
Trace elements (cations)	Co, Fe, Ni	10^{-4}	
Inert COD		1	
Microbes			

The acid content of a VFA-containing aqueous solution is a critical parameter to consider for choosing a suitable VFA separation method.[10] Since water forms the majority of fermented wastewater, the chosen method has to target the VFA molecules and limit water removal as much as possible. To separate VFAs from highly dilute aqueous streams, an affinity agent is required. Selection and design of an affinity agent is an important element of studies towards effective VFA recovery by affinity separation. A strong affinity may lead to an effective VFA

separation, but it makes recovering the VFAs from the affinity agent challenging. Both adsorption and liquid-liquid extraction have been examined as affinity separation methods for VFA recovery.[11-18] Adsorption enables separation of substances from dilute and complex solutions.[19] The effectiveness of adsorption is expressed with the term “capacity”, which is often defined as the mass of adsorbate per kilogram of adsorbent. After performing adsorption, the adsorbate has to be desorbed from the adsorbent to complete the recovery process and regenerate the adsorbent. When adsorption is applied to a complex solution such as fermented wastewater, a high selectivity of the adsorbent for the compound of interest is essential.[20]

In the literature, various adsorbents have been proposed for adsorption of carboxylic acids.[12, 17, 21-28] Primary, secondary and tertiary amines, and quaternary ammonium are the most common functional groups serving as reactive sites on these adsorbents. Quaternary ammonium-based adsorbents, also referred to as strongly basic adsorbents, are under normal fermentation conditions the only nitrogen-based adsorbents capable of recovering carboxylate anions through anion exchange.[23] The three amine forms can only adsorb carboxylic acids as charge-neutral units (either through hydrogen bonding or via proton transfer) to maintain the charge neutrality of the adsorbent phase. The pH of a VFA-containing fermented wastewater is typically 5–7, and as a result, the VFAs are mostly in their dissociated forms. Although a quaternary ammonium-based adsorbent appears beneficial for carboxylate recovery from fermented wastewater, the ion exchange makes regeneration of the adsorbent impossible without another ion exchange with the mineral acid of the replaced anion of the ammonium.[25, 29] This requires an extra chemical and processing stage, and moreover, the VFA obtained after adsorbent regeneration is not pure, but in an aqueous solution containing a significant mineral impurity.

Therefore, in this study, the use of a quaternary ammonium-based adsorbent was omitted, and adsorption of VFAs from a complex model solution mimicking fermented wastewater (composition given in Table 1) was studied with polystyrene-divinylbenzene (PS-DVB) resins which were either non-functionalized or functionalized with a primary, secondary or tertiary amine. The equilibrium selectivities and capacities of the adsorbents were determined in batch experiments. The breakthrough curves, as well as the column loadings in equilibrium with Feed were obtained in a packed bed.

With regard to regeneration of the loaded adsorbents, a few desorption techniques have been reported in the literature. They involve performing a solvent wash to recover the adsorbed organic acids from the adsorbent.[12, 24, 25, 29-33] The

solvent can be water (or steam), an alkali solution or an organic solvent (e.g. methanol). In all cases, the resulting stream has to be subjected to a post-treatment operation (e.g. distillation) to deliver a high purity organic acid stream. In this study, direct desorption of the adsorbed VFAs by nitrogen-stripping was studied as an alternative regeneration method that, after condensation of the desorbed VFAs, may yield highly concentrated VFAs. A complete process including both adsorption and desorption stages for recovery of VFAs from fermented wastewater was proposed as well.

2. Materials and methods

2.1. Chemicals

Acetic acid (HAc, >99.7%), propionic acid (HPr, >99.5%), butyric acid (HBu, >99%), potassium chloride (>99%), anhydrous sodium phosphate dibasic (>99%), and anhydrous sodium sulphate (>99%) were purchased from Sigma-Aldrich. Crystalline lactic acid (HLA, >98%) was kindly provided by Corbion. Potassium hydroxide (1 M) was supplied by Merck. All the adsorbents, Lewatit VP OC 1065 (primary amine), Amberlite IRA96 RF (secondary amine), Amberlite IRA96 SB (tertiary amine), and Lewatit VP OC 1064 MD PH (non-functionalized), were purchased from Lenntech. The water used was ultrapure (Milli-Q, with a resistance of 18.2 $\mu\Omega\cdot\text{cm}$ at 25 °C).

2.2. Model solutions

Two main model solutions were prepared for this study: a model solution for fermented wastewater referred to as “Feed”, and a more concentrated form of Feed referred to as “Concentrate” in which the concentration of each species was five times that in Feed.

Table 2: Composition of model solution representing fermented wastewater and its concentrated variety.

Solution	Concentration [wt%]				Concentration [mol/L]			pH
	HAc ^a	HPr ^b	HBu ^c	HLA ^d	KCl	Na ₂ SO ₄	Na ₂ HPO ₄	
Feed	0.25	0.25	0.25	0.25	0.05	0.05	0.1	4.98
Concentrate	1.25	1.25	1.25	1.25	0.25	0.25	0.5	4.95

^a Acetic acid

^b Propionic acid

^c Butyric acid

^d Lactic acid

Next to Feed and Concentrate, several model solutions, referred to as concentrates, were prepared by diluting Concentrate with water at Concentrate:water mass ratios of approximately 16:4, 13:8, 9:12, 4:16 and 1:90.

2.3. Experimental procedures

2.3.1. Batch adsorbent screening

To compare the capacities and selectivities of the adsorbents, Feed concentrates (see section 2.2) were used to construct competitive adsorption isotherms for the VFAs and minerals. A typical batch experiment was performed by contacting 1 g of an adsorbent (used as received, no pre-treatment) with 21 g of a Feed concentrate (both weighed on a balance with an accuracy of 0.0001 g) at room temperature (20 ± 1 °C). The exact mass of dry adsorbent was determined by correcting the initial value (~ 1 g) for the amount of moisture and preservatives. The mixtures were then stirred at >500 rpm for 1 h which was sufficient to reach equilibrium. The equilibrium concentrations were measured with HPLC and IC, and the capacities were calculated based on the differences between the initial and equilibrium contents. This method of preparing a multi-component batch isotherm was adopted from an earlier study by Zhou et al..[34]

2.3.2. Capacity determination in column

To determine the actual capacity of an adsorbent in a column after a complete breakthrough (thus in equilibrium with Feed), a glass column ($d = 2.5$ cm, $l = 6$ cm) was packed with the adsorbent as received. The adsorbent was then dried by flushing N_2 through the column at 120 °C for 3 h using the adsorbent regeneration mode of the setup depicted in Figure 1. The N_2 flow rate during the drying procedure was 0.2 L/min. Feed was then pumped through the column at room temperature (20 ± 1 °C) and 2 mL/min for >200 min which was sufficient to saturate the column with Feed. The column outlet was sampled periodically, and the samples were analysed by HPLC and IC. The amount of each species retained by the column was calculated by closing a mass balance over the fed Feed and the collected outlet samples. At the end of an adsorption experiment, before starting a desorption experiment, the column was flushed with N_2 at room temperature to drain a large fraction of Feed from the dead volume of the column. The mass of drained Feed was about twice the mass of Feed remaining in the column afterwards.

Figure 1: Schematic view of setup used for adsorbent drying, adsorption and desorption. The condenser was operated at 5 °C with water as the cooling liquid.

2.3.3. Desorption experiments

The desorption experiments were carried out by placing a weighed adsorption column containing an adsorbent in equilibrium with Feed in the adsorbent regeneration section of the setup shown in Figure 1. Several temperature profiles were applied during desorption (see Table 3).

Table 3: Temperature profiles applied for adsorption.

Temperature profile No.	Time period 1		Time period 2		Time period 3	
	Duration [min]	Temperature [°C]	Duration [min]	Temperature [°C]	Duration [min]	Temperature [°C]
1	60	180±1	-	-	-	-
2	30	120±1	50	180±1	-	-
3	180	20±1	60	120±1	40	200±1

The stripping N₂ flow rate was always set at 0.2 L/min. After completing a desorption experiment, the column was cooled down to room temperature while the N₂ flow was on. After reaching room temperature, the N₂ flow was stopped, and the difference in the mass of the column before and after desorption (typically about 5 g) was used to assist with the mass balance over each species. For each temperature profile, several condensate samples were taken to determine the VFA concentration profile in the condensate over time. The condensate samples were analysed by HPLC, representing evaporated species that were condensed in the condenser. It should be realized that not necessarily all the acids evaporated during desorption, and in addition, not all the VFAs condensed totally in the condenser. The desorption experiment performed with temperature profile 3 was chosen as an example to assess the mass balance closure during desorption. The amount of the VFAs escaping the condensate receiver through the vapour phase (see Figure 1) was calculated using the UNIFAC-Pitzer model for vapour-liquid equilibria. To determine the VFA mass which remained inside the column after the desorption procedure was complete, an alkali-wash on a sample of the regenerated adsorbent was performed with a 1 M KOH solution at a KOH solution:adsorbent mass ratio of around 15:1. The obtained alkaline phases were then analysed by HPLC for their VFA contents. A 1 M KOH solution:adsorbent mass ratio of 15:1 was sufficient for quantitative removal of the residual VFAs, as was experimentally validated with an additional wash.

2.4. Successive adsorption-desorption cycles

To examine the stability of an adsorbent over the course of successive adsorption-desorption cycles, the adsorption/desorption procedures described in sections 2.3.2 and 2.3.3 were performed consecutively to complete three cycles. The duration of desorption for each cycle was 3 h at a constant desorption temperature of 165 °C, 180 °C or 200 °C. An additional set of four successive adsorption-desorption cycles in which a 15 min water-wash (2 mL/min) was applied on the saturated column before desorption at 165 °C was performed as well. Only for this set of experiments, a 1 h water-wash (2 mL/min) was applied on the column containing fresh adsorbent before the first adsorption.

2.5. Analysis

The concentrations of HAc, HLa, HPr, HBu and $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ were measured with HPLC [Agilent Hi-Plex H column (300 × 7.7 mm) using a refractive index detector on a Agilent 1200 series HPLC system, mobile phase: 5 mM H_2SO_4 solution, column temperature: 65 °C, flow rate: 0.6 mL/min]. Cl^- and SO_4^{2-} concentrations were quantified with ion chromatography (IC) (Metrosep A Supp 16 - 150/4.0 column on a Metrohm 850 Professional IC, mobile phase: 7.5 mM Na_2CO_3 + 0.75 mM KOH solution, column temperature: 45 °C, flow rate: 0.8 mL/min). Na^+ and K^+ concentrations were measured with IC as well (Metrosep C6 - 150/4.0 column on a Metrohm 850 Professional IC, mobile phase: 1.7 mM HNO_3 + 1.7 mM dipicolinic acid solution, column temperature: 20±1 °C, flow rate: 1.0 mL/min). pH was measured with a Metrohm pH probe (6.0234.100) connected to a Metrohm 780 pH-meter.

3. Results and discussion

3.1. Batch adsorbent screening

In the batch adsorption experiments carried out with the Feed concentrates, the initial VFA and salt concentrations were varied, but their ratio was kept the same. The obtained capacities with the four adsorbents for all the species as a function of their equilibrium aqueous phase concentrations are displayed in Figure 2a to 2d. Although the analysis error was smaller than 1%, an analysis error of 1% was taken into account to calculate the error in the capacities, which was typically less than 5%, as reflected in the small error bars in Figure 2.

Figure 2: Multi-component competitive batch adsorption isotherms obtained with a Lewatit VP OC 1065 (primary amine), b Amberlite IRA96 RF (secondary amine), c Amberlite IRA96 SB (tertiary amine), d Lewatit VP OC 1064 MD PH (non-functionalized), $T = 20 \pm 1$ °C. Equilibrium concentrations of multivalent species represent the summation of the concentrations of all forms of that species present in the sample. The initial pH of the aqueous solutions was approximately 5.

The analysis of the aqueous phases obtained after adsorption showed that neither Na^+ nor K^+ was adsorbed by any of the adsorbents (see Table 4) which implies that the adsorbed mineral anions must have been adsorbed together with H^+ to obey the charge neutrality constraint. This implies that the deprotonation equilibria of the VFAs shifted, and the remaining VFAs in the aqueous phases were mostly present as carboxylate salts. The chloride, sulphate and phosphate loadings on the amine-functionalized adsorbents were very high, even exceeding capacities of 200 g/kg dry adsorbent for H_3PO_4 . Their capacity for H_2SO_4 was somewhat lower, slightly decreasing with increasing aqueous concentration after reaching a maximum of about 70 g/kg dry adsorbent, likely due to competitive adsorption. Competitive adsorption similarly affected the HCl isotherm obtained with the primary amine-based adsorbent. The major drawback of mineral acid co-adsorption was the remarkably lower capacity of the amine-based adsorbents for the VFAs. The mineral acid co-adsorption by the amine-based adsorbents was in fact so large that using idealized model solutions solely containing the VFAs may well lead to completely different findings.[30, 35] Besides losing capacity for the VFAs, mineral acid co-adsorption may result in problematic adsorbent regeneration, and if not removed, the mineral acids may accumulate on the adsorbent over time leading to a reduced adsorbent life time. Figure 2 also shows that the primary amine-based adsorbent has the highest H_3PO_4 capacity which implies that it might be a potential phosphate recovery agent in the presence of a H^+ source.

Table 4: Analysis of aqueous phases obtained after batch adsorption experiments for Na^+ and K^+ .

Batch adsorption with Concentrate:Feed (cation)	Lewatit VP OC 1065 (primary amine)		Amberlite IRA96 RF (secondary amine)		Amberlite IRA96 SB (tertiary amine)		Lewatit VP OC 1064 MD PH (non-functionalized)		Error [g]
	Mass before [g]	Mass after [g]	Mass before [g]	Mass after [g]	Mass before [g]	Mass after [g]	Mass before [g]	Mass after [g]	
16:4 (Na^+)	0.514	0.517	0.511	0.52	0.501	0.505	0.509	0.519	± 0.005
16:4 (K^+)	0.147	0.148	0.146	0.148	0.142	0.143	0.144	0.144	± 0.002
4:16 (Na^+)	0.132	0.138	0.132	0.136	0.128	0.133	0.156	0.166	± 0.002
4:16 (K^+)	0.038	0.039	0.038	0.038	0.036	0.038	0.044	0.044	± 0.001

As can be seen in Figure 2, the highest VFA capacities were achieved with the non-functionalized adsorbent (Figure 2d). The VFA molecules interact with the non-functionalized adsorbent through the hydrogen bond- π interactions between their carboxyl groups and the adsorbent's aromatic rings, and the hydrophobic interactions between the hydrocarbon chain and the adsorbent surface. With an increase in the length of the hydrocarbon chain, the hydrophobic section of the VFA molecule becomes larger resulting in a favoured adsorption. A similar trend was previously observed with extraction of VFAs using physical (non-complexing) solvents.[36] This behaviour was observed for the amine-based adsorbents in Figure 2 as well, which may be explained by the amine-based adsorbents sharing the same hydrophobic polymer matrix of the non-functionalized adsorbent, and thus having a similar hydrophobic interaction with the hydrocarbon chain. No measurable capacity for the strong acids H_2SO_4 and HCl was observed with the non-functionalized adsorbent, as they were fully dissociated. For the weaker mineral acid H_3PO_4 , a limited adsorption capacity was observed which can be explained with its dissociation equilibrium enabling some undissociated H_3PO_4 to adsorb. Where the interaction of the strong mineral acids with amines is supported through ion-pair formation with the lone pair of nitrogen [37], the non-functionalized adsorbent lacking these nitrogen lone pairs does not adsorb any strong mineral acid.

The high selectivity of the non-functionalized adsorbent for the VFAs makes it the most promising candidate for VFA separation from a VFA-containing fermented wastewater, and therefore, further studies were carried out with this adsorbent.

3.2. Capacity determination in column

The concentration profile of the eluent leaving the column packed with the non-functionalized adsorbent is shown in Figure 3.

As can be seen in Figure 3, after about 22 bed volumes, the column was saturated with all the adsorbates. A fast breakthrough was observed for HAc , as the adsorbent capacity for it was very limited (see Figure 3a and Table 5). The breakthroughs of HPr and HBU were slower due to the higher capacity of the adsorbent for them (see Figure 3a and Table 5). The sudden and significant drop in Cl^- concentration is an indication of the presence of Cl^- in the fresh adsorbent (Figure 3b). The aqueous solutions obtained after the batch adsorption experiments with the non-functionalized adsorbent contained extra Cl^- as well, and as indicated by the extra amounts of Na^+ in Table 4, Na^+ was the counter-ion. HLa , SO_4^{2-} and HPO_4^{2-} left the column with almost no interaction with the adsorbent. The capacities reported in Table 5 have been determined five times under identical conditions, and the reported error in Table 5 is the standard deviation of these five results.

Figure 3: Breakthrough curves for VFAs (a) and mineral acids (b) using an adsorption column packed with 6.15 g non-functionalized adsorbent, Feed flow rate: 2 mL/min, $T = 20 \pm 1$ °C.

Table 5: Capacities determined after complete breakthrough in column ($T = 20 \pm 1$ °C) compared with batch adsorption capacities.

Adsorbed compound	Column capacity [g/kg adsorbent, ± 3.5 %]	Batch capacity ^a [g/kg adsorbent]
HLa	0.0	9.7
HAc	1.5	12.5
HPr	13.3	26.5
HBu	60.7	65.2
H_3PO_4	0.0	13.4
H_2SO_4	0.0	0.0
HCl	0.0	0.0

^a Derived from Figure 4.

Due to the complexity of the aqueous solutions used in the batch experiments, and the competitive nature of multicomponent adsorption, the equilibrium aqueous concentrations varied from those in Feed. In the batch experiment that resulted in the equilibrium VFA concentrations closest to those in Feed (indicated with open symbols in Figure 4, a magnified view of Figure 2d), the corresponding mineral content was higher than that in Feed. This induced a salting-out effect resulting in VFA capacities higher than those obtainable in a column experiment. [38, 39] The capacities obtained with this batch experiment are compared with those obtained with a column experiment in Table 5. Although the absolute values of the adsorption capacities obtained in the column experiment varied from those obtained with the batch experiment, the conclusions regarding capacity and selectivity for the VFAs remained unchanged.

Figure 4: Batch experiments with non-functionalized adsorbent. The figure is very similar to Figure 2d. It now indicates deviation of the equilibrium concentrations (open symbols) from the concentrations in Feed.

3.3. Adsorbent regeneration

In order to produce concentrated VFA streams, performing a water- or strong alkali-wash on the adsorbent is not suitable, as the resulting stream will either have a large water content or contain carboxylate salts rather than free VFAs. [24, 25, 29-32] Therefore, adsorbent regeneration methods that involve a thermal operation have been investigated instead.[12, 40-42]

In the first desorption experiment (temperature profile 1, see Table 3), a saturated column (in equilibrium with Feed) was heated to 180 °C while being flushed with N₂ (at 0.2 L/min) for 1 h to investigate the feasibility of thermal regeneration. The VFA concentration profiles in the condensate in time are displayed in Figure 5.

Figure 5: Condensate concentration profile in time by applying temperature profile 1, adsorbent in column: 6.15 g, N_2 flow rate: 0.2 L/min.

As can be clearly seen in Figure 5, HPr and HBu concentrations increased simultaneously in time, following the same order seen in their column capacities and reaching a cumulative concentration of about 33 wt%. Considering that their cumulative concentration in Feed was only 0.50 wt%, the VFA concentration in the condensate exhibited a strong increase. The limited capacity of the adsorbent for HAc limited its concentration in the condensate. Integrated over time, the VFA concentration in the condensate amounted approximately 10 wt%. Thus, the selective adsorption of the VFAs led to a significant increase in the VFA concentration. The majority of the water was not adsorbed on the surface of the pores, but remained in the liquid phase inside the pores of the adsorbent. The continuous rise in the VFA concentrations during desorption was due to a faster evaporation of the non-adsorbed pore-water and its lower boiling point. This corresponds to a gradual temperature rise inside the column to eventually reach the set point of 180 °C. After 60 min, no condensate was collected anymore indicating that all the water and VFAs evaporated from the column, and therefore, the desorption procedure was stopped. A KOH-wash was then performed on a sample of the regenerated adsorbent to determine the residual adsorbate amounts in the column (see section 2.3.3), and hence, examine desorption efficiency. The obtained results are shown in Table 6.

Table 6: Condensate composition to be obtained by complete condensation of vapours after applying temperature profile No. 1 on Lewatit VP OC 1064 MD PH (non-functionalized adsorbent).

Species in Feed	Species on adsorbent and in condensate	Loading on adsorbent prior to desorption [g/kg dry adsorbent]	Cumulative concentration of all possible forms ^a [wt%]		Percentage desorbed ^b [%]
			Feed	Condensate	
HL _a /La ⁻	HL _a	0	0.25	0	-
HAc/Ac ⁻	HAc	1.5	0.25	0.45	100
HP _r /P _r ⁻	HP _r	13.3	0.25	1.77	100
HBu/Bu ⁻	HBu	60.7	0.25	7.27	99
PO ₄ ³⁻ /HPO ₄ ²⁻ /H ₂ PO ₄ ⁻ /H ₃ PO ₄	H ₃ PO ₄	0	0.96	0	-
SO ₄ ²⁻ /HSO ₄ ⁻ /H ₂ SO ₄	H ₂ SO ₄	0	0.48	0	-
Cl ⁻ /HCl	HCl	0	0.18	0	-
Water	Water (in pores)	926.9	96.47	90.5	100

^a Assuming all the VFAs and water desorbed by applying temperature profile 1 are condensed to form a single condensate.

^b Determined by performing a KOH-wash on the adsorbent after desorption.

As can be seen in Table 6, desorption using temperature profile 1 provides a significant purification step by which the total VFA concentration increases from 1 wt% to around 10 wt%, and the obtained condensate is solely composed of water, HAc, HPr and HBu, and it is essentially free of minerals. The adsorbed HAc, HPr and HBu were completely recovered from the adsorbent. The easy and complete thermal removal of the adsorbed VFAs from the non-functionalized adsorbent is an indication of the weak nature of the adsorbent–VFA interaction.

To isolate considerable fractions of the adsorbed VFAs in higher concentrations in the condensate, the use of temperature profiles with additional temperature increments for desorption was studied. By applying temperature profile 2, a significant amount of the water was evaporated at 120 °C in the first 30 min, while the VFA concentrations in the condensate stayed minimal. After 30 min, the temperature was raised to 180 °C to completely desorb the VFA-rich fraction. To examine the possibility of removing a fraction of the water at room temperature and improving the VFA-rich fraction of the condensate, temperature profile 3 was applied. Figure 6 shows the VFA concentration profile of the condensate obtained with temperature profiles 2 and 3.

Figure 6: Condensate concentration profile in time by applying temperature profiles 2 or 3, adsorbent in column for temperature profiles 2: 5.91 g; for temperature profiles 3: 5.76 g, N_2 flow rate: 0.2 L/min.

As can be seen in Figure 6, significantly higher VFA concentrations of up to 83.7 % for HBu were obtained by applying temperature profile 2. Temperature profile 3 boosted the VFA concentration profile in the condensate even further. During the first 180 min, no condensate was collected. However, measuring the mass of the column after 180 min indicated a significant mass loss, and if all associated with water, it accounted for around 10 wt% of the initial water mass. The HAc

and HPr concentrations in the condensate peaked at 270 min, whereas the HBU concentration continuously increased in time. This implies that, with a proper temperature profile, it may be possible to fractionate the VFAs during desorption. An additional stationary temperature step between the boiling points of HPr and HBU, and a proper column design can further improve fractionation of the VFA-rich fraction.

The mass balance over desorption while applying temperature profile 3 (see section 2.3.3) resulted in 93.5 % closure for HBU and 89.7 % closure for HPr, which is acceptable considering the vapour phase above the collected condensate was approximated with a VLE model.

Based on the results presented so far, it can be concluded that a single adsorption-desorption cycle in which the high temperature exposure duration of the adsorbent is <50 min (50 min for temperature profile 2 and 40 min for temperature profile 3) is promising for VFA recovery from a VFA-containing fermented wastewater.

3.4. Adsorbent life cycle assessment

To further assess the performance and stability of the adsorbent over several cycles of use, three series of three adsorption-desorption cycles were performed with desorption at 165, 180 or 200 °C for 3 h. The capacities were calculated with the procedure described in section 2.3.2. The obtained results are depicted in Figure 7. As can be seen in Figure 7, the adsorbent lost a significant part of its capacity after each adsorption-desorption cycle. A similar behaviour is often observed for other adsorbents reported in the literature.[25, 43]. However, Figure 7 also suggests that there is no correlation between capacity loss and temperature, and therefore, thermal degradation of the adsorbent was most likely not the reason behind the capacity loss. A potential reason for capacity loss could be deposition of the salts inside the pores of the adsorbent. During adsorption, the salts enter the pores without being adsorbed, and upon evaporation of water and the VFAs, they deposit inside the pores blocking the sites for the VFA in the next cycle. To verify this hypothesis, an additional set of adsorption-desorption cycles was performed with a water-wash stage prior to desorption at 165 °C (see section 2.3.4). The results are depicted in Figure 8.

Figure 8 shows that indeed short water-wash stages between adsorption-desorption cycles stopped capacity loss. However, during a water-wash stage that took about 15 min, approximately 5 wt% of the adsorbed HBU and 20 wt% of the adsorbed HPr was removed from the column. Optimization of the water-wash stages can reduce the VFA losses without compromising the stability. As the VFA removal from the column by water was almost linear with time (at a constant water

Figure 7: Capacity percentage retained on non-functionalized adsorbent over three successive adsorption-desorption cycles with a desorption temperature of 165, 180 or 200 °C.

flow), shortening the duration of a water-wash stage by more than a factor of two to 6 min, just enough to fill the column, appears well possible. The stable performance over four adsorption-desorption cycles indicating the potential for an extensive operation, high selectivity and low price (about 15 euro/L_{adsorbent}, bulk price) make the non-functionalized adsorbent ideal for VFA recovery from highly diluted and complex aqueous streams such as fermented wastewater. The adsorbent did not exhibit any capacity loss over four adsorption-desorption cycles which is an indication of no adsorbent loss. This is clearly an advantage for this process compared to liquid-liquid extraction-based processes where entrainment always causes small solvent losses and raffinate impurities.

Figure 8: Capacity of non-functionalized adsorbent during four successive adsorption-desorption cycles with water-wash and a desorption temperature of 165 °C.

Conclusions

Adsorption of volatile fatty acids (VFAs) from a complex solution mimicking fermented wastewater was studied using amine-functionalized polystyrene-divinylbenzene-based (PSDVB) resins as well as a non-functionalized PSDVB resin. The non-functionalized resin showed a very high selectivity for VFAs, while the amine-functionalized resins adsorbed mineral acids preferentially. Regeneration of the non-functionalized resin with a short water-wash stage followed by a temperature-profiled evaporation enabled fractionation of VFAs, and butyric acid was obtained with purities of up to 91 wt% (starting with a feed concentration of only 0.25 wt%). The non-functionalized resin proved very stable over four adsorption-desorption cycles each of which included a short water-wash stage between adsorption and desorption stages. Overall, the non-functionalized resin utilized in the proposed adsorption-desorption process can deliver high purity bio-based VFA streams in a sustainable manner, without any risk of solvent leaching associated with liquid-liquid extraction-based processes.

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The following calculations are based on a simple drying scheme presented in Figure S1. The heat-exchanger intends to recover a part of the latent heat of vaporization of water.

Certain assumptions had to be made to enable the calculations. The following is the list of assumptions:

- Water removal takes place at 70 °C, so $T_{Co} = 70$ °C.
- The vapor pressure of water in the outlet stream of the column is equal to the saturation pressure of water at 70 °C.
- The stripping gas is dry air at an inlet temperature (T_i) of 25 °C.
- Since, prior to water removal, the adsorption procedure takes place at room temperature, $T_c = 25$ °C.
- The heat-exchanger is efficient enough to achieve a temperature difference of 10 °C between the hot and cold fluids which implies that $T_{HE} = T_{Co} - 10 = 60$ °C.
- Under the applied conditions, air–water vapor mixtures are described as ideal gases.

2. Calculations

The procedure followed to estimate the cost of water removal per ton of produced VFAs is given below. The calculations are based on the above assumptions.

$$P_w^{\text{sat}}(70^\circ\text{C}) = 31.26 \text{ kPa} \quad (\text{S1})$$

Therefore, at a total pressure of 1 bar:

$$y_w^{\text{id}}(70^\circ\text{C}) = \frac{P_w^{\text{sat}}(70^\circ\text{C})}{P} = \frac{31.26 \times 10^3}{1 \times 10^5} = 0.3126 \text{ mol}_{\text{water vapor}}/\text{mol}_{\text{air-water vapor mixture}} \quad (\text{S2})$$

The amount of air needed to remove the water and result in a stream saturated with water vapor at 70 °C is:

$$m_{\text{air}}^{\text{eq}} = \frac{m_w}{M_w} \times \frac{y_{\text{air}}^{\text{id}}}{y_w^{\text{id}}} \times M_{\text{air}} = \frac{4.7821}{18.02} \times \frac{1-0.3126}{0.3126} \times 28.96 = 16.90 \text{ g} \quad (\text{S3})$$

The sensible heat needed to increase the temperature of the water from T_c at 20 °C (293.15 K) to T_{c_o} at 70 °C (343.15 K) is:

$$Q_1 = \frac{m_w}{M_w} \int_{293.15}^{343.15} c_{p_{\text{molar},w}} dT = \frac{4.7821}{18.02} \times \left(A(343.15-293.15) + \frac{B}{2}(343.15^2 - 293.15^2) + \frac{C}{3}(343.15^3 - 293.15^3) + \frac{D}{4}(343.15^4 - 293.15^4) \right) = 1.0 \text{ kJ} \quad (\text{S4})$$

A, B, C and D are taken from Chemical Properties Handbook by C. L. Yaws (1999). The latent heat of the water when it evaporates at T_{c_o} (70 °C, 343.15 K) is:

$$Q_2 = \frac{m_w}{M_w} A \left(1 - \frac{T}{T_c} \right)^n = \frac{4.7821}{18.02} \times A \times \left(1 - \frac{343.15}{T_c} \right)^n = 10.8 \text{ kJ} \quad (\text{S5})$$

T_c and n are taken from Chemical Properties Handbook by C. L. Yaws (1999). The total energy required to evaporate the water is then:

$$Q_T = Q_1 + Q_2 = 1.0 + 10.8 = 11.8 \text{ kJ} \quad (\text{S6})$$

The heat transferred to the dry air stream in the heat-exchanger increases its temperature from T_i at 20 °C (293.15 K) to T_{HE} at 60 °C (333.15 K). The amount of this heat is:

$$Q_{\text{air}} = \frac{m_{\text{air}}^{\text{eq}}}{M_{\text{air}}} R \int_{293.15}^{333.15} \frac{c_{p_{\text{molar},\text{air}}}}{R} dT = \frac{16.90}{28.96} \times 8.314 \times \left(A(333.15-293.15) + \frac{B}{2}(333.15^2 - 293.15^2) + \frac{C}{3}(333.15^3 - 293.15^3) - D(333.15^4 - 293.15^4) \right) = 0.7 \text{ kJ} \quad (\text{S7})$$

A, B, C and D are taken from Introduction to Chemical Engineering Thermodynamics (7th edition). The additional energy to be supplied to the dry air stream by the heater is then the difference between Q_T and Q_{air} :

$$Q_{\text{heater}} = Q_T - Q_{\text{air}} = 11.8 - 0.7 = 11.1 \text{ kJ} \quad (\text{S8})$$

Using the equation previously used to calculate Q_{air} this time with Q_{heater} , T_{Cin} can be calculated to be about 665 °C. It should be noted that such a high temperature is a result of a limited amount of dry air that is supplied to ensure that the air leaving the column is saturated with water. Q_{heater} can be calculated per kilogram of the VFA mixture that can be produced by this water removal procedure:

$$Q_{\text{heater}}^{\text{VFAs-based}} = \frac{Q_{\text{heater}}}{m_{\text{HAc}} + m_{\text{HPr}} + m_{\text{HBu}}} = \frac{11.1}{0.0201 + 0.0811 + 0.3258} = 26 \text{ kJ/g or MJ/kg} \quad (\text{S9})$$

The specifications of the air-water vapor stream that leaves the heat-exchanger was calculated by simulating the water removal scheme depicted in Figure S1 with Aspen Plus. The results show that this stream doesn't lose much energy after heat-exchanging with the dry air stream. In fact, its temperature decreases from 70 °C to about 69 °C and only about 2% of its water vapor content condenses.

3. Discussion

Based on the calculations presented above, it can be concluded that the energy demand of production of water-free VFA mixtures by the adsorption-based process proposed in chapter 7 can be up to $\sim 25 \text{ MJ/kg}_{\text{VFAs mixture}}$. This value can be compared with the heat of combustion of HBU $\sim 23 \text{ MJ/kg}_{\text{HBU}}$. It should be noted that such a comparison is not accurate enough to judge whether this procedure is economically appealing or not, as the commercial value of VFAs is much greater than their combustion value. Since dry air was used to evaporate the water, it was not possible to recover a large fraction of the energy content of the air-water vapor stream. Applying vapor recompression on the air-water stream after it leaves the heat-exchanger can make its energy content more accessible for another thermal operation.

Q_{heater} can be supplied by low-pressure saturated steam to be cost-effective. Using 15 psig saturated steam at a cost of about 1 $\$/\text{klb}_{\text{steam}}$ and assuming that all the steam can be condensed to maximize its energy output, the water removal cost will be under 50 $\$/\text{ton}_{\text{VFAs mixture}}$. Considering a price of around 1000–1500 $\$/\text{ton}$ for HBU and the fact that the raw materials for waste-derived VFAs are essentially free of charge, 50 $\$/\text{ton}_{\text{VFAs mixture}}$ is not such a high number. Naturally, the VFA fraction that contains HPr and HBU needs to undergo further purification which will raise the separation cost. Overall, the remarkable separation performance of this process and the reasonable preliminary values that were obtained for its most energy-intensive operation certainly suggest that it can be considered for further improvement.

Summary,
conclusions and
outlook

CHAPTER

8

1. Summary and conclusions

The aim of this thesis is to provide a practice to enable separation of volatile fatty acids (VFAs) from fermented wastewater. Two affinity separation techniques, namely liquid-liquid extraction (LLX) and adsorption, were initially proposed as the candidates which were to be assessed and compared. A sample of an actual fermented wastewater was represented by a few model solutions containing various VFAs and salts.

1.1. Part 1. Liquid-liquid extraction

The first candidate to examine was LLX. The practice of LLX can be seen as migration of a VFA from its home solution into a solvent, followed by removing it from the solvent to obtain a high purity VFA stream and reuse the solvent. This simple concept is the core of all elaborate LLX-based processes designed to meet various demands imposed by the nature of the carboxylic acid and its home solution.

To cover a wide range of basic and modified LLX-based practices involving carboxylic acids, Chapter 2 provides an overview on a large collection of studies reported as journal articles or patents. A comprehensive set of energy demand calculations provided a tool to assess economic feasibility of a selection of practices. To meet the selection criterion, a LLX-based practice had to be a complete carboxylic acid recovery process introducing a remarkable novelty to facilitate either extraction or solvent regeneration. The initial carboxylic acid concentration of the selected processes was then lowered to 1 wt% to see whether they can separate carboxylic acids from fermented wastewater in an economically desired fashion or not. A final carboxylic acid concentration of 99.7 wt% was set as the target. Most of the processes that were designed for the higher side of the concentration range ceased to be feasible when applied to a feed as dilute as fermented wastewater, due to the energy penalty imposed by evaporation of the extra water. Another outcome of this chapter was that a combined application of a low-boiling organic solvent and a CO₂-switchable solvent in a LLX-based practice can efficiently recover carboxylic acids from their dilute aqueous streams.

The ionic liquid [P_{666,14}][Phos] is proven promising for extraction of carboxylic acids in the literature. In Chapter 3, this ionic liquid was used to extract lactic, acetic, propionic and butyric acids from a complex model solution prepared to represent fermented wastewater. The extraction mechanism induced by [P_{666,14}][Phos] proved very similar to that induced by the benchmark molecular solvent trioctylamine (TOA) in n-octanol. Since, for this mechanism to proceed, the existence of molecular carboxylic acids is necessary, lowering the pH of the aqueous solution

can significantly improve extraction. Co-extraction of the mineral anions together with the H^+ originating from the VFAs as a charge neutral acidic unit reduced the selectivity of the solvents for the VFAs. $[P_{666,14}][Phos]$ exhibited a higher extraction capacity and selectivity than that of the benchmark molecular solvent.

In Chapter 4, acetic acid (HAc), representing VFAs, was extracted from a fermented wastewater model solution. $[P_{666,14}][Phos]$ was superior to the benchmark molecular solvent in terms of extraction capacity and selectivity. Extraction of carboxylic acids is facilitated in the presence of CO_2 as a result of acidification of the aqueous solution. The ionic liquid further outperformed the molecular solvent when VFA extraction was boosted by pressurized CO_2 . The improvement in the extraction capacity of the ionic liquid was higher than what had been predicted suggesting that CO_2 had most likely altered some of the physical properties of the ionic liquid. This implies that pressurized CO_2 may improve extraction of other compounds by this ionic liquid too.

Chapter 5 explored various techniques to regenerate $[P_{666,14}][Phos]$ and recover the extracted VFAs. HAc represented VFAs for this chapter. Unfortunately, it turned out that stripping with an inert gas at a reduced pressure or reactive regeneration by esterification were not capable of achieving a complete regeneration. Back-extraction of the VFAs from $[P_{666,14}][Phos]$ with a KOH solution was so successful that, for this thesis, it has been the standard laboratory method for determination of the ionic liquid's VFA loading. The drawback of this method is production of potassium carboxylate salts rather than free VFAs. To maintain a successful back-extraction and obtain free VFAs, the KOH solution was replaced with an aqueous solution of a volatile alkali, namely ammonia or trimethylamine (TMA). Both of these alternatives were capable of performing a successful back-extraction. However, the complexes of ammonia with propionic and butyric acids are irreversibly dehydrated to propionamide and butyramide at the temperatures needed for their decomposition. This made TMA the ultimate choice of volatile alkali for regeneration of the ionic liquid. Since the product stream of decomposition of TMA-VFA complexes is a gaseous mixture of TMA and VFAs, an entrainer has to be introduced to capture the VFAs with no interaction with TMA. This necessitates an extra distillation column to separate the VFAs from the entrainer. Chapters 3 to 5 describe the effort put to improve extraction of VFAs with an ionic liquid and regenerate the resulting loaded ionic liquid. A remarkable improvement was achieved in extraction specially in the presence of pressurized CO_2 . However, regeneration of the ionic liquid was challenging, and only a complex procedure of back-extraction with a TMA solution and decomposition of the forming complexes was successful. This procedure adds the following extra unit operations to the rather simple two-column operation shown in Figure 1 (see Figure 2):

- An extra extraction column for back-extraction
- A distillation column for recovering TMA from the ionic liquid
- A distillation column for separation of the entrainer from the VFAs

* Co-extracted

Figure 1. A simple hypothetical procedure for a liquid-liquid extraction operation to obtain highly concentrated VFAs. The solvent has a higher boiling point than that of VFAs and water.

The process depicted in Figure 2 is so complicated that it might be practically unfavorable for recovery of VFAs from fermented wastewater. On a bigger picture, it seems that the approach taken for this thesis to investigate the use of an ionic liquid for separation can be improved to enable a future researcher to simultaneously study extraction and solvent regeneration. Chapter 6 provides an alternative approach aiming at a substantial improvement.

Figure 2. Schematic view of a LLX-based separation process employing $[P_{666,14}][Phos]$ as the solvent and TMA-assisted back-extraction for solvent regeneration.

Chapter 6 evaluates the experimental approach taken for chapters 3 to 5. An alternative approach for an experimental work involving extraction with an ionic liquid is given. A mathematical demonstration of practicality/impracticality of such an experimental work is provided too. Since an ionic liquid does not have any vapor pressure, regenerating it in a distillation column to achieve a deep recovery of the solute it carries is impractical. Any attempt to perform a deep recovery will express itself as a drastic increase in the temperature of the ionic liquid in the reboiler, and eventually degrade it. The provided mathematical method describes this impracticality as an unreasonably high reboiler temperature, higher than the degradation temperature of the ionic liquid to be regenerated.

1.2. Part 2. Adsorption

Adsorption was the second candidate to study. The affinity needed to adsorb VFAs from an aqueous solution is induced by a solid, namely an adsorbent, often immobilized in a column. The following step, referred to as desorption, removes the adsorbed VFAs from the adsorbent and prepares it to be reused. To avoid transportation of the adsorbent, an adsorption-based operation is intrinsically semi-continuous, and performed with multiple columns undergoing adsorption or desorption at the same time.

Chapter 7 explores the principles of adsorption of the VFAs from the complex model solution containing lactic, acetic, propionic and butyric acids and salts. Four adsorbents including a primary, secondary or tertiary amine supported on a crosslinked polystyrene support, and the support itself were tested for their adsorption capacity and selectivity. The support, referred to as the non-functionalized adsorbent, outperformed the others by having no capacity for mineral acid units, which in turn gave it an excellent selectivity for acetic, propionic and butyric acids. The mineral acid units formed as pairs of the salt-originating anions and the VFA-originating H^+ . Further adsorption and desorption experiments in a column proved that the non-functionalized adsorbent was very stable. Temperature-profiled desorption resulted in formation of three condensate fractions:

- Fraction 1. A mixture of water and acetic acid to be returned to fermentation for acetic acid to undergo chain elongation to propionic and butyric acids
- Fraction 2. A mixture of propionic and butyric acids to be distilled to obtain two pure streams
- Fraction 3. A pure stream of butyric acid to merge with that obtained with distillation

Chapter 7 includes an appendix providing a brief energy-ordinated evaluation of the proposed adsorption-desorption scheme. The energy demand of evaporation of water when a heat exchanger recovers a fraction of its latent heat of vaporization is about $15 \text{ MJ/kg}_{\text{VFAs mixture}}$ costing under $50 \text{ \$/ton}_{\text{VFAs mixture}}$.

2. Outlook

Recovery of waste-derived volatile fatty acids (VFAs) from fermentation broths was thoroughly studied in this thesis. Since, VFAs are currently among bulk petrochemicals, to ever consider waste-derived VFAs as alternatives, an efficient recovery process has to be proposed. The depth of this need for an efficient recovery process becomes more clear by realizing that their cumulative concentration in fermented waste streams can barely exceed 1 wt%, plus they are accompanied by minerals. Two affinity separation techniques, liquid-liquid extraction (LLX) and adsorption that have passed their test on robustness and efficiency over many years, were to address this recovery challenge in this thesis. An efficient extraction of VFAs from fermented wastewater was so demanding that it overshadowed assessment of regeneration of the extraction solvent, an ionic liquid. Unfortunately, regeneration of this ionic liquid turned out to be as demanding as extraction. The only regeneration technique that could deliver a completely regenerated ionic liquid and keep the VFAs intact was back-extraction with a volatile alkali solution and thermal decomposition of the VFA-alkali complexes. A simplified sequence of this recovery process is as follows:

- Extraction of VFAs with an ionic liquid
- Back-extraction of the extracted VFAs from the ionic liquid with a volatile alkali solution
- Thermal decomposition of the VFA-alkali complexes in the presence of an entrainer to capture the VFAs and release the volatile alkali
- Separation of the entrained VFAs from the entrainer by distillation to obtain a product stream and recycle the entrainer

Such a complex process might never be a worthy competitor to well-optimized petrochemical routes. On the plus side, it is applicable to recovery of non-volatile carboxylic acids from fermentation broths as well. Thermal decomposition of the complexes of a non-volatile carboxylic acid and a volatile alkali can even be performed in the absence of an entrainer.

Adsorption with a non-functionalized cross-linked polystyrenic resin was very successful in isolating VFAs from fermented wastewater with practically no interaction with its mineral content. Temperature-profiled desorption of the adsorbed VFAs enabled fractionation of the VFAs mixture itself. A high-purity butyric acid stream and a mixture of propionic acid and butyric acid were the product streams. When the VFAs are treated as final products, the propionic acid and butyric acid mixture has to undergo distillation. Unfortunately, the non-functionalized adsorbent retained a significant amount of water together with the

adsorbed VFAs. Although extremely selective for VFAs when processing a mixture of VFAs and minerals, such a high water uptake imposes a significant energy demand on this adsorption-based separation process. Other non-functionalized cross-linked polystyrenic resins with a smaller pore volume might reduce the water uptake during adsorption and consequently lower the energy demand of desorption.

Samenvatting en conclusie

Het doel van het onderzoek in deze thesis is om een methode te ontwikkelen die het mogelijk maakt om vluchtige vetzuren (Volatile Fatty Acids, VFAs) te scheiden van gefermenteerd afvalwater. Initieel werden twee technieken gekozen, die beide gebaseerd zijn op een verschil in affiniteit, namelijk vloeistof-vloeistof extractie (liquid-liquid extraction, LLX) en adsorptie. Deze technieken werden onderzocht en vergeleken. Enkele modeloplossingen van echt gefermenteerd afvalwater werden samengesteld uit verschillende VFAs en zouten.

Deel 1. Vloeistof-vloeistof extractie (liquid-liquid extraction, LLX)

De eerste techniek die onderzocht werd was LLX. Het principe van LLX kan worden gezien als een migratie van een VFA vanuit de originele oplossing naar een oplosmiddel, waarna het weer verwijderd wordt uit het oplosmiddel om zo een VFA stroom te krijgen met een hogere concentratie en daarnaast het oplosmiddel te kunnen recycleren. Dit eenvoudige concept vormt de basis van alle uitgebreide processen die op LLX gebaseerd zijn en ontworpen zijn om aan de verschillende voorwaarden te voldoen die opgelegd zijn door de aard van de vetzuren en die van de oorspronkelijke oplossing waarin ze voorkomen.

Om het brede scala aan eenvoudige en gemodificeerde processen die op LLX gebaseerd zijn en betrekking hebben op carbonzuren uiteen te zetten, biedt hoofdstuk 2 een overzicht van een grote verzameling aan studies die in artikelen of patenten gepubliceerd zijn. Door middel van uitgebreide berekeningen van de energiebehoefte, kon de economische haalbaarheid van een selectie van processen geëvalueerd worden. Om aan het selectiecriterium te voldoen moest het op LLX gebaseerde proces voor een volledige terugwinning van het carbonzuur kunnen zorgen. Daarnaast moest het proces op een innovatieve manier de extractie of de regeneratie van het oplosmiddel mogelijk maken. De beginconcentratie van het carbonzuur was voor de geselecteerde processen verlaagd naar 1 wt% om na te gaan of het door middel van het proces mogelijk is om op economisch gunstige wijze carbonzuren te scheiden van gefermenteerd afvalwater. De productstroom van het proces moest 99.7 wt% carbonzuur bevatten. De meeste processen die ontworpen waren voor het scheiden van stromen met hogere concentraties waren niet meer economisch gunstig wanneer ze werden toegepast op een voedingsstroom die zo verdund was als gefermenteerd afvalwater. Dit wordt veroorzaakt door de extra energie die benodigd is voor het verdampen van de grotere hoeveelheid water. Een ander resultaat van dit hoofdstuk was dat een gecombineerde toepassing van een laagkokend organisch oplosmiddel en een 'CO₂-switchable' oplosmiddel in een proces dat op LLX gebaseerd is, effectief de carbonzuren kan winnen uit hun

verdunde waterige stromen.

In de literatuur is bewezen dat de ionische vloeistof (ionic liquid) $[P_{666,14}][Phos]$ veelbelovend is voor de extractie van carbonzuren. In hoofdstuk 3 is deze ionische vloeistof gebruikt om melkzuur, azijnzuur, propionzuur en boterzuur te extraheren uit een complexe modeloplossing van gefermenteerd afvalwater. Het door $[P_{666,14}][Phos]$ geïnduceerde extractiemechanisme bleek sterk gelijkend aan het mechanisme dat geïnduceerd wordt door het moleculaire referentie-oplosmiddel trioctylamine (TOA) in n-octanol. Omdat voor het plaatsvinden van dit mechanisme de aanwezigheid van moleculaire carbonzuren vereist is, kan het verlagen van de pH van de waterige oplossing de extractie significant verbeteren. Co-extractie van de minerale anionen met de H^+ afkomstig van de VFAs, samen een ladingneutrale zure component, verlaagde de selectiviteit van de oplosmiddelen voor de VFAs. De extractie capaciteit en de selectiviteit van $[P_{666,14}][Phos]$ was hoger dan die van het referentie-oplosmiddel.

In hoofdstuk 4 werd azijnzuur (HAc), als modelcomponent voor VFAs, geëxtraheerd uit een modeloplossing van gefermenteerd afvalwater. In termen van extractiecapaciteit en selectiviteit was $[P_{666,14}][Phos]$ superieur ten opzichte van het moleculaire referentie-oplosmiddel. Extractie van carbonzuren is mogelijk in aanwezigheid van CO_2 als gevolg van verzuring van de waterige oplossing. De ionische vloeistof overtrof het moleculair referentie-oplosmiddel verder toen de extractie van het VFA werd versterkt door CO_2 onder druk. De verbetering van de extractiecapaciteit van de ionische vloeistof was groter dan verwacht. Dit suggereerde dat het CO_2 zeer waarschijnlijk enkele fysieke eigenschappen van de ionische vloeistof had veranderd. Dit impliceert dat de aanwezigheid van CO_2 ook de extractie van andere componenten door deze ionische vloeistof zou kunnen verbeteren.

Hoofdstuk 5 verkende verschillende technieken om $[P_{666,14}][Phos]$ te regenereren en de geëxtraheerde VFAs terug te winnen. HAc was de modelcomponent voor VFAs in dit hoofdstuk. Het bleek niet mogelijk om volledige regeneratie te bereiken door het strippen met een inert gas bij verlaagde druk of door middel van reactieve regeneratie door esterificatie. Terug-extractie van de VFAs van $[P_{666,14}][Phos]$ met een KOH oplossing was zo succesvol dat het, voor deze thesis, de standaard laboratoriummethode is geweest om de VFA belading van de ionische vloeistof te bepalen. Het nadeel van deze methode is dat er kalium carboxylaat zouten gevormd worden in plaats van vrije VFAs. Voor een succesvolle terug-extractie waarbij vrije VFAs verkregen worden, is de KOH oplossing vervangen door een waterige oplossing van een vluchtig alkali, namelijk ammonia of trimethylamine (TMA). Met deze twee alternatieven werd een succesvolle terug-extractie bereikt. De

complexen van ammonia met propionzuur en boterzuur zijn echter onomkeerbaar gedehydrateerd tot propionamide en butyramide, bij de temperaturen die nodig zijn voor hun decompositie. Dit zorgde ervoor dat TMA de uiteindelijke keuze was voor de regeneratie van de ionische vloeistof. Aangezien de productstroom van de decompositie van TMA-VFA complexen een gasmengsel is van TMA en VFAs, moet een entrainer toegevoegd worden om de VFAs af te vangen zonder interactie met TMA. Hierdoor is een extra destillatiekolom nodig die de VFAs scheidt van de entrainer. Hoofdstuk 3 en 5 beschrijven het werk dat gewijd is aan het verbeteren van de extractie van VFAs met een ionische vloeistof en het regenereren van de hierbij gevormde ionische vloeistof waarin de VFAs zijn opgenomen. In de aanwezigheid van een druk van CO_2 werd een opmerkelijke verbetering van de extractie bereikt. Regeneratie van de ionische vloeistof was echter uitdagend en alleen een complexe procedure was succesvol. Deze procedure was gebaseerd op terug-extractie met een TMA oplossing en decompositie van de gevormde complexen. Deze procedure voegt de volgende extra onderdelen toe aan het vrij eenvoudige proces op basis van twee kolommen dat in Figuur 1 getoond wordt (zie Figuur 2):

- Een extra extractiekolom voor de terug-extractie
- Een destillatiekolom voor het terugwinnen van TMA uit de ionische vloeistof
- Een destillatiekolom voor het scheiden van de entrainer van de VFAs

* Door co-extractie

Figuur 1. Een eenvoudige hypothetische procedure voor een proces gebaseerd op vloeistof-vloeistof extractie voor het verkrijgen van VFAs in hoge concentraties. Het oplosmiddel heeft een hoger kookpunt dan dat van de VFAs en water.

Hoofdstuk 6 evalueert de experimentele aanpak die gebruikt is in hoofdstuk 3 tot en met 5. Een alternatieve aanpak wordt beschreven voor experimenteel werk met betrekking tot extractie met een ionische vloeistof. Ook is een wiskundige beschrijving van de uitvoerbaarheid of onuitvoerbaarheid van zulk experimenteel werk gegeven. Aangezien een ionische vloeistof geen dampdruk heeft, is regeneratie in een destillatiekolom om een volledige terugwinning van de geëxtraheerde componenten te krijgen onuitvoerbaar. Iedere poging voor het bereiken van volledige terugwinning van de geëxtraheerde componenten zorgt voor een drastische verhoging van de temperatuur van de ionische vloeistof in de reboiler van de destillatiekolom en zorgt uiteindelijk voor degradatie. De gegeven wiskundige methode beschrijft deze onuitvoerbaarheid als een onredelijk hoge temperatuur in de reboiler, hoger dan de degradatietemperatuur van de ionische vloeistof die geregenereerd dient te worden.

Deel 2. Adsorptie

Adsorptie was de tweede techniek die bestudeerd is. De affiniteit die benodigd is om VFAs te adsorberen van een waterige oplossing wordt bij adsorptie geïnduceerd door een vaste stof, namelijk een adsorbent. Het adsorbent is in veel gevallen geïmmobiliseerd in een kolom. De volgende stap, de desorptie genaamd, verwijderd de geadsorbeerde VFAs van het adsorbent en zorgt ervoor dat het adsorbent hergebruikt kan worden. Om transport van het adsorbent te voorkomen, is een proces dat gebaseerd is op adsorptie intrinsiek semi-continu en wordt het uitgevoerd met verschillende kolommen die tegelijkertijd adsorptie en desorptie ondergaan.

Hoofdstuk 7 verkent de uitgangspunten van adsorptie van de VFAs van de complexe modeloplossing met melkzuur, azijnzuur, propionzuur, boterzuur en zouten. Vier adsorbentia, waaronder een primair, secundair of tertiair amine op een gecrosslinked support van polystyreen en het support zelf werden onderzocht. Er werd gekeken naar hun adsorptiecapaciteit en selectiviteit. Het support, aangeduid als niet-gefunctionaliseerd adsorbent, presteerde beter dan de andere adsorbentia doordat het geen capaciteit had voor de minerale zuren, waardoor het een uitstekende selectiviteit had for azijnzuur, propionzuur en boterzuur. De minerale zuren werden gevormd van de uit zout afkomstige anionen en de protonen afkomstig uit de VFAs. Aanvullende experimenten met adsorptie en desorptie in een kolom bewezen dat het niet-gefunctionaliseerde adsorbent erg stabiel was. Desorptie met een temperatuur-profiel zorgde voor de vorming van drie condensaatfracties:

- Fractie 1. Een mengsel van water en azijnzuur dat terug gestuurd kan worden naar de fermentatie zodat de keten van azijnzuur verlengd kan worden en propionzuur en boterzuur gevormd worden
- Fractie 2. Een mengsel van propionzuur en boterzuur dat gedestilleerd kan worden waarbij twee pure stromen verkregen worden
- Fractie 3. Een pure stroom van boterzuur die gemengd kan worden met de stroom van boterzuur verkregen in de destillatie

Hoofdstuk 7 bevat een appendix waarin een korte evaluatie gegeven wordt van het voorgestelde adsorptie-desorptie schema met betrekking tot de benodigde energie. De energiebehoefte voor de verdamping van water is ongeveer $15 \text{ MJ/kg}_{\text{VFAs mengsel}}$ en kost minder dan $50 \text{ \$/ton}_{\text{VFAs mengsel}}$, wanneer een warmte-wisselaar een deel van de latente warmte van verdamping terugwint.

List of publications

Field: Separation of carboxylic acids from aqueous solutions

- **Reyhanitash, E.**, Zaalberg, B., IJmker, H. M., Kersten, S. R. A., Schuur, B., CO₂-enhanced extraction of acetic acid from fermented wastewater, *Green Chemistry*, **2015**, 17, 4393-4400.
- **Reyhanitash, E.**, Zaalberg, B., Kersten, S. R. A., Schuur, B., Extraction of volatile fatty acids from fermented wastewater, *Separation and Purification Technology*, **2016**, 161, 61-68.
- **Reyhanitash, E.**, Kersten, S. R. A., Schuur, B., Recovery of volatile fatty acids from fermented wastewater by adsorption, *ACS Sustainable Chemistry & Engineering*, **2017**, 5, 9176-9184.
- **Reyhanitash, E.**, Brouwer, T., van der Ham, A. G. J., Kersten, S. R. A., Schuur, B., Extractive processes for recovery of carboxylic acids from aqueous solutions, submitted to *Separation & Purification Reviews*.
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Field: Transformation of biomass into fuels

- **Reyhanitash, E.**, Tymchyshyn, M., Yuan, Z., Albion, K., van Rossum, G., Xu, C., Upgrading fast pyrolysis oil via hydrodeoxygenation and thermal treatment: effects of catalytic glycerol pretreatment, *Energy & Fuels*, **2014**, 28, 1132-1138.
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About the author

Ehsan Reyhanitash was born on June 9, 1989 into a family of two, his mother who was an elementary school teacher and his father who was an elementary school principal. Later on, when he was six, his family got a new member, his brother who grew up to be slightly taller than he is and a lot heavier than he is. After finishing elementary school, middle school and high school at his hometown, he took the nationwide public universities entrance exam to compete against about another 400000 students. His remarkable score put him among the top 0.5% and granted him admission to Sharif University of Technology which was and still is the top technical university of Iran. After graduating from Sharif University of Technology with a BSc in chemical engineering, he moved to Canada to pursue his studies as a MEng student at The University of Western Ontario and work on upgrading pyrolysis oil to produce transportation fuels. After graduating from The University of Western Ontario with a MEng in chemical and biochemical engineering, he moved to The Netherlands to start his PhD in Sustainable Process Technology group at University of Twente where he worked on separation of organic acids from their aqueous streams. During his PhD, he investigated separation of volatile fatty acids from fermented wastewater by liquid-liquid extraction and adsorption. Despite all his efforts to come up with a capable liquid-liquid extraction-based process, his rather simple adsorption-based process outperformed his elaborate liquid-liquid extraction-based process and taught him one more time that sometimes easy solutions are the right solutions.