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Emulsion-Enhanced Biphasic Esterification: Applied Reactive Separations for Valorization of Dilute Carboxylic Acids

DOCTORAL THESIS

to achieve the university degree of

Doktor der technischen Wissenschaften

submitted to

Graz University of Technology

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Graz, December 2019

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"Opportunities multiply
as they are seized."

—

"Chancen multiplizieren sich,
wenn man sie ergreift."

Sun Tzu (544–496 v. Chr.)

Acknowledgements

My way through this doctoral thesis in the past four years would not have been the same without the company of a number of special people. This page is dedicated to these special people.

First and foremost, my gratitude belongs to Matthäus Siebenhofer. As my supervisor, he supported me and my work with guidance when necessary, an open ear and door when needed, opportunities when least expected, and Gin-Tonics whenever deserved. The chance to defend my work at more than 20 scientific conferences is by no means self-evident, but an example of his support.

My thanks and respect belongs to the second in row in terms of support: my co-supervisor Susanne Lux. She always managed to find time for assistance, motivation and coffee, beside caring for her three boys.

Further, I want to thank Prof. Markus Lehner, who kindly agreed to review and assess my doctoral thesis without hesitation.

Thanks are also due to my students contributing to this thesis: Markus Gschiel, Daniela Grosinger, Valentin Kotzmaier, Michael Christopharo, Moritz Donauer, Lukas Koweindl, Rafaela Greil, Andrea Stachel, Michael Tschurtschenthaler, Gregor Paster and Silke Schnedl.

For all the experiences and opportunities provided in the past four years I want to thank the whole team at our institute, especially our laboratory team and our secretaries.

A life without friends is a lonely one, therefore I want to thank all of my friends who accompanied me during the last years. A few special of them are to be named here: Daniela, who I had the pleasure of working and cooking with, Helmut, Elisabeth and Josef, who took care about my emotional and creative balance and Lisa, who despite the geographical distance is the most loyal friend anybody could wish for.

The last lines of this page are dedicated to the one thing that should always stay on top: my family. My father Franz, my (step-)mother Petra, my brother Christian and my (step-)sister Nadine backed me up and set me straight whenever I needed it. Unconditional support as they provided for me is of inestimable value.

The very last line belongs to the person who was inspiration, protection and guidance for me – during her lifetime and beyond: my mother Anita.

Affidavit

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present doctoral thesis.

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Abstract

Sustainable use of biobased resources requires appropriate technology concepts. Whether in pulping of wood or fermentation of any biobased sources, low-molecular-weight carboxylic acids (e.g., formic acid, acetic acid, propionic acid, butyric acid) are formed intentionally or unintentionally. The waste of these carboxylic acids as a consequence of their low concentration, and the lack of suitable economic separation technologies limits economics and sustainable use of the processed resources. With this thesis, an attempt was made to improve sustainability by developing a valorization concept for dilute low-molecular-weight carboxylic acids based on reactive separation technologies. Core of the proposed concept is emulsion-enhanced biphasic esterification of the carboxylic acids with 1-octanol to produce a value-added product (esters). Emulsion formation and catalysis in this step were based on the use of 4-dodecylbenzenesulfonic acid, a highly active Brønsted-acid-surfactant catalyst. Conversions of carboxylic acids (e.g., acetic acid) beyond 60 % were possible despite a more than 20-fold molar excess of water (compared to maximum 4 % conversion in the native broth). Even higher conversion was possible, limited only by formation of stable emulsions induced by the surfactant catalyst. This limitation of the catalyst was subject to specific modifications, allowing to control the degree of emulsification through increasing the interfacial tension of the biphasic system. Combination of 4-dodecylbenzenesulfonic acid with nickel, taking advantage of the ion-exchange capability of the catalyst, yielded the metallosurfactant catalyst $Ni(DBSA)_2$. Lower catalyst activity was the price for preventing the formation of stable emulsions. Regeneration of the solvent phase is proposed *via* reactive distillation with transesterification. The high-boiling esters formed in the esterification step were transesterified with methanol to enhance distillative separation and form the final product, low-boiling methyl esters. High regeneration rates of up to 86 % could be achieved in continuous operation of a benchtop reactive distillation setup with a 6-fold methanol excess. Separation of volatile low-boiling constituents from the regenerated solvent as a matter of energy input is feasible. The proposed concept for valorizing dilute low-molecular-weight carboxylic acids was proven applicable for an acid concentration of even less than 1 mol l^{-1}.

Kurzfassung

Nachhaltige Nutzung biogener Rohstoffe ist nur durch geeignete Technologien möglich. Niedermolekulare Carbonsäuren (z.B.: Ameisensäure, Essigsäure, Propionsäure oder Buttersäure) entstehen gewollt oder ungewollt in biobasierten Prozessen wie der Zellstoffherstellung oder Fermentation. Die Verschwendung dieser Carbonsäuren verhindert eine nachhaltige Nutzung dieser Ressource, es fehlt aber an geeigneten Technologien, die der niedrigen Konzentration der Carbonsäuren in den Prozessströmen entsprechend, eine ökonomische Verwertung ermöglichen. Im Rahmen dieser Doktorarbeit wurde ein Prozesskonzept entwickelt, das eine wertgesteigerte Nutzung dieser niedrigkonzentrierten Carbonsäuren ermöglichen und so die Nachhaltigkeit der zugrundeliegenden Prozesse steigern soll. Das Kernstück des reaktiven Trennkonzepts ist eine zweiphasige Veresterung der Carbonsäuren mit 1-Octanol in emulgiertem Zustand. Der Brønsted-Säure-Tensidkatalysator 4-Dodecylbenzolsulfonsäure beschleunigt zum einen die Veresterung, und zum anderen liefert er durch die Emulgierung eine hohe Stoffaustauschfläche. So sind Umsätze über 60 % (im Vergleich zu maximal 4 % in der wässrigen Trägerlösung) trotz eines mehr als 20-fachen Wasserüberschusses möglich. Höhere Umsätze sind möglich, der Einsatz größerer Mengen des Katalysators hat aber die Bildung stabiler Emulsionen zur Folge. Aus diesem Grund wurde die 4-Dodecylbenzolsulfonsäure unter Ausnutzung ihrer Ionentauscheraktivität mit Nickel zu einem Metalltensidkomplex ($Ni(DBSA)_2$) modifiziert. Die Bildung von stabilen Emulsionen konnte dadurch verhindert werden; jedoch zulasten der Katalysatoraktivität. Die Lösungsmittelphase des Veresterungsschrittes wurde in einem Reaktivdestillationsschritt regeneriert. Dazu wurden die hochsiedenden Octylester mit Methanol in einer kontinuierlich betriebenen Reaktivdestillationskolonne im Labormaßstab umgeestert. Mit einer Regenerierungseffizienz von bis zu 86 % bei 6-fachem Methanolüberschuss im kontinuierlichen Betrieb konnte die Machbarkeit der Lösungsmittelregnerierung mit diesem Konzept bewiesen werden. Die vollständige destillative Abtrennung der flüchtigen Komponenten aus dem regenerierten Lösungsmittel ist durch ensprechenden Energieaufwand möglich. Das entwickelte Prozesskonzept zur wertgesteigerten Nutzung von verdünnten niedermolekularen Carbonsäuren aus biogenen wässrigen Mischungen konnte für Säurekonzentrationen um 1 $mol\ l^{-1}$ untersucht und seine Anwendbarkeit bewiesen werden.

Contents

Part I.

Introduction

1. Motivation

’Sustainability’ is an abstract catchphrase used in many contexts throughout the chemical and chemical engineering community in recent years, not least since the United Nations [1] defined 17 Sustainable Development Goals (SDG) to be achieved for improving life for all human beings. These goals are loosely defined to address all fields of human life. Anastas and Zimmerman [2] and Horváth [3] have made an attempt to derive consequences for the fields of chemistry and chemical engineering. The two goals especially chemical engineering can contribute to, are Goal 9 and Goal 12. Goal 9 is entitled ’Industries, Innovation and Infrastructure’, which i.a. sets the frame for technological innovation. Goal 12 defined as ’Responsible Consumption and Production’ complements Goal 9 by referring to the handling of resources. Regarding ’sustainable’ chemical engineering, both goals are strongly intertwined. In this more specific context, ’sustainable’ denotes to efficiently using renewable resources through appropriate processes with least impact on future generations and the environment. For biomass (renewable resource) processing fields of chemical engineering, a few subgoals can be concluded: full valorization of existing resources and waste, development of suitable processes and concepts and value-added treatment of waste streams. This work aims to contribute to these subgoals in terms of developing a valorization concept for biobased low-molecular-weight carboxylic acids.

Low-molecular-weight carboxylic acids (LMCA; volatile fatty acids, VFA) are widely present in biobased industry. Such LMCAs (e.g., formic acid, acetic acid, propionic acid or butyric acid) are considered platform chemicals for further chemical synthesis. [4, 5] Lee et al. [6] reviewed the production and application of LMCAs from waste feedstock. The origin of LMCAs can either be process intended to produce LMCAs, like fermentation or decomposition processes, or unintended in side products during pulping or pyrolysis. Examples for fermentation processes include investigations of Angenent et al. [7], producing carboxylic acids from waste water, or of Grootscholten et al. [8], converting municipal waste to carboxylic acids. Decomposition processes yielding carboxylic acids were studied by Di Marino et al. [9] (decomposition of lignin to carboxylic acids) or Pola et al. [10], who used hydrolysis to convert non-lignin residues. The OxFA process as investigated by Reichert et al. [11] decomposes non-food biomass to formic acid.

Overwhelmingly, LMCAs are formed as byproducts of other processes that use biomass as renewable feedstock. Acetic acid is formed during pyrolysis of non-food biomass for the production of biogenic fuel in the BioCRACK process, as described by Ritzberger et al. [12] and Painer et al. [13]. Pulping of biomass also produces LMCAs through degradation of hemicellulose during the pulping process. [10, 14–17] In case LMCAs are formed as side products, they are often considered as waste problem to downstream processing. They inhibit fermentation of waste streams from pulping and therefore cause limited conversion, as described by Kumar et al. [18] or Yang et al. [19]. Further, they can deactivate catalysts in downstream processing of pyrolysis oil as mentioned by Painer et al. [13]. No matter, if they are intended products, and product isolation is sought, or if they are byproducts and inhibit downstream processing, the separation of LMCAs is necessary. This separation is a bottle-neck as the concentration of the carboxylic acids is low and they are mostly present in aqueous streams, making any isolation an economic challenge.

The valorization of low-molecular-weight carboxylic acids from biobased processes is the point of action of the present work. In order to contribute to the Sustainable Development Goals, an innovative way of valorizing LMCAs (e.g. through value-added production of chemicals) is necessary to reduce waste streams and avoid wasting valuable resources.

2. Problem definition

The major problem of valorizing low-molecular-weight carboxylic acids from biobased processes is the high water excess. Separation and utilization is well investigated for concentrated systems, while dilute LMCAs cause problems to conventional technologies. The concentration range of dilute systems associated with biobased processes is below 10 wt%. [20] Therefore, more than 90 wt% of LMCA-laden effluents is water. This high water excess and the unfavorable vapor-liquid equilibrium (VLE) makes separation with conventional technologies inefficient and uneconomic. A value-added valorization of the LMCAs through *in-situ* chemical conversion is not possible, due to their low concentration. Increasing the concentration prior to conversion is therefore essential. To illustrate the problem with separations in dilute systems, the VLEs of formic acid, acetic acid, propionic acid and butyric acid, each in a binary mixture with water, are shown in Figure 2.1. In every case, water is to be considered as the low boing component with 100 °C at atmospheric pressure.

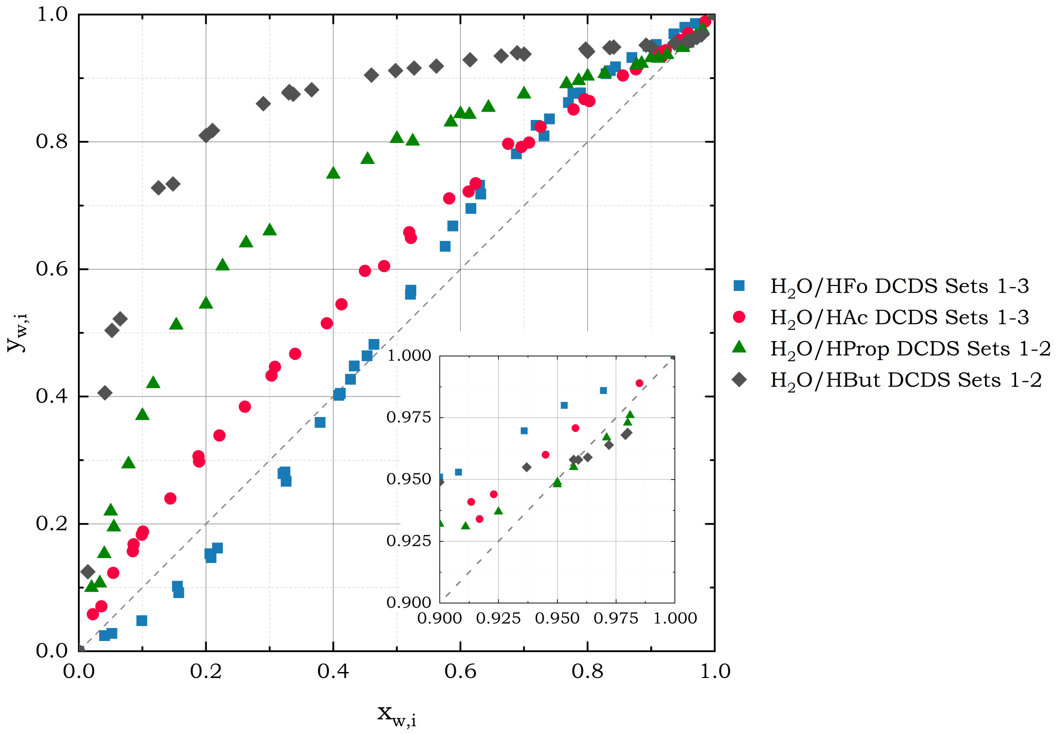


Figure 2.1.: Isobaric vapor-liquid equilibria of water (w) and low-molecular-weight carboxylic acids (i) from Dechema Chemistry Data Series (DCDS) at 1.013 bar; HFo - formic acid, HAc - acetic acid, HProp - propionic acid, HBut - butyric acid; Data sets in Appendix C; Inset: focused area of low acid concentration between $x_{w,i}$=0.9 and pure water.

Formic acid has an azeotrope with water which prevents simple separation from the scratch. Acetic acid shows a low relative volatility, demanding a high separation effort. The inset diagram in Figure 2.1 highlights the concentration range of interest for dealing with dilute LMCAs. For all of the carboxylic acids shown in the diagram, the VLE above 90 wt% water shows either azeotropic (propionic and butyric acid) or quasi-azeotropic behavior (formic and acetic acid).

The low-energy unit operation of liquid-liquid extraction (LLX) is often applied as an alternative to the high energy demand for conventional separation technologies. Main problems of LLX in dealing with dilute LMCAs include the struggle with efficient recovery and the loss of the solvent to the aqueous stream. Especially the loss of reactive extractants (e.g., tri-alkylamines) is harmful to microorganisms in fermentation and the environment and therefore needs further treatment. [21]

3. Scope

The present work aims to provide an approach capable of coping with the problem of efficient and economic valorization of dilute low-molecular-weight carboxylic acids. The development of an innovative process concept is supported by heuristic tools, which are briefly described. Literature dealing with the separation of LMCAs and the scientific background is summarized for clarification. This includes state-of-the-art separation technologies for dilute LMCAs as well as basic information on emulsions and chemical reactions in emulsions. The valorization process concept is introduced, based on emulsion-enhanced biphasic esterification. In this concept, acetic acid and other LMCAs are esterified with 1-octanol to form octyl acetate and allow efficient extraction. Emulsification is induced by the Brønsted-acid-surfactant catalyst 4-dodecylbenzenesulfonic acid (4-DBSA). Development of a metallosurfactant catalyst, based on 4-DBSA and nickel, is presented. This metallosurfactant aims at increasing operability of the process in terms of phase separation. Finally, solvent regeneration and product isolation is suggested by transesterifying the octyl ester with methanol to methyl ester and 1-octanol. Performed in a reactive distillation column, this allows the closing of the solvent cycle and efficient isolation of the low-boiling methyl esters.

4. Scientific background

This chapter gives an overview and a review of literature on tools for structured process development, separation technologies for utilizing carboxylic acids as well as basics on emulsions, surfactants and chemical reactions in micellar systems.

4.1. Tools for structured process development

In the following section two tools for developing and investigating a suitable separation process for the problem defined in Chapter 2 are explained. One is the Theory of Inventive Problem Solving (TIPS) for creative problem solving and the other is Design of Experiments for planning the experimental investigation.

4.1.1. TIPS - Theory of Inventive Problem Solving

Complex problems in general need creative and innovative solution approaches. These can hardly be derived by intuitive methods like trial and error or brainstorming. [22] A structured, heuristic alternative to find suitable solutions is the Theory of Inventive Problem Solving (TIPS, TRIZ). [22–29] This principle was developed by Genrich Altshuller after screening a huge number of patents and analyzing the described problems and solutions. He derived 40 basic principles which he identified in all of these patents. As TIPS was originally focused more on mechanical engineering problems, the principles need to be reinterpreted in the context of chemical engineering. [23] Jack Hipple published such an adaption of the 40 principles to chemical engineering applications. [24] Across the subject limits, the general procedure is the same: transfer the specific problem to a general problem, find a solution for the general problem and from that, derive the specific solution. The general procedure of TIPS revolves around three steps:

1. Analyze the system and determine all relevant characteristics
2. Reformulate the task as a contradicting problem
3. Utilize an appropriate principle of TIPS to solve the problem

In this context, a contradicting problem is defined by a pair of parameters of which one parameter needs improvement and the other worsens through the improvement of the first parameter. Compiled in a so called contradiction matrix, TIPS provides a tool correlating the contradicting problem with the 40 principles for solution. An extension of the classical contradiction matrix by parameters specifically for chemical engineering was proposed by Pokhrel et al. [22] and Srinivasan et al. [25]. An excerpt to clarify the application of the contradiction matrix is given in Table 4.1 based on the work of Pokhrel et al. [22].

In this table, the complexity of the system, the concentration, and the conversion are listed as examples for parameters. In the case of improving the concentration (e.g., increasing the concentration of a component in a process stream) the complexity of the overall system increases (worsens) as additional unit operations are necessary to achieve this concentration. The present contradiction matrix suggests principle 6 as a possible solution. According to the adaption of the 40 principles by Hipple [24], principle 6 '*universality*' states to integrate multiple functions in one apparatus or unit operation. This could be, for example, a reactive distillation or a reactive extraction step achieved by integrating a reactor into a separation technology.

Table 4.1.: Excerpt of the modified contradiction matrix for chemical engineering applications according to Pokhrel et al. [22]

		worsening parameter			
		complexity	concentration	conversion	…
improving parameter	complexity	x		1,3,8	⋮
	concentration	6	x	1,3,6	⋮
	conversion	3	4	x	⋮
	⋮	⋮	⋮	⋮	⋱

1: principle of segmentation
3: principle of local quality
4: principle of asymmetry
6: principle of universality
8: principle of anti-weight

By repeatedly applying this procedure, a suitable solution for any given problem can be found. The crucial step is the second one (abstraction or transformation of the specific problem to a general problem), which requires highly networked thinking across topical boundaries.

4.1.2. DoE - Design of Experiments

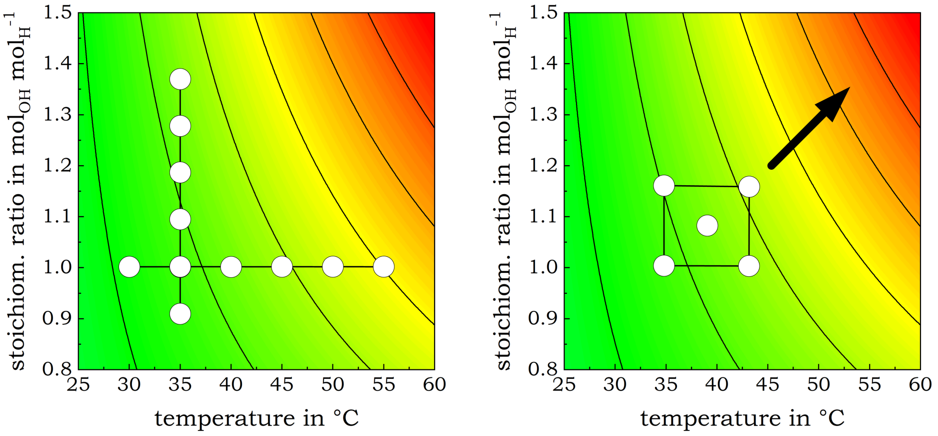
Once a concept is found, work starts regarding experimental investigation. Especially in unexplored processes a structured approach to these investigations is necessary to save resources in terms of time, material and money. Still, most investigations are performed intuitively as structured approaches always include statistics, which are avoided by many researchers. Lazić [30] indicates the problem with statistics as its abstractness in the preface of his book 'Design of Experiments in Chemical Engineering'. For further reading and in-depth information on necessary statistical basics, design of experiments and its application this book is a recommended base. This thesis just outlines a rough description of the basic idea and application of DoE for introducing utilization of the commercial software MODDE Pro version 12.0.1 from Umetrics/sartorius stedim biotech. Details are explained in the corresponding book of Eriksson [31] titled 'Design of Experiments: Principles and Applications'. The software was used for the DoE for efficient experimental investigation in the research article in Chapter 6.

Two main benefits from using DoE for experimental investigation (screening and optimization alike) can be identified: one is the significant reduction of experimental runs to learn as much as possible about the investigated system and therefore save time and material. The other benefit is the possibility to evaluate the results with statistical means to identify optima and interactions of significance. Based on this evaluation, a model for description and prediction of the investigated process can be developed.

DoE-based investigation follows six steps:

1. Define 'factors': parameters influencing the system (e.g., reaction temperature)
2. Define 'responses': outcome of the experiments allowing to evaluate them (e.g., conversion, separation efficiency)
3. Choose/Create a design: the statistical selection of expressive experiments (combination/variation of factors)
4. Perform the experiments
5. Develop a model describing the investigated system (e.g., a simple linear or a quadratic model)
6. Evaluate the system behavior and interpret the retrieved data

For better understanding of the difference between intuitive and statistic experimental planning, Figure 4.1 schematically compares the intuitive COST (Changing One Separate factor at a Time) approach for experimental investigation to the statistical DoE approach. The contour plot displays the separation efficiency (response) of the process described in Chapter 6, depending on the molar ratio of alcohol and reaction temperature (factors). A maximum of the separation efficiency is indicated in the upper right corner by the red color. Yellow color expresses medium and green color low separation efficiency. In the left diagram in Figure 4.1 the intuitive COST approach is illustrated. As the acronym reveals, one factor at a time is changed in the COST approach: the molar ratio is fixed to 1 and the temperature is varied between 30 °C and 55 °C.; in the next step, the temperature is kept constant at 35 °C and the molar ratio is varied. In contrast, the DoE approach is depicted in the right diagram in Figure 4.1. A statistical design set of experiments allows more insight into the system's behavior and therefore allows approaching the maximum separation efficiency (optimum) much faster and much more economically.



a) COST approach

b) DoE approach

Figure 4.1.: Schemes of intuitive and statistical approaches to experimental planning adapted from Eriksson [31]. a) intuitive COST approach (**C**hanging **O**ne **S**eparate factor at a **T**ime); b) statistical DoE approach (**D**esign **o**f **E**xperiments); Contour plot from the research article discussed in Chapter 6.

The case described in Figure 4.1 represents a regular two dimensional problem, speaking of two factors influencing one response. For three factors, three possible designs are illustrated in Figure 4.2. The regular three factor designs can be visualized as a (three-dimensional) cube with each axis representing one factor. For each factor an interval is defined with a low and a high level of the respective factor. A full factorial design uses an experimental run in each node of the cube, representing either a lower or a higher value of the investigated factors and a center point in the spatial center of the cube. In order to distinguish significant changes of the responses from experimental noise, the center point is usually investigated at least three times to determine the baseline of the experimental noise. A reduction of experimental runs can be achieved by using fractional factorial designs by maximizing the volume of the experimental space between the selected points, as shown by the middle design in Figure 4.2. Further optimization can be done with composite designs as exemplarily represented by the right hand design in this figure.

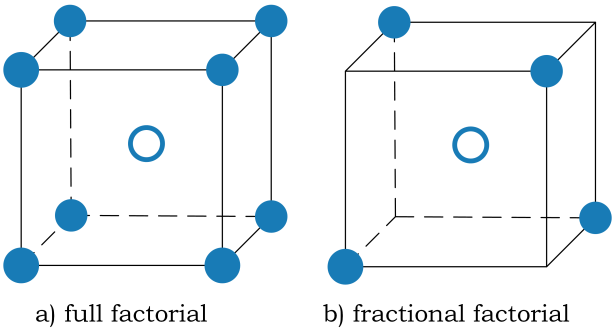

a) full factorial
b) fractional factorial
c) composite

Figure 4.2.: Scheme of typical designs in DoE for three factors, adapted from Eriksson [31]. a) full factorial design with center point; b) fractional factorial design with center point; c) composite design with center point.

While a three dimensional problem can easily be imagined, a multi-dimensional problem, starting with four factors is very abstract in imagination. The concept of maximizing the experimental space can still be achieved by statistics, e.g., in a D-optimal design as applied in Chapter 6. The selection of the appropriate design depends on the purpose of the investigation (screening or optimization) and can be aided by software solutions like MODDE.

The evaluation of the randomized experimental runs feeds development of an appropriate model, capable of describing and predicting the system within the defined boundaries. Leaving aside fancy diagrams like contour plots and other statistical diagrams for evaluation of the retrieved data, a very useful tool is the interaction plot. It allows interpretation of interaction between two parameters and its impact on a response similar to a sensitivity analysis. Such an interaction plot is exemplarily shown in Figure 4.3, again based on data from Chapter 6. It depicts the interaction between stirrer speed and phase ratio and its influence on the conversion. The blue points represent the conversion at the high level of the phase ratio for three different stirrer speeds. The conversion rises insignificantly with the stirrer speed and lies at about 29.5 %. In contrast, the conversion drops with increasing stirrer speed for the low level of the phase ratio. One of several conclusions that can be drawn from this plot is, that the process must be operated at a low phase ratio (solvent to aqueous). A high stirrer speed is disadvantageous for a high conversion in this case.

An example of applied DoE is presented in Chapter 6. Especially for users new to the topic of DoE, the use of a commercial software like MODDE, providing condensed background information and short descriptions of the features and

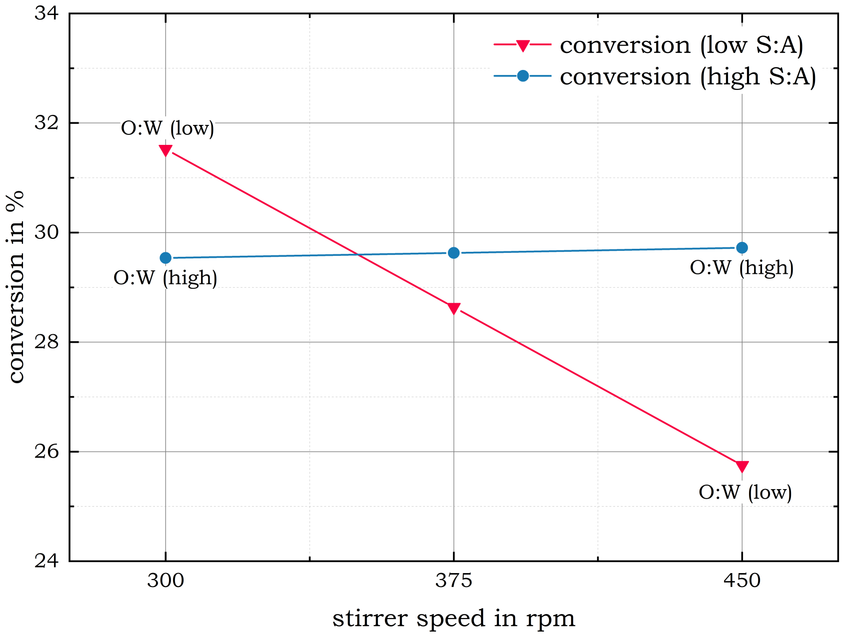


Figure 4.3.: Interaction plot as a tool for evaluation of parameter interaction in DoE. Interaction of solvent to aqueous ratio (S:A) and stirrer speed and its impact on conversion in reactive liquid-liquid extraction in emulsion as described in Chapter 6.

statistical terms, offers an appropriate access. The statistical approach allows revealing interactions and trends that would perish in an intuitive approach.

4.2. Separation technologies for carboxylic acid utilization

Carboxylic acids originating from fermentation or other means of biomass processing struggle with feasible downstream processing/utilization as discussed in chapter 2. Separation technologies beyond standard mass transfer unit operations (distillation, physical liquid-liquid extraction,...) are reviewed in the following section. Emphasis is put on reactive extraction and reactive distillation, as they are the most common and most developed technologies in the field. Additionally, research stage technologies like membrane technologies, electro-dialysis or pervaporation are introduced. Literature on suitable process concepts was reviewed in 2014 by Talnikar et al. [32] and in 2018 by Atasoy et al. [33], Djas et al. [34] and Reyhanitash et al. [35].

4.2.1. Liquid-liquid extraction: principle and application

The most common separation technology for carboxylic acid utilization is liquid-liquid extraction (LLX). For in-detail background on LLX it is referred to the chapter of Müller et al. [36] in Ullmann's encyclopedia of industrial chemistry or to chemical engineering textbooks, i.e. Sattler [37] or Wankat [38]. The three basic principles of LLX applied for acetic acid extraction are shown in Figure 4.4 for better understanding of the present work and the differentiation to other extraction based approaches. These principles are physical LLX (Figure 4.4 A), reactive LLX *via* adduct formation (Figure 4.4 B) and reactive extraction coupled with chemical conversion of the solute (Figure 4.4 C). The latter represents the main topic of this thesis and, thus, is discussed in Part II. It relies on the chemical conversion of the carboxylic acid to a different chemical species and thereby changing its distribution behavior between the aqueous phase and the solvent phase.

Physical extraction (Figure 4.4 A) is rarely applied for carboxylic acid extraction, especially when they occur in low concentrations. Physical extraction is solely based on solvation of the solute and its distribution equilibrium between the solvent and the feed. As mentioned by Reyhanitash et al. [35] physical solvents have little interaction with low-molecular-weight carboxylic acids (LMCA), causing a low extraction efficiency. Solvents for the physical extraction of LMCA include ketones, higher carboxylic acids, alcohols or esters. Recent examples for the use of esters are given in the section on LLX-processes based on low-boiling solvents.

Reactive extraction (Figure 4.4 B), mostly performed with high-boiling solvents is more suitable for the task of extracting LMCAs from dilute aqueous solutions. Opposite to physical extraction, reactive solvents strongly interact with the carboxylic acid molecules *via* ion exchange or chelating reactions (adduct formation). [35, 36] These active constituents (reactive extractant agent, REA) are commonly diluted to allow better handling in the processes or increase their extraction efficiency. As shown in Figure 4.4 B for the example of acetic acid (HAc) extraction, the REA reacts with the carboxylic acid and forms an adduct or a complex. Most commonly used REAs are tri-alkylamines and tri-alkylphosphine oxides.

Solvents and LLX-processes have been evaluated and reviewed by various research groups. [14, 34, 35, 39] Subsequently, processes based on low- and high-boiling solvents are presented as discussed in literature.

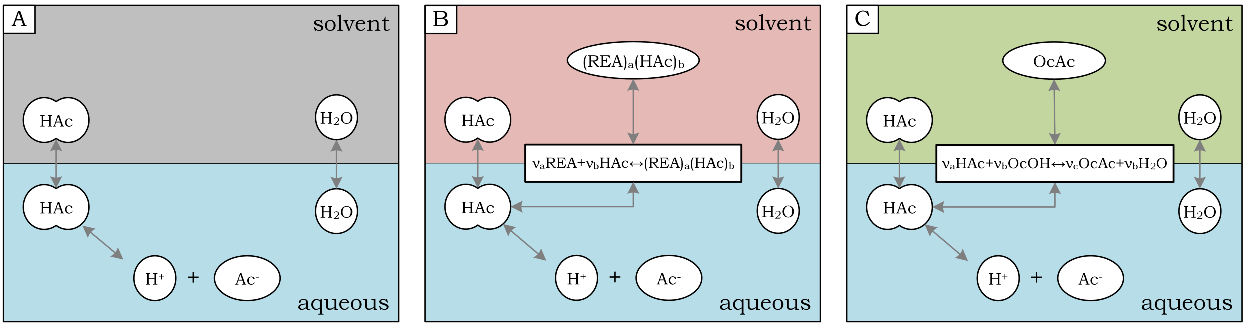


Figure 4.4.: Principle schemes of liquid-liquid extraction types. A: physical extraction. B: reactive extraction *via* adduct formation. C: reactive extraction *via* chemical conversion.

LLX-processes based on low-boiling solvents

As low-boiling solvents exhibit low interaction with the LMCA, only little effort has been made to include them in a primary process step. Yet, they may be used for regeneration of a laden high-boiling solvent in terms of back-extraction. [35, 40]

Esters. Ethyl acetate was used as a solvent by Aghazadeh et al. [41, 42] and Cebreiros et al. [43]. Aghazadeh et al. chose ethyl acetate for the extraction of acetic acid from a biobased hydrolyzate determined for ethanol fermentation. The main reason for ethyl acetate was its high volatility and low toxicity to the microorganisms used in fermentation. They further evaluated the economics of implementing a LLX-step in the existing fermentation process and the impact of the LLX on the fermentation performance. Removing 90 % of the initial acetic acid increased the ethanol yield by 11 %.

The intention of Cebreiros et al. [43] was similar, as they tried to improve a hydrolyzate stream from a pre-pulping extraction for bio-ethanol producing fermentation by removing acetic acid. The hydrolyzate stream originates from extraction of eucalyptus wood chips with green liquor in a Kraft pulping process. They could remove 82 % of acetic acid in a single stage extraction, however, they used a concentration step prior to LLX, adding another energy demanding step to the process.

Low-boiling hydrocarbons. In 2010 Schon [44] patented a process for acrylic acid extraction from dilute aqueous streams, using pressurized liquefied propene or propane as low-boiling solvents. The acid concentration in the aqueous effluent of acrolein production is below 10 %. The process allows removing more than 60 % of the acrylic acid and high regeneration yield of the solvent through evaporation. The low boiling point and high volatility of propene and propane allows regeneration of the solvent at very low temperatures. Nevertheless, the liquefaction of the hydrocarbon solvent and the necessity to add polymerization inhibitors are crucial drawbacks of the process.

LLX-processes based on high-boiling solvents

In contrast to low boiling solvents, high boiling solvents for carboxylic acid extraction commonly act as reactive solvents. The most frequently used representatives of this solvent class are higher amines and organophosphorus compounds.

Amines. Higher amines have been thoroughly investigated for carboxylic acid extraction in the last century. Since then, much effort has been made to improve amine-based extraction processes. [19, 20, 33–35, 39, 40, 45–55] Common amines for LMCA extraction include tri-*n*-butyl amine (TBA) [47, 50], tri-*n*-decyl amine [46] and tri-*n*-octyl amine (TOA) [19, 20, 33–36, 39, 45, 48, 51–54]. The biggest advantage of these tertiary amines is the high extraction efficiency reported throughout the literature. Drawbacks are the formation of amine salts [36], the need of appropriate diluents, the decreasing extraction efficiency due to co-extraction of other residues and a complex solvent regeneration. The selection of the diluent is crucial, as formation of emulsion or a third phase leads to breakdown of the process. To avoid this, often aromatic compounds (e.g., phenol, naphthol) or other polar solvents (e.g., 1-octanol) are used. Further, aliphatic hydrocarbons exhibit low load capacity for amines. [19, 34, 36, 48] The use of aliphatic alcohols as diluents may cause unwanted esterification of the LMCA during distillative regeneration of the amine-based reactive solvent. [47, 54] As most of the recent processes for carboxylic acid extraction with high-boiling solvents need to deal with biobased streams, co-extraction of matrix constituents from the upstream processes needs consideration. For example, amine-based reactive solvents may be laden with such higher extracts and therefore suffer from limited extraction efficiency. [45]

An extensive review on the influence of diluents on the performance of tri-*n*-octyl amine/tri-*iso*-octyl amine (TIOA) is provided by Yang et al. [19]. In their review, an industrial sample of pre-hydrolysis liquor with an acetic acid concentration of about 1 wt% served as a feed. They screened four polar and non-polar diluents and mixtures thereof in dependency of pH, time, temperature and amount of REA. TIOA diluted in 2-ethyl-1-hexanol performed best with 68.79 % extraction efficiency within 10 min at 25 °C. An increased temperature was found to be disadvantageous as extraction efficiency decreased for temperatures above 25 °C.

The acetic acid laden solvent was regenerated with sodium hydroxide (NaOH), resulting in recovery rates between 50 and 79 %, highly depending on a sufficient molar excess of NaOH. Repeated extraction/regeneration cycles led to a reduction of the acetic acid recovery. This reduction, presumably caused by matrix constituents (e.g., lignin), was counteracted by increasing the amount of REA in the reactive solvent.

Patented processes based on reactive extraction with higher amines date back to 1981 (Baniel et al. [46]) and 1988 (Wojtech et al. [54]). The patent of Wojtech et al. describes the treatment of dilute aqueous streams containing less than 8 wt% acetic acid with amine/phenol or amine/naphthol reactive solvents. The higher amines used were tri-*n*-octyl amine and tri-*n*-decyl amine. In a six-stage extraction, they could remove 99.2 % of the initial acetic acid (1.4 wt% in waste water).

Organophosphorus extractants. In chelating-based reactive extraction the REAs competing with amines are organophosphorus extractants. Therefore, they serve as benchmark in reactive extraction of dilute carboxylic acids and are thoroughly investigated. [13, 33–36, 39, 45, 53, 56–60] The most established representative of the REA-class is tri-*n*-octylphosphine oxide (TOPO). Recently, mixtures of various tri-alkylphosphine oxides (TRPO) have gained importance, as they have improved extraction efficiency, and as they are easier to handle in the processes (pure TOPO is solid at ambient temperature). Another frequently used phosphorus based REA is tri-butyl phosphate (TBP).[49, 56] Similar to amines, organophosphorus extractants have been subject of investigation for decades. Patents for reactive extraction of LMCAs date back to 1976 by Grinstead [61] or 1981 by Kanzler et al. [58]. A more recent patent was developed by van Heiningen et al. [60] in 2014. The latter two patents explicitly suggest the use of TOPO diluted in *n*-undecane for the extraction of acetic acid from biobased effluents (initial concentration below 10 g l^{-1}). While Kanzler et al. emanate from an aqueous condensate stream, van Heiningen et al. based their process on an aqueous wood extract stream. The major difference between the two feeds is the presence of matrix constituents in the aqueous wood extract stream. These constituents are potentially blocking the reactive solvent, analogous to the findings of Yang et al. [19]. Both patents propose distillative regeneration of the high-boiling reactive solvent. The patent of Kanzler et al. provides a process scheme thereof, which is shown in Figure 4.5. The proposed regeneration consists of four distillative steps including a stripper (D1), a 200 mbar vacuum distillation (D2), a distillation step at ambient pressure (D3) and an entrainer distillation (D4). All of the distillation top products need phase separation as indicated by the separators (S1 to S4). The proposed entrainers, provided *via* the entrainer dosage (V), are di-*n*-propyl ether or ethyl-*n*-propyl ether. This scheme gives an insight in the complex solvent regeneration and product isolation.

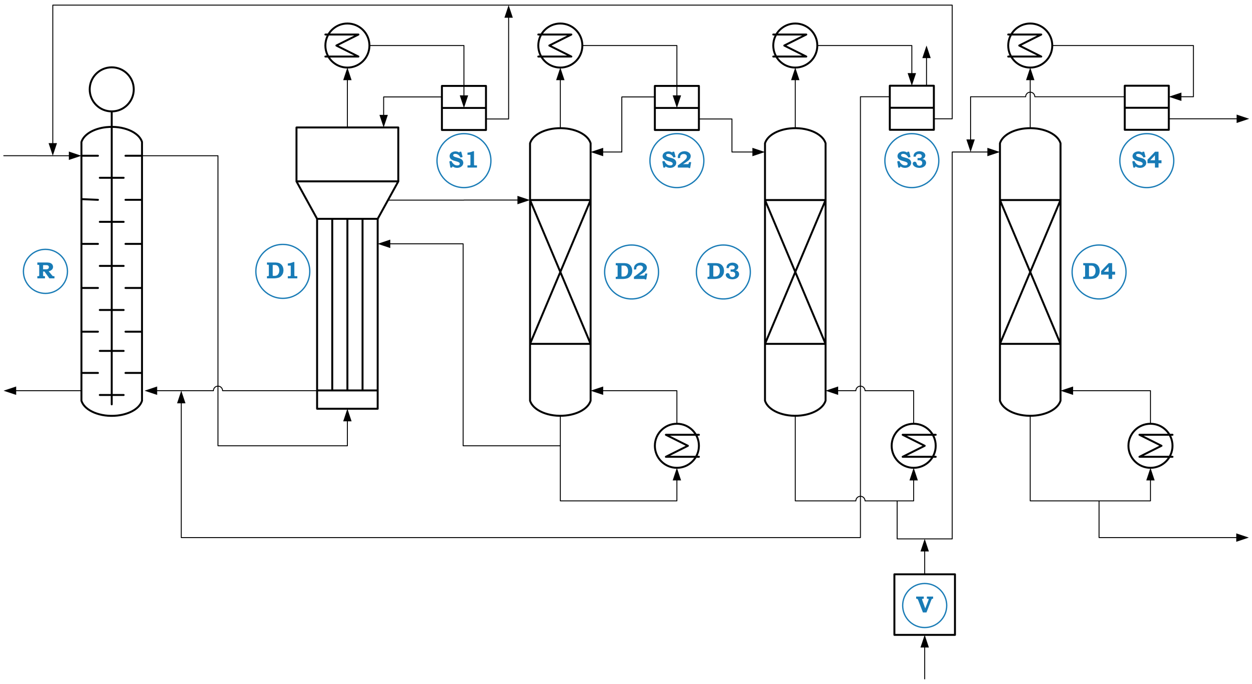


Figure 4.5.: Reactive extraction process including solvent regeneration as patented by Kanzler et al. [58]. Reactive solvent: TOPO in *n*-undecane; reactive extraction R, stripper D1, 200 mbar vacuum distillation D2, distillation D3, entrainer distillation D4, phase separators S1 to S4, entrainer dosage V.

Abdulrahman et al. [45] tested the extraction performance in single stage extraction of acetic acid with TOPO compared to TOA, in dependence of the pH. TOPO performed best at lower pH (<3) while TOA had a maximum extraction efficiency around a pH of 4. This trend is confirmed by the results of van Heiningen [60]. The latter reasoned this behavior with the necessity of protonated acetic acid for adduct formation and extraction with TOPO. It can be concluded, that whether amines or organophosphorus compounds perform better, highly depends on the operation conditions.

Similar to the process of van Heiningen et al. the group of Kwon et al. [57] used TOPO to recover LMCAs from Kraft black liquor prior to fermentation for bio-ethanol production. Acetic acid and formic acid were present in the feed at around 10 g l^{-1} and 5.2 g l^{-1}, respectively. Their investigations yielded a separation efficiency of 69.87 %. A model was developed based on statistical DoE to allow optimization through analysis of response surface plots. The investigated factors were temperature, pH and residence time; the response was the extraction yield of the respective acid.

The extraction step in the discussed patents with TOPO is performed at elevated temperatures (around 70 °C) due to the upstream process steps. This allows the use of TOPO which is solid at ambient conditions. Reactive extraction at ambient conditions requires TRPOs like the commercially available mixture Cyanex®923. This blend of four different TRPOs was used by Tirronen et al [62] in their patent for recovery of carboxylic acids from dilute aqueous streams (less than 15 wt% acids). Recently, Painer et al. [13] applied Cyanex®923 for the reduction of the total acid number of liquid-phase-pyrolysis oil (LPP oil). The total acid number of about 80 mg g^{-1} was mainly due to acetic acid, which causes problems with downstream catalytic hydrodeoxygenation. In a three-stage extraction/regeneration cycle they were able to remove 81 % of the acids. Regeneration was performed with vacuum distillation at 200 mbar.

A major drawback of all so far discussed high-boiling solvents and most diluents is their loss to the aqueous stream, causing problems with sewage treatment or fermentation. Avoiding this secondary pollution is an aim of the work of Ren et al. [56]. They used tri-butyl phosphate, another organophosphorus extractant. An aqueous mixture of LMCAs (i.e. acetic acid, propionic acid and butyric acid) which was used as a feed was synthesised to match a fermentation broth from municipal sewage sludge. Their process yielded an extraction efficiency of 98.47 % in a three-stage process with solvent regeneration by vacuum evaporation at 950 mbar. Extraction with TRPO served as a benchmark for the extraction with TBP. Although TRPO had an extraction efficiency twice as high as TBP, formation of a third phase occurred, as no diluent was added.

LLX-processes based on special solvents

Aside the innovative approach of Schon [44] with liquefied lower hydrocarbons, attempts have been made to use (supercritical) carbon dioxide or ionic liquids for reactive extraction of LMCAs.

Supercritical CO_2. Supercritical CO_2 acts rather poor as physical solvent, but has shown good performance in combination with high-boiling REAs like TOA. Literature on this topic was reviewed by Djas et al. [34] in 2018. Despite high extraction efficiency above 90 %, i.e. in combination with TOA for extraction of propionic acid as performed by Henczka et al. [63], operation of the process at pressures above 160 bar may be troublesome in terms of process operability and safety. CO_2 may also be used subcritical, as proposed by Reyhanitash et al. [52] for enhancing reactive extraction with ionic liquids with CO_2 at a pressure of 40 bar.

Ionic liquids. Reyhanitash et al. [20, 40, 52] worked on reactive extraction of LMCA with ionic liquids (IL). The IL of choice is a phosphonium phosphinate ([$Ph_{666,14}$][Phos]) which was investigated for extraction of acetic acid, propionic acid and butyric acid. The performance of the phosphor-based IL was reported twice as high as of 20 wt% TOA in 1-octanol under comparable conditions. Further, leaching of the IL into the aqueous phase was confirmed negligible by HPLC analysis. Regeneration was suggested by back-extraction with a lower amine (tri-methyl amine) after evaluation of different regeneration concepts. [40]

Solvent regeneration concepts

A suitable solvent regeneration with a high regeneration efficiency is crucial for any LLX-process. Nevertheless, solvent regeneration is often treated negligently. Regeneration concepts range from distillative processes (ambient distillation, vacuum distillation, entrainer distillation,...) to back-extraction or simple evaporation. The choice of the appropriate solvent regeneration highly depends on the solvent used (low- or high-boiling) and the carboxylic acids extracted. Investigation on solvent regeneration was for example done by Reyhanitash et al. [40], Ren et al. [56], Sprakel et al. [53] and Painer et al. [13, 64]. Reactive distillation as a highly potent technology for solvent regeneration and production of value-added products is described in more detail in the following section (section 4.2.2).

4.2.2. Reactive distillation: principle and application

A technology complementary to liquid-liquid extraction is reactive distillation (RD). For basic information on the reactive distillation process the overview article of Sakuth et al. [65] in Ullmann's encyclopedia of industrial chemistry or the textbook of Kai Sundmacher titled 'Reactive Distillation: Status and Future Directions' [66] are recommended. Benefits of the reactive distillation technology comprise lower investment costs compared to conventional technologies and higher selectivity towards the reaction product. [65] Reduction of investment costs is achieved by combining reactor and separation in one apparatus. Immediate separation of reactants and products in the reaction zone provides an increased selectivity. The prime example of an established RD process in industry is the Eastman-Kodak process for production of methyl acetate dating back to the patent by Agreda et al. [67] from 1984. Acetic acid is catalytically converted with methanol to methyl acetate and water, yielding a highly pure top product stream of methyl acetate. Talnikar et al. [68] worked on a similar process for the esterification of acrylic acid with 2-ethyl-1-hexanol. While Agreda et al. proposed sulfuric acid for catalysis, Talnikar et al. tested various solid acidic catalysts (e.g., Amberlyst® 15). Both achieved high yields and high purity of their product streams, yet they used undiluted acid feed streams. The lack of water excess simplifies the reaction in contrast to dilute aqueous feed streams. In the frame of carboxylic utilization, there are two possible applications of RD: either for solvent regeneration or direct processing of dilute carboxylic acid streams. In either way, the desired product is not the original carboxylic acid, but a value-added product (i.e. an ester).

Solvent regeneration by RD

A process for solvent regeneration by reactive distillation was patented by Tirronen et al. [62]. As mentioned in the paragraph on organophosphorus extractants (section 4.2.1) this patent proposes the use of Cyanex®923 as a REA. For value-added use of the extracted carboxylic acids suggestions for possible regeneration concepts are given in the patent. One of these concepts for multi-acid utilization is depicted in Figure 4.6. After the reactive extraction the solvent laden with carboxylic acid/REA complexes is transferred to a first reactive distillation. This RD 1 is fed with methanol to produce methyl esters of a lower carboxylic acid (i.e. acetic acid). The solvent is then moved to a second reactive distillation. Here higher carboxylic acids (i.e. levulinic acid) are esterified with a second alcohol (i.e. ethanol) to their corresponding esters. After this second RD the solvent is purified before reentering the reactive extraction.

This process was designed for highly diluted carboxylic acid feed streams. Painer et al. [64] worked on a similar process for a multi-acid feed containing formic acid and acetic acid. Focus of their work was the determination of the liquid-liquid equilibria of single- and multi-acid extraction and the impact of the catalyst 4-dodecylbenzenesulfonic acid (4-DBSA) on these equilibria. Discontinuous reactive distillation experiments were performed with 4-DBSA as homogeneous catalyst. Conversion of 100 % for formic acid and 88 % for acetic acid was achieved in multi-acid reactive distillation with methanol as alcohol for esterification.

Direct processing of dilute LMCA by RD

In contrast to the solvent regeneration applications of reactive distillation, some research groups worked on direct processing of dilute LMCA. An early approach was made by Niemann et al. [69] in 1984 for converting dilute acetic acid with methanol to methyl acetate. This early approach already clearly states the vague definition of 'dilute feed streams', as the feed used by Niemann et al. contains 60 wt% acetic acid. All other RD concepts presented hereinafter use a minimum

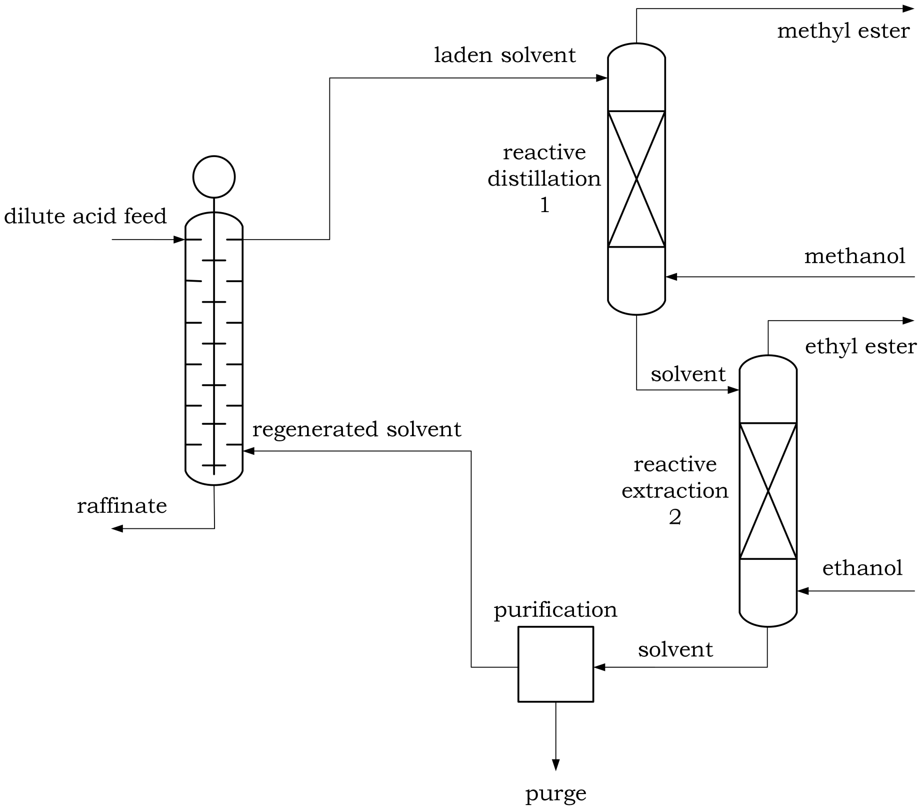


Figure 4.6.: Solvent regeneration *via* reactive distillation in a reactive extraction process as patented by Tirronen et al. [62]. Reactive extractant agent: Cyanex®923.

acid concentration of 30 wt%, clearly above the concentration range subject of biorefinery sources in the present thesis. Niemann et al. and similar processes of Saha et al. [70] from 2000 or of Singh et al. [71, 72] from 2006 use solid acidic catalyst (e.g., DOWEX®50W, Indion®130 or Amberlyst®CSP2) for enhancing the esterification. The major problem of solid catalysts in reactive distillation is the change of the catalyst bed after exceeding its lifetime, as stated by Sakuth et al. [65].

Niemann et al. achieved a maximum acetic acid conversion of about 80 % for their 60 wt% acetic acid feed. The investigations of Saha et al. yielded 58 % and 51 % for esterification with *n*-butanol or *iso*-amyl alcohol for a 30 wt% feed of acetic acid. The latter produced a biphasic top product as a consequence of the used alcohols. A sensitivity analysis was performed by Saha et al. and Singh et al. on different aspects of the reactive distillation processes investigated. Saha et al. identified the feed stages of the acid and the alcohol relative to each other as important for reaction yield and purity of the product stream. A counter current application was most beneficial with the acid feed at the top of the reaction zone and the alcohol at the bottom of the reaction zone. Singh et al. used acetic acid (30 wt%) and methanol, as did Niemann et al. in their research. They found the overall system behavior to be highly non-linear, expressing in possible multiple steady-states during operation.

The choice for methanol as the reactant for esterification is among others, subject to the investigations of Hung et al. [73]. They performed a cost analysis of the total annual costs (TAC) for ester production in reactive distillation with various alcohols and found methanol and *n*-pentanol to cause the lowest TAC. Additionally they analyzed the impact of the feed concentration within a range of 100 to 30 wt% of acetic acid. Target was a process without increasing the feed concentration in an azeotropic distillation prior to the RD. While the process with pre-concentration is more favorable with methanol, the direct processing of the acid prefers the use of *n*-pentanol.

4.2.3. Separation technologies in research stage

In addition to the so far discussed established separation technologies, literature reviews of Talnikar et al. [32] from 2014 and of Atasoy et al. [33] from 2018 list a number of conceptual technologies, which are to the best of our knowledge not yet applied in industrial scale. They can be classified into membrane and non-membrane technologies. Membrane technologies include nanofiltration, reverse osmosis, pervaporation or electro dialysis. The most discussed separation technology in the non-membrane class is adsorption.

Membrane technologies

Membrane-based separation technologies are particularly interesting for fermentation processes, as the membrane can prevent leaching of (toxic) solvents to the fermentation broth. Further, selective separation of multi-acid mixtures is possible, depending on the membrane used. Not limited to purification only, Pal et al. [74] reviewed processes for the production of acetic acid *via* fermentation in a membrane reactor.

Nanofiltration and reverse osmosis. The two technologies, nanofiltration (NF) and reverse osmosis (RO), are often discussed conjointly for treatment of hydrolyzate streams to separate monosaccharides [75] or hemicellulose [51] and carboxylic acids. One such combination of nanofiltration and reverse osmosis was investigated by Kaur et al. [51] to produce furfural and acetic acid from a feed stream of pre-hydrolysis liquor containing 1 wt% of acetic acid. This liquor, originating from a Kraft pulping process, was first subject to nanofiltration to remove the acetic acid. The permeate of the NF was then treated by RO to concentrate the acetic acid and purify the water. A drawback of this process is that an extraction step is needed after the RO to further purify the acetic acid.

Pervaporation. Already in 1998, Ray et al. [76] proposed pervaporation for the separation of water from acetic acid. They evaluated different membranes for an acetic acid concentration range of 0-100 %. Acrylonitrile membranes exhibited best performance in both, selectivity and flux. Nevertheless, selectivity drastically dropped at low acetic acid concentrations. These results disqualify pervaporation for isolation of dilute acetic acid, but pervaporation is promising for purification. A more encouraging application of pervaporation was investigated by Yesil et al. [77] in 2018. The target of their work was the isolation of carboxylic acids (acetic acid, propionic acid, butyric acid, valeric acid and caproic acid) from a synthetic fermentation broth. The total acid concentration in the feed was 10 g l^{-1} with 2 g l^{-1} of each carboxylic acid. The best performing membrane was a PTFE (polytetrafluoroethylene) membrane functionalized with tri-dodecylamine (TDDA). The amine/carboxylic acid interaction already known from reactive LLX highly enhanced the separation efficiency. Nevertheless, selectivity is significantly higher for the carboxylic acids with higher molecular mass (e.g., selectivity for valeric acid is four times the selectivity of acetic acid).

Vapor permeation. A separation technology closely related to pervaporation is vapor permeation. Aydin et al. [78] proposed a vapor permeation process for the separation of LMCA from a waste fermentation broth. Like Yesil et al. [77], they used a PTFE membrane with an amine as functional group (i.e. TOA). They achieved a separation efficiency of 45 % of acetic acid and up to 86 % for propionic acid and butyric acid. The limitation of this process is a pH below 4 on the feed side of the membrane, as the LMCAs need to be present in their unionized form to permeate through the membrane. The permeate side was operated with a sodium hydroxide solution, maintaining a pH above 12. Vapor permeation therefore produces a permeate containing the salts of the alkaline solution and the corresponding LMCA (e.g., sodium acetate). To generate a product from these salts, further processing is necessary.

Electro-dialysis. Reported by Talnikar et al. [32] and Atasoy et al. [33], electro-dialysis is a promising, yet costly separation technology. It uses electric potential to let cations and anions pass through alternating cation-exchange and anion-exchange membranes. As shown by Jones et al. [79] for acetic acid, the acetate anions move towards the anode, permeating through the anion-exchange membranes, incapable of passing through the cation-exchange membranes. This whole process leads to a concentration of the acid in one compartment and purified solution in the other compartment. Jones et al. achieved a separation efficiency of above 92 % with their model feed solution containing 1.2 g l^{-1} of LMCA (e.g., acetic acid, butyric acid).

Membrane extraction. To remove inhibitors for fermentation from hydrolyzate streams, Grzenia et al. [80] proposed a membrane extraction process. With TOA diluted in 1-octanol as reactive solvent, they achieved 60 % regeneration of acetic acid in a hollow-fibre extraction setup. Additional to acetic acid, sulfuric acid was extracted and leaching of the amine to the fermentation broth was prevented. Not only the amines, which are toxic to fermentation microorganisms, but other harmful species, like phenols, were removed as a consequence of using 1-octanol as a diluent.

Non-membrane technologies

Melt crystallization. An interesting approach through melt crystallization was proposed by Choi et al. [81]. Unfortunately it only works for purification of undiluted acetic acid. They used the single-eutectic solid-liquid equilibrium of water/acetic acid to remove water from an acetic acid feed with a concentration above 60 wt%. Yet, they lack an energy demand evaluation and comparison for providing the low temperatures.

Adsorption. The most promising among the separation technologies in research stage is adsorption. In this concept, the LMCAs are adsorbed at the surface of functionalized resins similar to the interactions in reactive LLX. In 1995, Cloete et al. [82] proposed the use of weakly basic ion exchange resins (e.g., Duolite®A-375) based on tertiary amines to separate acetic acid from a 1 wt% solution. Desorption was performed with lime slurry, resulting in calcium acetate as the obtained product. The drawback of necessary further treatment to obtain the acids from their salts is compensated by the insensibility of the adsorption process to solids in the feed. Further, no solvents toxic to the environment or fermentation are used. Eregowda et al. [83] screened 11 ion exchange resins (i.e. Amberlite®IRA-67, DOWEX®optipore L-493) in 2019 for application in LMCA adsorption. In their sequential batch process with two different resins, they where able to selectively recover 85 % of acetic acid in the first step and 75 % of propionic acid in the second step of the acids initially present in the feed. Regeneration was again performed with a salt forming alkaline solution, in this case sodium hydroxide. The desorption or regeneration is crucial for adsorption processes. Using alkaline solvents produces acid salts and using water generates dilute aqueous solutions of LMCAs again. Reyhanitash et al. [84] circumvented these problems by using a temperature profile and by flushing with nitrogen (N_2). They also found the high adsorption capacity of amine-based resins problematic in case of other salts present in the feed solution. In this case, they observed a drastic reduction of the adsorption capacity due to co-adsorption of hydrochloric acid, sulfuric acid or phosphoric acid. Better adsorption behavior was observed with non-functionalized resins, allowing an adsorption capacity for carboxylic acids of 76 g kg^{-1} for a 1 wt% feed solution.

4.3. Emulsions and chemical reactions

A dispersion of two immiscible liquids is defined as an emulsion. While emulsions may show disadvantageous limitations in conventional industrial processes (e.g., physical liquid-liquid extraction), they are essential in other fields (e.g., pharmacy, food industry, chemical synthesis). In the following section, a brief introduction to the important topic 'emulsions' is given, and their application as an active reaction medium for chemical reactions is discussed. Detailed theory on emulsions can be found in the books of Tharwat F. Tadros [85, 86], and the chapters of van der Schaaf [87], Hloucha [88], and Holmberg [89] in Ullmann's encyclopedia of industrial chemistry. Additionally, the book of Lagaly et al. [90] and the doctoral thesis of Robert Macher-Ambrosch [91] provide details on emulsions and the splitting thereof.

4.3.1. Emulsion basics and classification

In an emulsion, droplets of a dispersed liquid phase are distributed in the continuous liquid phase. As both liquids must be immiscible, a stabilizer is needed to avoid immediate phase separation. Such stabilizers are surface-active substances (surfactants), which are discussed later in this section. Most common types of emulsions are oil-in-water (O/W) and water-in-oil (W/O) emulsions. Classification of emulsion depends on the field of interest and application. Alongside the dispersion type (e.g., O/W or W/O), classification can be done by dispersed phase holdup φ (volume ratio of the dispersed phase) or the droplet size range, as summarized in Table 4.2. *Via* phase holdup of the dispersed phase emulsions can be classified as dilute, concentrated and highly concentrated. The droplet size range also provides the three classes macroemulsions, nanoemulsions and microemulsions. Due to their special behavior, microemulsions are the topic of an independent chapter by Hloucha [88] in Ullmann's encyclopedia of industrial chemistry. Macroemulsions are mostly milky mixtures, while nanoemulsions can also be transparent (colloidal).

Table 4.2.: Classification of emulsions based on dispersed phase holdup φ and droplet size range

criterion	range	classification
dispersed phase holdup φ	$\varphi < 0.3$	dilute emulsion
	$0.3 < \varphi < 0.74$	concentrated emulsion
	$\varphi > 0.74$	highly concentrated emulsion
droplet size range	0.1 µm - 100 µm	macroemulsion
	50 nm - 1 µm	nanoemulsion
	<100 nm	microemulsion

Formation and occurrence

Emulsions may occur in any process involving two immiscible liquids. This may be intentional as in production of paints, as delivery system form of pharmaceuticals or in food industry (e.g., milk, mayonnaise). [87] An example for unwanted/unintended formation of emulsions is the field of liquid-liquid extraction. Due to high dispersion rates or due to the presence of biobased surfactant molecules, the biphasic system may emulsify. A special form of such an unintentionally formed emulsion in LLX is turbidity (a microemulsion with very low dispersed phase holdup). [91] Formation of emulsions, intended or not, requires two preconditions: a low interfacial tension and sufficient sheer stress. The latter can be applied by a stirrer, shaker or the rotating internals of a LLX-column. The low interfacial tension can be provided by adding a surfactant to the biphasic system.

Surfactants (surface-active substances)

Surface-active substances (surfactants) highly reduce the interfacial tension between two liquids by self-assembling at the interface. This self-assembly is driven by the molecular structure of the surfactants, as they consist of a polar and a non-polar group. [86, 89] In case of a biphasic liquid system of water and a non-polar solvent, the surfactant molecules gather at the liquid interface with the non-polar tail in the solvent and the polar head in the water. An example of a typical surfactant molecule structure is shown in Figure 4.7 with the example of 4-dodecylbenzenesulfonic acid. Surfactants may be classified by the charge of their polar head. This allows to distinguish between anionic, cationic, amphoteric and non-ionic surfactants. While anionic surfactants, as shown in the example in Figure 4.7, have a negatively charged head, cationic surfactants own a positively charged head. As a special case, amphoteric surfactants have two opposingly charged heads. Non-ionic surfactants do not have a charged head.

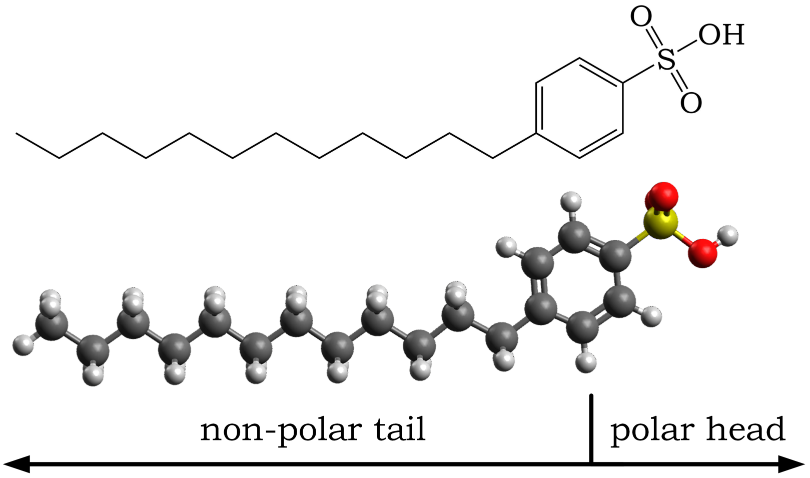


Figure 4.7.: Molecular structure of a surfactant (i.e. 4-dodecylbenzenesulfonic acid) with non-polar tail and polar headgroup.

Two characteristic values are used to specify the activity of surfactants: the hydrophilic-lipophilic balance (HLB) and the critical micelle concentration (CMC). The HLB-system was proposed by Griffin [92] in 1954 and indicates the preferred phase of the surfactant. A similar assessment can be derived from the logP-value. Holmberg [89] summarized the correlation between HLB and logP as an increase in HLB equaling a decrease in logP. The information drawn from the HLB of a surfactant allows interpretation of its applicability. This is compiled by Table 4.3. A strong anionic surfactant, like 4-dodecylbenzenesulfonic acid, exhibits a high HLB in the range of 13-15, characteristic for surfactants used as detergents, causing O/W emulsions.

Table 4.3.: Application of surfactants depending on the hydrophilic-lipophilic balance (HLB) according to Tadros [86]

HLB range	application
3 – 6	W/O emulsifier
7 – 9	wetting agent
8 – 18	O/W emulsifier
13 – 15	detergent
15 – 18	solubiliser

The second characteristic value of a surfactant is the critical micelle concentration (CMC). Van der Schaaf [87] simply describes the CMC as the concentration of surfactant, at which the interface is completely occupied by surfactant molecules. Above the CMC, the interfacial tension is almost constant. Further admixture of surfactant to the system causes formation of micelles. Figure 4.8 displays schematic drawings of a spherical micelle and an inverse spherical micelle. Micelle bodies are not limited to spherical shape, but may also form rods or lamellar structures. Micellar systems are for example used as reaction media for chemical reactions as described in section 4.3.4.

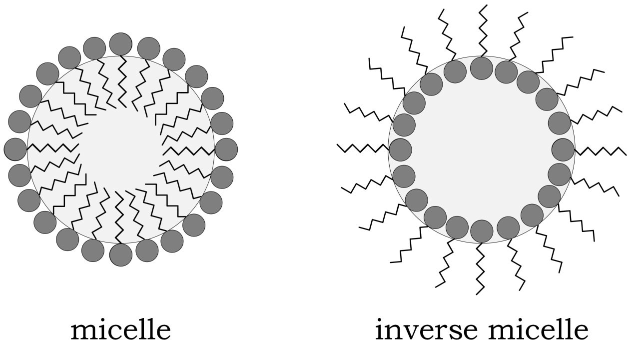


Figure 4.8.: Scheme of a spherical micelle (water surrounding, organic phase in the micelle) and of an inverse spherical micelle (water in the micelle, organic phase surrounding).

The phase behavior of emulsions above the CMC is mainly influenced by temperature and the amount of surfactant in the system. Investigations thereof were done by Hohl et al. [93] and Kraume et al. [94]. In Figure 4.9 the so called 'fish'-diagram described by Kahlweit [95] is shown for systems with constant mass ratio between solvent and water. Switching between different phase types can be achieved by either varying the temperature or the amount of surfactant.

4.3.2. Stability of emulsions

Surfactants crucially influence the stability of emulsions, which is the reason for their addition in the first place. No matter, if the emulsification is intended or not, the stability of an emulsion is essential for the corresponding process. While the splitting or separation of emulsions is unwanted for example in the food industry, a stable emulsion leads to breakdown of any continuous LLX. Stability of emulsions changes with the type of emulsion: macroemulsions and nanoemulsions are only kinetically stable, while microemulsions are thermodynamically stable. The kinetically stable emulsions are subject to various breakdown phenomena.

Droplet phenomena in emulsions

Breakdown phenomena, as described by Tadros [86] or van der Schaaf [87], include creaming, sedimentation, flocculation, phase inversion, coalescence and Ostwald ripening. All these phenomena sooner or later lead to splitting of the emulsion, if not counteracted by mechanical measures. Creaming and sedimentation is caused by the density difference between dispersed and continuous phase. As a consequence, the dispersed phase (droplets) accumulates at the top or at the bottom of the system. Flocculation describes the agglomeration of dispersed phase droplets without changing the initial droplet size. Phase inversion can be caused by a change of temperature, i.e. according to the 'fish'-diagram of Kahlweit et al. [95] in Figure 4.9.

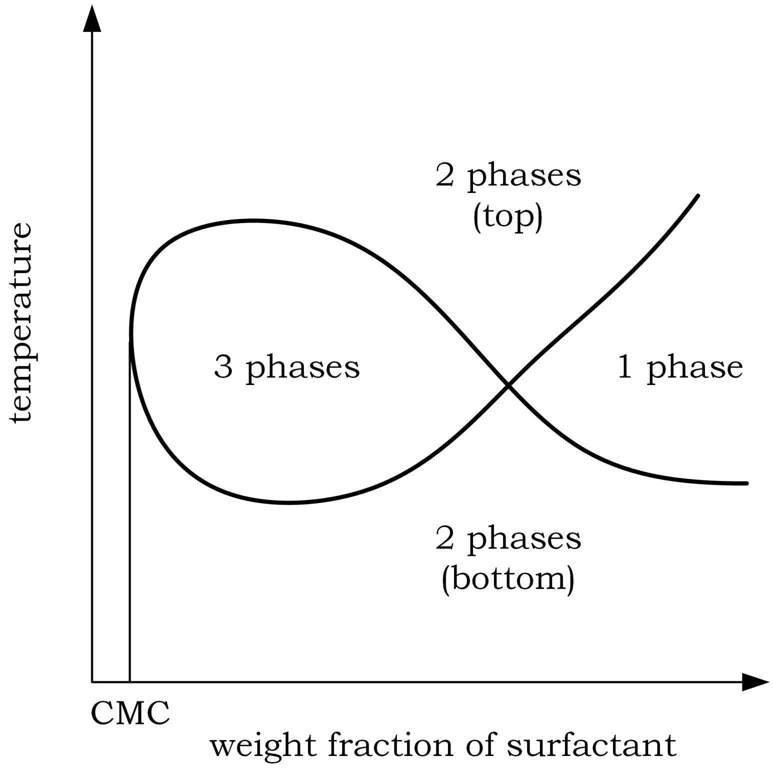


Figure 4.9.: Scheme of the phase behavior of an emulsion system at constant mass ratio of solvent to water, in dependency of the temperature and the amount of surfactant according to Kahlweit et al. [95]. 3 phases: bicontinuous microemulsion with solvent top phase, high surfactant load middle phase and aqueous top phase; 2 phases (top), 2 phases (bottom): O/W emulsion with solvent-rich top phase or W/O emulsion with water-rich bottom phase, respectively; 1 phase: single microemulsion phase at high surfactant concentration.

Coalescence occurs as a consequence of droplet-droplet interaction in the emulsion (e.g., collision). These interactions are described by the DLVO-Theory (developed by Derjaguin, Landau, Verwey, and Overbeek), correlating the energy potential and the distance between the droplets. Tadros [86] and Heusch et al. [96] provide a compact summary of the single steps of coalescence and the application of the DLVO-Theory to coalescence in emulsions.

The last droplet phenomenon is Ostwald ripening. Ostwald ripening requires partial mutual solubility of the two phases. As a consequence, smaller droplets dissolve in the continuous phase while larger droplets grow. The droplet size distribution shifts towards larger droplet diameters by this diffusion-driven process over time.

4.3.3. Emulsion splitting techniques

Breaking or splitting of emulsions must mainly be performed for unintended emulsification or for intended phase separation i.e. after finished chemical reaction in the emulsion. Several technological approaches may be applicable for this task: chemical splitting, electrical splitting, thermal splitting and mechanical splitting. A summary of these approaches is given by Macher-Ambrosch [91].

Chemical spitting The breaking of an emulsion by chemical means is achieved through admixture of a demulsifier. This approach is industrially applied, for example in the petrochemical industry, as described by Angle [97]. Most demulsifying substances are surfactants themselves or simply solubilizers like alcohols. Although effective, chemical splitting is problematic as an additional chemical species is added to the system demanding an additional downstream treatment.

Electrical spitting Electrical splitting depends on dipole-dipole interactions, electrophoresis and di-electrophoresis and differs for W/O and O/W emulsions. For W/O emulsions the application of alternating current (AC) or pulsed direct current (DC) is to be applied according to Mhatre et al. [98]. O/W emulsions are proposed to be split through DC by Ichikawa [99]. The application of DC splitting of O/W emulsions was investigated by Macher-Ambrosch [91] in his doctoral thesis with the target of turbidity control in aqueous raffinate phases from LLX processes.

Thermal spitting W/O emulsions can be split by applying heat (e.g., microwave radiation, simple heating). Referring to the diagram in Figure 4.9, splitting or shifting phases by temperature change is reasonable. Larson et al. [100] explained this phenomenon with the lower solubility of water in the solvent at increasing temperature. Nevertheless, this approach is reported to be slow compared to other techniques.

Mechanical spitting Mechanical breakage of emulsions can be achieved by filtration, flotation or forced sedimentation. Sedimentation in the gravitational field is easy to implement, but extremely slow, especially for emulsions with surfactant concentrations above the CMC. Application of an external force field, i.e. through centrifugation, significantly decreases splitting time.

4.3.4. Chemical reactions in emulsions and micellar systems

The unique conditions in emulsified systems, especially in micellar systems, have drawn attention of chemists to make use of emulsions as reaction media. One such condition is the high mass transfer area provided through emulsification. Another one, important for reactions in aqueous media, is the increased local concentration of reactants within the micellar structures.

Aqueous environment for organic reactions

The evolution of solvents for organic synthesis has been evaluated by Lipshutz et al. [101]. Subsequently, they propose the shift from conventional solvents towards water, not least for environmental reasons. Manabe et al. [102], Hamerla et al. [103], Dwars et al. [104], and Kaur et al. [105] have reviewed emulsions and micellar systems as reaction media. Reactions performed in micellar systems require suitable catalysts to achieve reasonable conversion, but also the reaction itself needs to be suitable for this special reaction medium. As stated by Shiri et al. [106] dehydration reactions generally exhibit the problem that water is a reaction product and conversion suffers from the aqueous environment. Therefore, they are suggested for being performed in micellar systems. Basically, the surfactant inducing and stabilizing the emulsion can serve two purposes: either the surfactant is used for emulsification only or it offers the properties of a surfactant and a catalyst in the same molecule.

Surfactant-enhanced mass transfer

An example for the admixture of a surfactant to generate a micellar environment with high mass transfer area was investigated by Kraume et al. [94] and Hamerla et al. [103]. Their model reaction was a hydroformylation, in which the surfactant served the sole purpose of enhancing contact between reactants, solvent and catalyst solution.

Surfactant-type catalysts

Surfactants can act as catalysts through Brønsted-acid or Lewis-acid interactions. This was investigated for a variety of reactions as for example for ether synthesis by Mandal et al. [107], to use water as a reaction medium. Kobayashi et al. [108] performed selective organic synthesis reactions in aqueous media with the help of Lewis-acid-surfactant catalysts (LASC). As mentioned before, dehydration reactions like esterifications are predestined for surfactant-catalyst systems. Zhao et al. [109] used a Brønsted-Lewis-surfactant hetero-polyacid for catalyzing an esterification reaction. Zheng et al. [110] used a Brønsted-acid surfactant ionic liquid for the synthesis of ethyl oleate. More process related aspects were investigated by Milano-Brusco et al. [111] by evaluating the product isolation and catalyst recycling of a hydrogenation reaction in a surfactant system. Catalyst recycling with micellar-enhanced ultrafiltration (MEUF) showed promising results.

4-DBSA as catalyst A catalyst often mentioned especially for esterification and transesterification reactions, is 4-dodecylbenzenesulfonic acid (4-DBSA). Application of this strong anionic surfactant was reported by Hagen et al. [112] as highly potent for transesterification of fatty acids with ethanol. Also Alegria et al. [113] used 4-DBSA for the catalysis of transesterification of triglycerides with methanol to biodiesel. They highlighted the high performance at even mild conditions. 4-DBSA is further reviewed in the work by Kaur et al. [105], Manabe et al. [102] and Shiri et al. [106] as a Brønsted-acid-surfactant catalyst. The catalysis of solvent free esterification of higher carboxylic acids at room temperature with 4-DBSA was investigated by Gang et al. [114].

Part II.

Reactive separation based process concept

5. Overall process concept and problem solving strategy

Applying the creative, heuristic mechanism of TIPS allows the development of a suitable process concept for value-added valorization of low-molecular-weight carboxylic acids (LMCA), as described in Chapter 2. The main problem to be tackled is the low concentration of the LMCAs in the feed stream. Increasing the concentration *via* distillation is not economic as confirmed by the vapor-liquid equilibria shown in Figure 2.1. TIPS suggests using reactive separation technologies (e.g., reactive extraction) to increase the concentration and avoid a higher complexity of the process. Reactive extraction provides the possibility of applying a low-energy technology for isolation of the LMCAs. Conventional reactive extraction uses complex-forming/adduct-forming/salt-forming reactions to enhance extraction efficiency. Through regeneration, the LMCAs are isolated. To implement the generation of value-added products, a chemical conversion is necessary. Instead of using complexation, esterification can be performed to generate the corresponding ester of the LMCAs. The esterification enhances extraction through the TIPS principle 'change of properties', as the esters exhibit a higher affinity to the solvent phase. The problem with esterification in the given setting is the high water excess, as water is the basic carrier of the target constituent (LMCA) and it is produced as a byproduct. According to Le Chatelier's law, the initial excess of water prevents sufficient conversion. TIPS again provides options for solution: changing the state and 'pseudo-states'. Changing the state in this case suggests to remove the desired constituents from the feed stream. This is achieved by extraction of the reaction product (esters) and the low-molecular-weight carboxylic acids. The choice of a higher aliphatic alcohol provides the benefit of significantly decreasing the water-solubility of the produced esters. As a consequence, the extraction efficiency improves and secondary pollution of the aqueous feed is counteracted by low solubility of products in water. Increasing the conversion is achieved by introducing a 'pseudo-state': addition of a surfactant, to allow formation of a quasi-homogeneous state. This measure drastically decreases the mass transfer limitation of the esterification reaction in the aqueous environment. The choice for a catalytically active surfactant (e.g., 4-dodecylbenzenesulfonic acid) provides high mass transfer area in a quasi-homogeneous state by emulsification together with an increased reaction rate.

Regeneration of the product-laden solvent is crucial for closing the process cycle. The high boiling point and the vapor-liquid equilibria of the solvent, the alcohol used for esterification and the, thus, produced esters make simple distillation less suitable. Yet, again changing the properties of the product through chemical conversion can provide a solution. The high-boiling esters are transesterified with a low-molecular weight alcohol (e.g., methanol or ethanol) to form low-boiling equivalents. These low-boiling esters can easily be separated by distillation at a reasonably low temperature level. Complexity and efficiency of this regeneration step can be improved by implementation in a reactive distillation. The transesterification provides the additional benefit of regenerating the higher aliphatic alcohol for the emulsion-enhanced esterification step. Ideally, the catalyst from the esterification step is also capable of enhancing the transesterification reaction, and it is recycled with the solvent stream.

Combining all of these considerations in a conceptual process seems a reasonable approach to meet the target of valorization of low-molecular-weight carboxylic acids from dilute biobased streams. A scheme of this process concept is shown in Figure 5.1 for a representative feed concentration of LMCA of 1 mol l^{-1} and methanol as low-molecular-weight alcohol for transesterification.

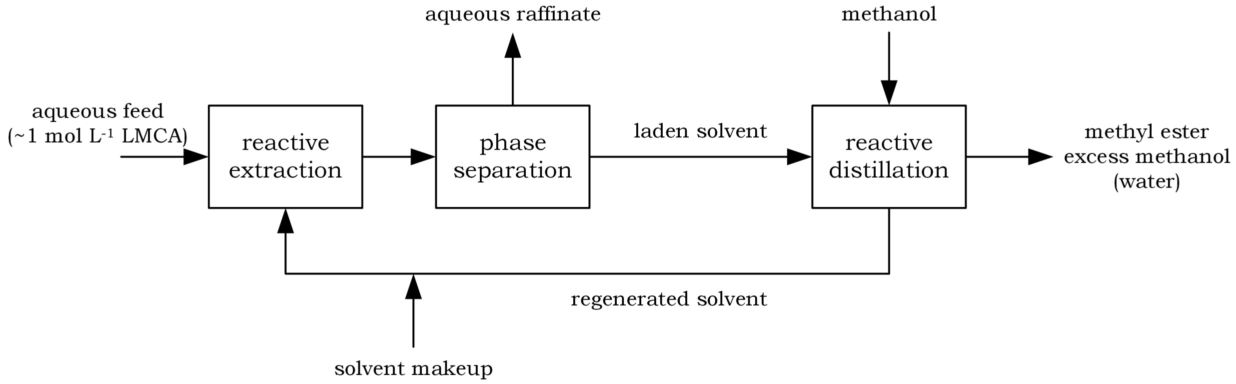


Figure 5.1.: Scheme of the proposed overall process concept for valorization of dilute low-molecular-weight carboxylic acids (LMCAs) from aqueous biobased feed.

The proposed process concept consists of three crucial steps:

1. **Step** emulsion-enhanced biphasic esterification with *in-situ* extraction
2. **Step** phase separation and emulsion splitting
3. **Step** solvent regeneration *via* transesterification in reactive distillation

The first step requires a reaction system with low water solubility of the alcohol and the produced esters. The solvent for extraction needs high affinity to the esters, the alcohol and the LMCAs, yet it should cause low co-extraction of water. Further, the solvent must allow high regeneration rates without loss or decomposition. Crucial step for the overall process is a high conversion at low to moderate temperatures and a high mass transfer area in the biphasic system.

As a resolution to this requirements, 1-octanol was chosen as reaction educt and *n*-undecane as an inert solvent. Increasing the reaction rate and inducing a quasi-homogeneous state for enhanced mass transfer can be achieved by using the Brønsted-acid-surfactant catalyst 4-dodecylbenzenesulfonic acid (4-DBSA).

The second step demands a high phase separation efficiency obtained with simple means. This step should not add more components to the system to avoid secondary pollution of the aqueous phase. Sedimentation in the gravity field or accelerated by centrifugation is preferred. As 4-DBSA is a strong anionic surfactant, even low concentrations thereof cause formation of stable emulsions. This can be prevented by adapting the 'change of properties' to the catalyst. Modification of the surfactant properties of 4-DBSA grants access to a nearly water-insoluble catalyst with improved surfactant-activity. Such a catalyst was developed by coupling of 4-DBSA with nickel to form a metallosurfactant ($Ni(DBSA)_2$) which provides sufficiently low interfacial tension for high mass transfer area in a quasi-homogeneous state.

The third step demands a high regeneration efficiency for best removal of the low-boiling constituents from the laden solvent. Transesterification needs to be accelerated to ensure maximum conversion of the octyl esters formed in the first step, ideally with the same catalyst as used in the esterification step. As temperatures may be higher than in the esterification step, the catalyst needs to be thermally stable. The third step further needs to be insensible to residual LMCAs and co-extracted water. All requirements stated so far for the solvent regeneration step can be met with transesterifying the octyl esters with methanol or ethanol in presence of 4-DBSA or $Ni(DBSA)_2$.

Summing up, the octyl esters are used as 'shuttle'-species for valorizing the low-molecular-weight carboxylic acids. The proposed process concept therefore uses 1-octanol in the first step to esterify the LMCAs in an emulsified environment to their respective octyl esters, according to the reaction in Equation 5.1.

$$R_1COOH + R_2OH \overset{\text{CAT}}{\rightleftharpoons} H_2O + R_1COOR_2 \tag{5.1}$$

As residual LMCAs and unreacted 1-octanol are present in the laden solvent, transesterification (Equation 5.2) and direct esterification of the residual LMCAs (Equations 5.3 and 5.4) are observed in reactive distillation.

$$R_1COOR_2 + R_3OH \overset{\text{CAT}}{\rightleftharpoons} R_2OH + R_1COOR_3 \tag{5.2}$$

$$R_1COOH + R_2OH \overset{\text{CAT}}{\rightleftharpoons} H_2O + R_1COOR_2 \tag{5.3}$$

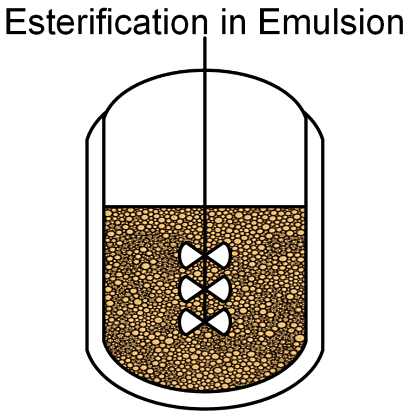
$$R_1COOH + R_3OH \overset{\text{CAT}}{\rightleftharpoons} H_2O + R_1COOR_3 \tag{5.4}$$

6. Intensification of esterification through emulsification: isolation of dilute low-molecular-weight carboxylic acids

This part of the thesis discusses the first part of the reactive separation concept: liquid-liquid extraction coupled with esterification in an emulsified regime. The research article was published on 8th October 2018 in Reaction Chemistry & Engineering and is available *via* DOI: 10.1039/c8re00194d.

Synopsis

A concept for isolation of dilute low molecular weight carboxylic acids, based on surfactant-catalyst enhanced esterification, is proposed.



$$R_1COOH + C_8H_{17}OH \xleftrightarrow{4DBSA} R_1COOC_8H_{17} + H_2O$$

Reaction
Chemistry &
Engineering

PAPER

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View Journal | View Issue

Cite this: *React. Chem. Eng.*, 2018, **3**, 905

Received 4th September 2018,
Accepted 8th October 2018

DOI: 10.1039/c8re00194d

rsc.li/reaction-engineering

Intensification of esterification through emulsification: isolation of dilute low molecular weight carboxylic acids

Andreas Toth, * Susanne Lux, Daniela Painer and Matthäus Siebenhofer

A concept for isolation of low molecular weight carboxylic acids (*e.g.*, acetic acid) from dilute aqueous streams was developed. This concept of combining chemical conversion of the carboxylic acids with *in situ* liquid–liquid extraction enhanced by catalysis and emulsification was proven applicable for carboxylic acid concentration of 1 mol l^{-1}. Chemical conversion was achieved by esterification with 1-octanol, catalysed by the surfactant 4-dodecylbenzenesulfonic acid. Emulsification induced by the catalyst was confirmed to be essential for high conversion and separation efficiency. Investigations were supported and evaluated by design of experiments and yielded conversions beyond 54.3% and separation efficiencies beyond 57.5% for acetic acid. Evaluation of process parameters yielded a quadratic model for prediction of process performance. Applicability of the concept for formic acid, propionic acid and butyric acid isolation from aqueous feed was confirmed.

1 Introduction

Sustainable utilization of biobased feedstock to its full extent embodies one of the main aims of the biorefinery concept. This aim requires efficient and environmentally sound separation technologies.[1] Such processes are widely available for feed streams with highly concentrated constituents, in sharp contrast to the isolation of constituents from dilute aqueous streams/effluents. Dilute effluent streams occur throughout the biorefinery, exemplarily in pulping processes. These processes generate effluents containing valuable constituents such as (hydroxy-)carboxylic acids at varying concentrations, which are either flushed or incinerated.[2,3]

A compilation of separation technologies for isolation of carboxylic acids from dilute aqueous streams is given by Talnikar *et al.*,[4] including reactive separations. The latter have shown great potential for dealing with dilute aqueous streams *e.g.*, reactive distillation for isolation of acetic acid or formic acid.[2,5,6] While these processes work well for a concentration of 30 wt% carboxylic acid in the feed, for lower concentrations (6 wt% and below) the only industrial applied technology is reactive extraction.[7] This technology is based on adduct formation of the carboxylic acid with a reactive extractant and requires complex solvent regeneration. Sustainability and application range of such processes are critically lowered due to the preferred use of organophosphorous compounds and various aliphatic amines as reactive extractants.[4,7] Some of the reactive extraction processes reviewed by Talnikar *et al.*[4] require residence times of up to 24 h, hindering an industrial implementation.

In order to provide a simple, yet efficient alternative technology for isolation of low molecular weight carboxylic acids, the present work presents the concept of combining the two main benefits of reactive distillation and reactive extraction. These are the (catalysed) chemical conversion of reactive distillation and the moderate, easy-to-implement process of liquid–liquid extraction. In this context, chemical conversion does not refer to adduct formation in the sense of conventional reactive extraction, but rather to the transformation of the constituent to a product (*e.g.*, esterification of carboxylic acids). For esterification, low concentration of reactants and a high excess of water inhibit the reaction rate and shift the reaction equilibrium composition to the reactant side. Nevertheless, high conversion rates may be achieved by utilizing surfactant catalysts like 4-dodecylbenzenesulfonic acid (4DBSA). The catalyst activity and its influence on the reaction was stated by Manabe *et al.*,[8] who achieved high yields in dehydrative esterification of lauric acid with 3-phenyl-1-propanol in water. Emulsification induced by surfactant catalysts like 4DBSA has been reported to be beneficial for etherification reactions in water[9] and various organic reactions in aqueous and biphasic media.[8,10–12] Although the benefits of emulsification are highlighted *e.g.*, for dehydration reactions,[8] the work of Hohl *et al.*[12] indicates the complexity of emulsified multiphase systems. Thorough evaluation of

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process parameter influence on emulsification and process performance is essential for applicability and modeling of the concept.

The proposed concept of combining extraction with chemical conversion targets the limitation of the state of the art separation processes by using a reactive, catalytically active solvent phase. For this purpose, the solvent phase (*e.g.*, *n*-undecane) contains a higher aliphatic alcohol for esterification (*e.g.*, 1-octanol) and a surfactant catalyst (*e.g.*, 4-dodecylbenzenesulfonic acid) for enhancing reaction rate and mass transfer. While esterification of higher molecular weight carboxylic acids is investigated more frequently, less effort has so far been spent on low molecular weight carboxylic acids, which occur more frequently in biobased effluents. The concept was thus applied for acetic acid isolation (1 mol L^{-1}) and extended to other low molecular weight carboxylic acids. In order to meet requirements of efficient and environmentally sound separation processes, the proposed concept aims at meeting the "24 principles of green engineering and green chemistry" summarised by Tang *et al.*[13] and the CHEM21 selection guide for solvents by Prat *et al.*[14]

2 Materials and methods

2.1 Chemicals

Acetic acid (CAS: 64-19-7; Sigma-Aldrich) with a purity of 99–100% and 1-octanol (CAS: 111-87-5; Sigma-Aldrich) with a purity of >98% were used as reactants. *n*-Undecane (CAS: 1120-21-4; Sigma-Aldrich) with a purity of >99% was used as diluent and 4-dodecylbenzenesulfonic acid (4DBSA; CAS: 121-65-3; Sigma-Aldrich; mixture of isomers) with a purity of >95% was used as catalyst. Formic acid (CAS: 64-18-6; Chem-Lab), propionic acid (CAS: 79-09-4; Sigma-Aldrich) and butyric acid (CAS: 109-92-6; Merck) all with a purity of >99% were used as reactants for reference experiments. Hydrochloric acid (CAS: 7647-01-0; Carl Roth) with a purity of 37% p.a. and Amberlite® IR120$^+$ (CAS: 39389-20-3; Sigma-Aldrich) were used as reference catalysts. Amberlite® IR120$^+$ was rinsed with deionized water and dried before use; all other chemicals were used without further pretreatment.

2.2 Experimental procedure

Esterification experiments were performed in a 1000 ml jacket batch reactor stirred with a triple Rushton turbine impeller. For sealing the batch reactor, a custom-made PTFE-lid with sockets for the stirrer, a thermometer and for sampling was used. The batch reactor temperature was kept constant with water using a Lauda RC20 thermostat; the temperature was measured with a digital thermometer (TFA Dostmann; ±0.8 °C). Discharging of the reaction mass was done *via* a PTFE-sealed outlet at the bottom of the batch reactor.

Water was filled into the batch reactor together with the solvent phase and heated up to the desired operation temperature under constant stirring. The solvent phase consisted of 1-octanol as reactant, 4-dodecylbenzenesulfonic acid (4DBSA) as catalyst and *n*-undecane as diluent. After reaching the reaction temperature, admixing the carboxylic acid initiated the reaction. The experiments were stopped after an arbitrarily chosen reaction time of 3 h. At this time, the stirrer was stopped and after primary phase separation of 3 min samples of 10 ml were taken from the top and the bottom of the reaction mixture with a syringe. These samples were centrifuged for 10 min to generate enough clear sample for GC analysis to avoid distorting process performance by uncontrolled reaction progress. For the mass balance, the remaining reaction mass was split by centrifugation for 30 min to achieve adequate phase separation with minimum entrainment of the two phases into each other. A Heraeus Labofuge 400 benchtop centrifuge was used for emulsion splitting at rcf 2383.

2.3 Analytics

Both liquid phases were analysed by gas chromatography in a Shimadzu GC 2010 plus equipped with an AOC 20i/s autosampler, a flame ionization detector (FID) and a thermal conductivity detector (TCD) in parallel operation. A Phenomenex column of type Zebron ZB WAXplus (60 m × 0.32 mm × 0.5 μm) was used. The samples were injected undiluted (0.3 μl) in split mode with a split ratio of 120 and an injection temperature of 250 °C. Helium was used as carrier gas. The temperature program started at 45 °C for 5 min and ramped up to 150 °C with a rate of 25 °C min^{-1} and a final hold for 3.3 min. Both detectors were operated at 270 °C. The relative standard error of the GC measurements was in the range of 1.9% for all components analysed *via* FID and 4.1% for water.

Reaction progress of the reference experiments with formic acid, propionic acid and butyric acid as well as 4DBSA and hydrochloric acid was determined with a SI Analytics TitroLine 7800 autotitrator. A potassium hydroxide solution (0.1 mol L^{-1}) was used for acid/base titration. The solvent phase was dissolved in a mixture of 2-propanol and deionized water prior to titration.

2.4 Design of experiments (DoE)

Investigations were planned based on the concept of design of experiments in order to minimize experimental effort, while gaining insight into parameter interaction and influence. The design of experiments was developed and evaluated with the commercial software MODDE® Pro 12 (Umetrics). Table 1 shows the chosen process parameters with the investigated ranges. Carboxylic acids were used at a feed

Table 1 Investigated process parameters (factors) with minimum and maximum values

Process parameter	Min	Max	Unit
Temperature (T)	25	60	°C
Stoichiometric ratio (OH : H)	0.8	1.5	mol_{OcOH} $mol_{A,0}^{-1}$
Phase ratio (S : A)	0.5	2.0	—
Catalyst load (CAT)	0.015	0.060	eq. $mol_{A,0}^{-1}$
Stirrer speed (n)	300	450	rpm

concentration of 1 mol l^{-1} for all experiments; the total reaction volume was fixed with 600 ml. Catalyst load and stoichiometric ratio were based on the initial amount of carboxylic acid at the reaction start.

Two characteristic numbers were defined as response factors to enable comparison and evaluation of the single experiments. The first is the overall conversion of carboxylic acid as defined in eqn (1), which allows assessment of the reaction kinetics. In this equation, X_A is the overall conversion, $m_{A,0}$ the initial mass of carboxylic acid and $m_{A,sol}$ and $m_{A,aqu}$ the mass of carboxylic acid at the end of the experiment in the solvent and in the aqueous phase, respectively.

$$X_A = \frac{m_{A,0} - \left(m_{A,sol} + m_{A,aqu}\right)}{m_{A,0}} \tag{1}$$

The second characteristic number is the separation efficiency SE_A based on the carboxylic acid (defined in eqn (2)) providing information on total carboxylic acid removal from the aqueous phase. Eqn (2) represents the separation efficiency SE_A, which is defined as the ratio of the mass of the carboxylic acid removed from the aqueous phase to the initial mass of carboxylic acid.

$$SE_A = \frac{m_{A,0} - m_{A,aqu}}{m_{A,0}} \tag{2}$$

3 Results and discussion

3.1 Catalyst comparison and impact of emulsification

Comparing different types of catalysts confirmed the necessity of emulsification for high process performance. Emulsification induced by the surfactant catalyst 4-dodecylbenzenesulfonic acid requires attention, as catalyst loads above 0.06 eq. $mol_{A,0}^{-1}$ produce stable emulsions. This high emulsion stability is to be avoided, since splitting of such emulsions by centrifugation is not possible. Impact of emulsification on both response factors was determined by comparing the uncatalysed esterification to esterification enhanced with three different catalysts. Hydrochloric acid and Amberlite® IR120$^+$ were used as non-surfactant catalysts at the same molar equivalents as the surface-active catalyst 4DBSA. Attrition of the solid catalyst was not observed during the experiments due to the reactor geometry and the small amount of catalyst. Fig. 1 displays the results of these experiments with conversion in white and separation efficiency in grey.

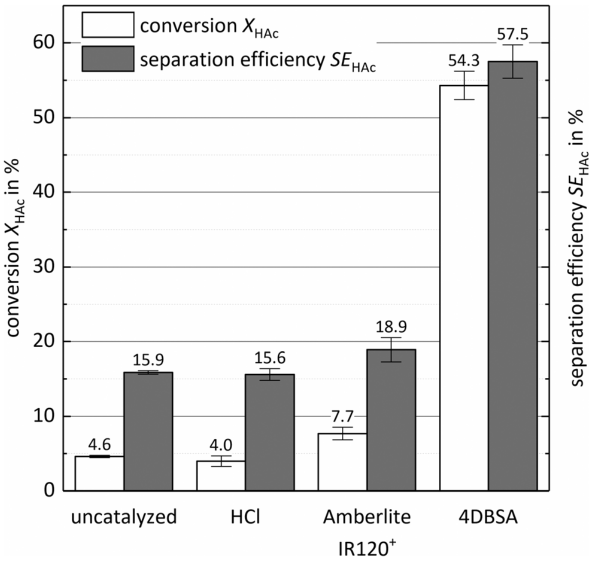

Fig. 1 Impact of emulsification induced by 4DBSA on acetic acid conversion X_{HAc} (left bars; white) and separation efficiency SE_{HAc} (right bars; grey) compared to catalysis with HCl, Amberlite® IR120$^+$ and an uncatalysed reference. Catalysts used at 0.06 eq. $mol_{A,0}^{-1}$, reaction time 3 h, reaction temperature 60 °C, phase ratio 2, stirrer speed 300 rpm and 1.5-fold stoichiometric excess of alcohol.

The uncatalysed reference experiment yielded a conversion of about 4.6 ± 0.2% and a separation efficiency of 15.9 ± 0.2%. These results were confirmed to be the maxima for the given process conditions as a consequence of the phase and reaction equilibria. As shown in Fig. 1, catalysis with hydrochloric acid and Amberlite® IR120$^+$ yielded 4 ± 0.7% and 7.7 ± 0.8% conversion and 15.6 ± 0.8% and 18.9 ± 1.6% separation efficiency, respectively. For these two catalysts, the slight increase of SE_A can be explained by the change of extraction properties of the solvent phase due to reaction progress. This improved reaction progress increases the concentration of ester in the solvent phase. The slightly better performance of the HCl-catalysed experiment compared to the uncatalysed reference is negligible and explained by a higher deviation of the HCl-catalysed results. As a result, the catalysis with a homogeneous catalyst in the aqueous phase has no significant influence on process performance.

Comparing these results with the performance of 4DBSA confirms the positive impact of emulsification on the process. The induced emulsification highly increases the mass transfer area up to quasi-homogeneous state and thus enhances phase contact, overriding mass transfer limitation. As

Table 2 Scaled and centered parameters for the DoE-based models predicting conversion X_{HAc} and separation efficiency SE_{HAc} of acetic acid esterification with a confidence interval of 95%

Parameter	X_{HAc}	SE_{HAc}
β_i	29.13 ± 0.72	34.62 ± 0.82
β_T	11.50 ± 0.85	10.30 ± 0.96
$\beta_{S:A}$	0.50 ± 0.82	0.88 ± 0.94
β_{CAT}	4.04 ± 0.81	3.47 ± 0.92
$\beta_{OH:H}$	3.50 ± 0.88	5.06 ± 1.00
β_n	−1.40 ± 0.82	−1.43 ± 0.93
$\beta_{T\cdot OH:H}$	3.80 ± 0.97	4.00 ± 1.08
$\beta_{T\cdot n}$	−1.18 ± 0.92	−1.32 ± 1.04
$\beta_{S:A\cdot CAT}$	0.91 ± 0.85	1.07 ± 0.97
$\beta_{S:A\cdot n}$	1.49 ± 0.87	1.30 ± 0.99
$\beta_{CAT\cdot OH:H}$	1.52 ± 0.92	Not used
$\beta_{OH:H\cdot n}$	1.00 ± 0.94	Not used

a result, an overall conversion of 54.3 ± 1.9% and a separation efficiency of 57.5 ± 2.2% was achieved with 4DBSA. As low molecular weight carboxylic acids like acetic acid are preferably present in the aqueous phase and the higher alcohol 1-octanol has a much higher solubility in the solvent phase, catalysis at the interphase or in the solvent phase is more efficient. Targeting this necessity much better than HCl and Amberlite® IR120$^+$ (both mainly present in the aqueous phase), the surface active catalyst 4DBSA is assumed to accumulate at the interphase as well as in the solvent phase due to its hydrophobic dodecyl group.[15]

3.2 Parameter screening and process modeling for acetic acid esterification

Parameter screening and process modeling was done for acetic acid as model carboxylic acid. The concept of design of experiments was used to determine the main influence parameters *via* parameter screening and optimisation. The models shown in eqn (3) for overall conversion and in eqn (4) for separation efficiency were derived from DoE-results. Quadratic models were simplified by dismissing insignificant parameters. The remaining parameters including confidence intervals for 95% probability are given in Table 2 for both models.

$$\begin{aligned}X_{\mathrm{HAc}} = {}& \beta_{X_{\mathrm{HAc}}} + \beta_T\cdot(T) + \beta_{\mathrm{S:A}}\cdot(\mathrm{S:A}) + \beta_{\mathrm{CAT}}\cdot(\mathrm{CAT}) \\ & + \beta_{\mathrm{OH:H}}\cdot(\mathrm{OH:H}) + \beta_n\cdot(n) + \beta_{T\cdot\mathrm{OH:H}}\cdot(T)\cdot(\mathrm{OH:H}) \\ & + \beta_{T\cdot n}\cdot(T)\cdot(n) + \beta_{\mathrm{S:A\cdot CAT}}\cdot(\mathrm{S:A})\cdot(\mathrm{CAT}) + \beta_{\mathrm{S:A}\cdot n}\cdot(\mathrm{S:A})\cdot(n) \\ & + \beta_{\mathrm{CAT\cdot OH:H}}\cdot(\mathrm{CAT})\cdot(\mathrm{OH:H}) + \beta_{\mathrm{OH:H}\cdot n}\cdot(\mathrm{OH:H})\cdot(n)\end{aligned} \tag{3}$$

Twelve parameters enable prediction of acetic acid conversion with R^2 = 0.984, Q^2 = 0.956 and a reproducibility of 0.993. While the high R^2 indicates a good fit of the model for the experimental data, Q^2 close to 1 confirms a good response prediction within the investigated parameter ranges. Experimental noise level is very low, which is confirmed by the high reproducibility. A graphical comparison of experimental data and predicted conversions and separation efficiencies is shown in Fig. 2 and 3.

Fig. 4 (left diagram) shows the influence of scaled and centered parameters on the conversion of acetic acid. Temperature (*T*) is the main influence parameter followed by catalyst load (CAT) and stoichiometric ratio (OH : H). Although the impact of the phase ratio (S : A) is not significant in itself, its interaction with catalyst load and stirrer speed (*n*) influences the overall conversion. The only parameters causing a retarding effect on the overall conversion are an increased stirrer speed and the interaction of stirrer speed and temperature. This may be explained by a shift of the drop size distribution towards smaller droplet diameters. The surface of small droplets becomes rigid due to the surfactant molecules and thus hinders mass transfer.[15]

$$\begin{aligned}\mathrm{SE}_{\mathrm{HAc}} = {}& \beta_{\mathrm{SE}_{\mathrm{HAc}}} + \beta_T\cdot(T) + \beta_{\mathrm{S:A}}\cdot(\mathrm{S:A}) + \beta_{\mathrm{CAT}}\cdot(\mathrm{CAT}) \\ & + \beta_{\mathrm{OH:H}}\cdot(\mathrm{OH:H}) + \beta_n\cdot(n) + \beta_{T\cdot\mathrm{OH:H}}\cdot(T)\cdot(\mathrm{OH:H}) \\ & + \beta_{T\cdot n}\cdot(T)\cdot(n) + \beta_{\mathrm{S:A\cdot CAT}}\cdot(\mathrm{S:A})\cdot(\mathrm{CAT}) + \beta_{\mathrm{S:A}\cdot n}\cdot(\mathrm{S:A})\cdot(n)\end{aligned} \tag{4}$$

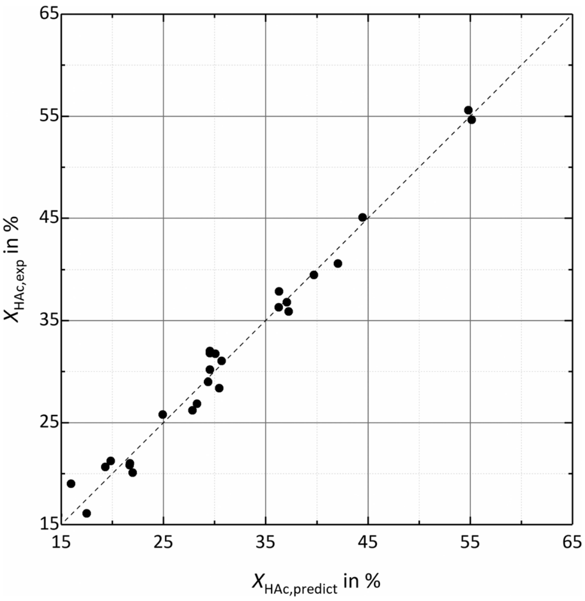

Fig. 2 Comparison of experimental conversion $X_{\mathrm{HAc,exp}}$ and predicted conversion $X_{\mathrm{HAc,predict}}$ based on the DoE-model (R^2 = 0.984; Q^2 = 0.956; reproducibility = 0.993).

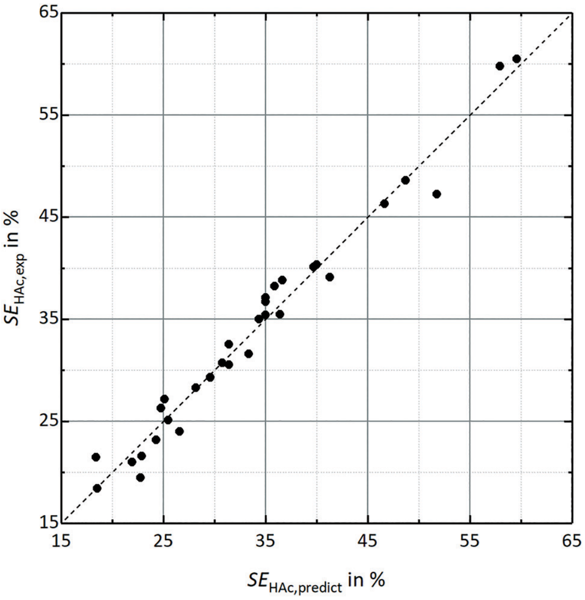

Fig. 3 Comparison of experimental separation efficiency $\mathrm{SE}_{\mathrm{HAc,exp}}$ and predicted separation efficiency $\mathrm{SE}_{\mathrm{HAc,predict}}$ based on the DoE-model (R^2 = 0.974; Q^2 = 0.931; reproducibility = 0.993).

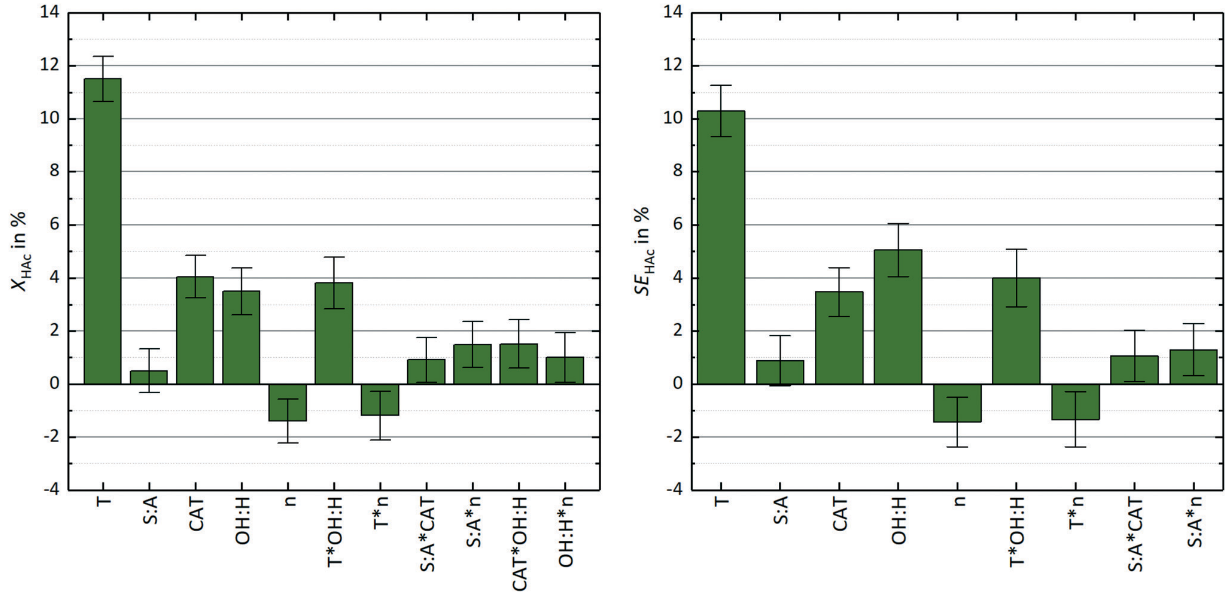

Fig. 4 Coefficient plot for the DoE-models showing their influence on conversion X_{HAc} (left-hand side plot) and separation efficiency SE_{HAc} (right-hand side plot) of acetic acid esterification with a confidence interval of 95%.

Similar results were found for the separation efficiency, which is influenced by 9 parameters as shown in eqn 4 and Table 2. In contrast to the overall conversion, the interaction between catalyst load and stoichiometric ratio ($\beta_{CAT\cdot OH:H}$) and stoichiometric ratio and stirrer speed ($\beta_{OH:H\cdot n}$) has no significant impact on SE_A. Nevertheless, the model predicts the separation efficiency as displayed in the diagram in Fig. 3 very well. This is confirmed by a R^2 of 0.974, a Q^2 of 0.931 and a reproducibility of 0.993.

The right-hand side diagram in Fig. 4 gives an overview of the parameter influence on the separation efficiency including the 95%-confidence intervals. Reaction temperature is still the most important parameter, but compared to the overall conversion it has slightly less impact on separation efficiency. By contrast, the influence of the stoichiometric ratio is increased for the separation efficiency, as it corresponds with the composition and therefore the extraction capacity of the solvent phase. The limiting effect of an increased stirrer speed is observed in the same magnitude as for overall conversion.

3.2.1 Interpretation of parameter influence on acetic acid separation efficiency *via* contour plot analysis. Fig. 5 illustrates the predicted separation efficiency in dependence on all investigated process parameters in a contour plot. Within this contour plot, three effects are revealed. The first effect is a trend of rising separation efficiency from the lower left corner (all parameters at minimum level; plot A3) to the upper right corner (all parameters at maximum level; plot C1). High O : H, CAT and T are expected to increase conversion and thereby positively influence the extraction towards higher separation efficiencies and thus confirming the observed trend.

A second effect is the enhanced mass transfer due to a high catalyst load which is best observed in plot C1 of Fig. 5. With a CAT_{max} of 0.06 eq. $mol_{A,0}^{-1}$ even at a stoichiometric ratio of 0.8 and nearly ambient temperature separation efficiencies in the range of 35% are possible at a stirrer speed of 475 rpm. The latter leads to the third effect: decreased separation efficiency for high stirrer speeds. This effect is assumed to be caused by too small droplets with highly rigid surfaces due to the surfactant (catalyst) molecules. Such rigid surfaces increasingly hinder mass transfer, hence limiting the separation efficiency and boosting unwanted emulsion stability.

3.2.2 Mass transfer capacity limitation due to exceeding extraction capacity of the solvent phase. Two experiments (T = 60 °C, CAT = 0.06 eq. $mol_{A,0}^{-1}$, OH : H = 1.5, n = 300 rpm) differed only in phase ratio with one at minimum $S:A_{min}$ = 0.5 and the other at maximum $S:A_{max}$ = 2. Evaluation after 3 h reaction time revealed nearly the same results for both experiments ($X_{HAc} \approx 55\%$; $SE_{HAc} \approx 60\%$). The thereby indicated mass transfer limitation could be confirmed by extending reaction time for both experiments to 12 h. While both response factors remained nearly unchanged for $S:A_{min}$ ($X_{HAc} \approx 57\%$; $SE_{HAc} \approx 63\%$), a significant increase was achieved for $S:A_{max}$ to $X_{HAc} \approx 74\%$ and $SE_{HAc} \approx 75\%$. This increase supports the necessity of higher phase ratios in order to avoid exceeding the solvent's extraction capacity. In addition, the difference between conversion and separation efficiency for the maximum phase ratio experiment decreases. This implies approaching both reaction and extraction equilibrium in the system.

3.2.3 Increase of the reaction temperature to 75 °C and 95 °C. A further approach to increase both response factors was

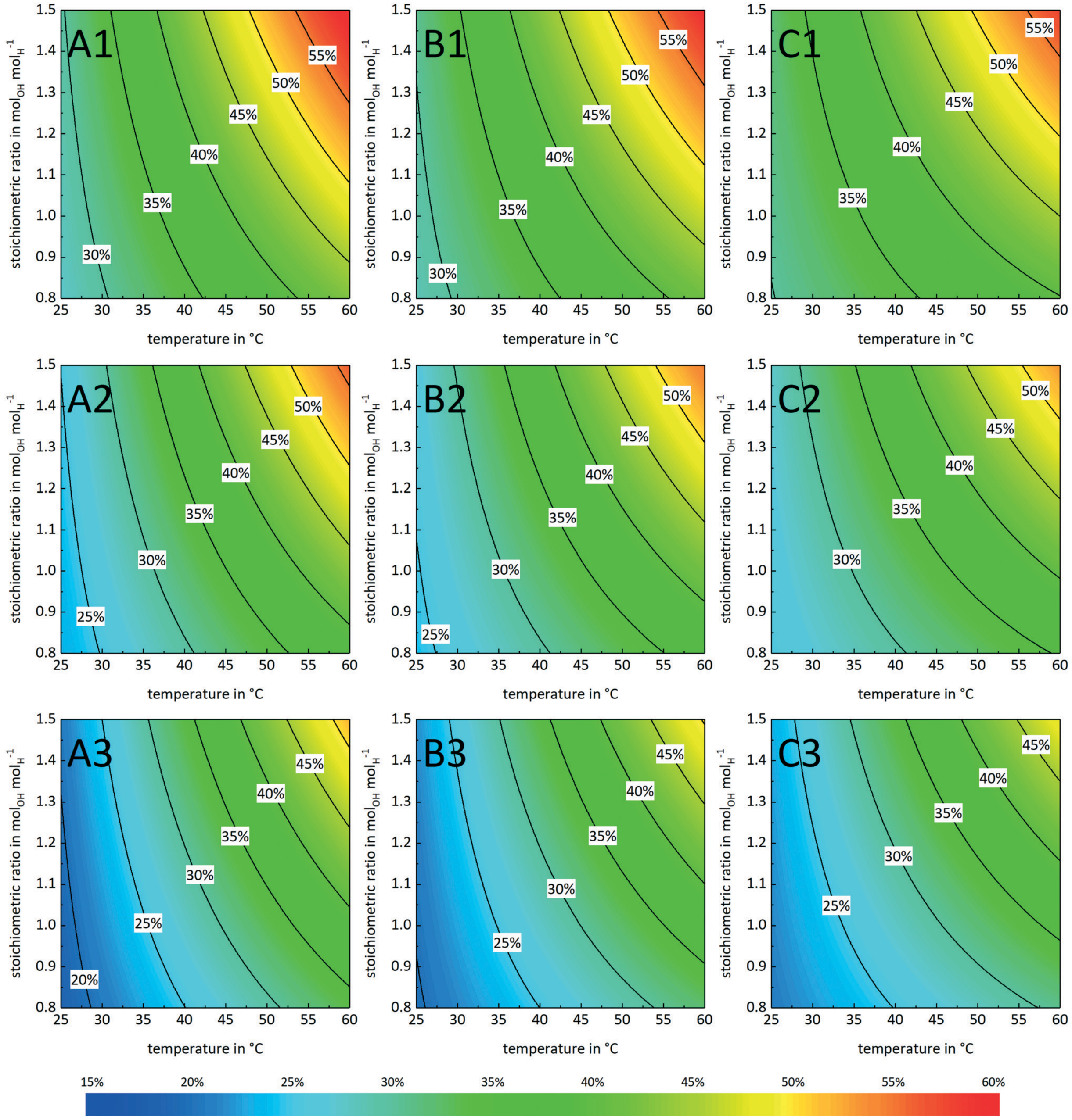

Fig. 5 Contour plot of predicted acetic acid separation efficiency $SE_{HAc,predict}$ in% for a fixed phase ratio S : A of 2 in dependency of stirrer speed (columns A, B and C), catalyst load (row 1, 2 and 3), stoichiometric ratio and temperature. Column A: 300 rpm, column B: 375 rpm, column C: 450 rpm; row 1: 0.06 eq. $mol_{A,0}^{-1}$, row 2: 0.03 eq. $mol_{A,0}^{-1}$, row 3: 0.015 eq. $mol_{A,0}^{-1}$.

increasing the reaction temperature from 60 °C to 75 °C and 95 °C, exceeding the limits of the DoE-set. All process parameters were kept constant at CAT = 0.06 eq. $mol_{A,0}^{-1}$, OH : H = 1.5, n = 300 rpm and S : A = 2 for 3 h reaction time. A reaction temperature of 75 °C yielded an overall conversion of 70.8 ± 0.0% and a separation efficiency of 72.8 ± 0.1%. Compared to this, 95 °C provided 73.7 ± 0.7% conversion and 75.5 ± 1.1% separation efficiency. From these results, two facts can be observed: on the one hand, a temperature increase above 75 °C does not yield a significant increase in either response factor. On the other hand, a temperature of 95 °C offers the possibility of decreasing the reaction time, as the system approaches its equilibrium conversion faster.

Additionally enhancing the extraction would shift the equilibrium composition to the product side and eliminate mass transfer limitation. Thus, a multi-step process similar to a mixer–settler cascade in counter-current operation is proposed. The multi-stage process concept maximises extraction

Table 3 Partition coefficients and corresponding separation efficiencies for investigated low molecular weight carboxylic acids

Carboxylic acid	$\log K_{OW}$[16]	SE_i
Formic acid	−0.54	61.4 ± 2.3%
Acetic acid	−0.17	57.5 ± 2.2%
Propionic acid	0.33	70.5 ± 2.7%
Butyric acid	0.79	79.6 ± 0.4%

driving force and may give access to nearly complete conversion. Finding an optimal temperature range with respect to conversion and reaction time requires further investigation.

3.3 Esterification of other low molecular weight carboxylic acids

The 4DBSA-catalysed concept was applied to other low molecular weight carboxylic acids, namely formic acid, propionic acid and butyric acid. Experiments were performed at 60 °C, CAT = 0.06 eq. $mol_{A,0}^{-1}$, OH : H = 1.5, n = 300 rpm and S : A = 2 for 3 h. The concept was proved to be applicable for the investigated carboxylic acids, which is best displayed by the separation efficiencies. Separation efficiencies were 61.4 ± 2.3% for formic acid, 70.5 ± 2.7% for propionic acid and 79.6 ± 0.4% for butyric acid compared to 57.5 ± 2.2% for acetic acid. Increasing chain length of the carboxylic acid and thus decreasing $\log K_{OW}$-values result in increasing separation efficiency, except for formic acid as displayed in Table 3. Although formic acid prefers the aqueous phase based on its $\log K_{OW}$-value, a higher reactivity compared to acetic acid allows a higher separation efficiency.

4 Conclusions

In accordance with the "24 principles of green engineering and green chemistry",[13] a concept was proposed to prevent loss of unused carboxylic acids from renewable resources. This is achieved by using catalytic reagents for isolation at moderate temperatures and ambient pressure with low toxicity of the products in a safe and simple process. The concept of utilizing emulsification with the surfactant-catalyst 4-dodecylbenzenesulfonic acid in order to enhance the reaction rate for isolation of low molecular weight carboxylic acids *via* esterification with 1-octanol was confirmed in single-stage batch operation. Further improvement of process performance can be achieved by multi-stage operation with adequate phase separation between the reaction stages.

Indices and symbols

Indices

A	Acid
0	Initial
sol	Solvent phase
aqu	Aqueous phase
exp	Experimental
predict	Predicted
HAc	Acetic acid
OcOH	1-Octanol

Symbols

X	Conversion
SE	Separation efficiency
β	Parameter of the models derived by design of experiments
DoE	Design of experiments
4DBSA	4-Dodecylbenzenesulfonic acid
HCl	Hydrochloric acid
R^2	Coefficient of determination
Q^2	Percent of variation
$\log K_{OW}$	n-Octanol/water partition coefficient

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge the contribution of Andrea Stachel and Michael Christopharo in performing the experimental work.

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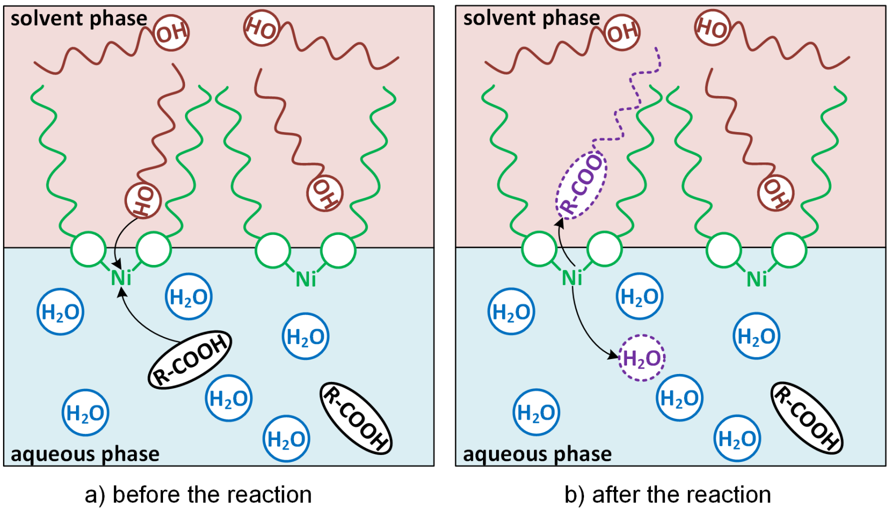
7. Interfacial catalysis in biphasic carboxylic acid esterification with a nickel-based metallosurfactant

This part of the thesis discusses the development and evaluation of a catalyst suitable for the reactive separation concept. The research article was published on 12th October 2019 in ACS Sustainable Chemistry & Engineering and is available *via* DOI: 10.1021/acssuschemeng.9b04667.

Synopsis

A nickel-based metallosurfactant is used to enhance valorization of low molecular weight carboxylic acids from aqueous biobased effluents.



a) before the reaction   b) after the reaction

ACS Sustainable Chemistry & Engineering
Research Article
Cite This: ACS Sustainable Chem. Eng. 2019, 7, 18547−18553
pubs.acs.org/journal/ascecg

Interfacial Catalysis in Biphasic Carboxylic Acid Esterification with a Nickel-Based Metallosurfactant

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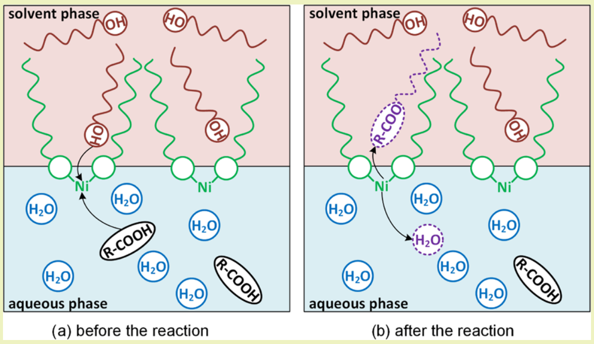
Supporting Information



(a) before the reaction (b) after the reaction

ABSTRACT: A metallosurfactant catalyst was developed to address the requirements for the utilization of low-molecular-weight carboxylic acids from dilute effluents. The catalyst $Ni(DBSA)_2$ combines transition-metal catalysis of nickel ions and surfactant catalysis of 4-dodecylbenzenesulfonic acid (4-DBSA). Requirements for the metallosurfactant catalyst are low water solubility, high catalytic activity in biphasic esterification, and self-assembling properties at the interface. $Ni(DBSA)_2$ was tested for applicability in the interfacial catalysis of esterification of dilute acetic acid with the solvent 1-octanol and resulted in an octyl acetate yield of 31.3%. Under identical reaction conditions, $Ni(DBSA)_2$ performed better than sulfuric acid with a yield of 1.7%. The limited catalytic performance of sulfuric acid is caused by the presence of sulfuric acid mainly in the aqueous phase. In contrast, $Ni(DBSA)_2$ is dissolved in the solvent and assembles at the aqueous/solvent interface where the reaction takes place. Additionally, the metallosurfactant lowers the interfacial tension between 1-octanol and deionized water by up to 75%, thus enhancing mass transfer. Compared to catalysis with 4-DBSA in emulsion, the catalytic performance of $Ni(DBSA)_2$ dropped by 62%, but this drawback is compensated by the complete suppression of emulsification. With $Ni(DBSA)_2$, the development of a catalyst was achieved, which self-enhances its catalytic performance in the interfacial catalysis through increased mass transfer area due to its surfactant properties.

KEYWORDS: *esterification, transition-metal, reactive extraction, metallosurfactant, interfacial catalysis*

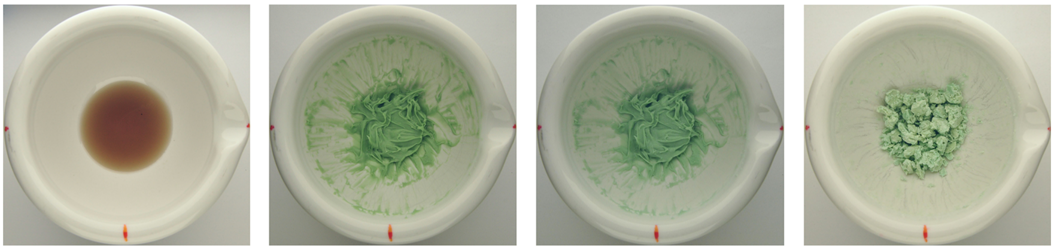
■ INTRODUCTION

Low-molecular-weight carboxylic acids are formed during the processing of biomass, such as pulping of wood, and are mostly present at low concentrations in aqueous effluents. These carboxylic acids represent a potential source for renewable products and holistic use of biomass feedstock. Acetic acid as a platform chemical is one of the main low-molecular-weight byproducts formed during pulping via the cleavage of the acetyl group from hemicellulose. Common practice in industry to treat these byproducts is to thicken the effluent containing mainly lignin and carboxylic acids followed by incineration. Referring to the global annual pulp capacity, the incineration of such valuable constituents represents a huge waste of resources but is accepted state of the art due to economic reasons. Using this source requires appropriate process technologies. High excess of water, low concentration of the carboxylic acids, and formation of (quasi-)azeotropic mixtures specify the major problems to be tackled for distillative or reactive separation.[1]

Esterification combined with simultaneous extraction of the low-molecular-weight carboxylic acids, i.e., formic acid, acetic acid, propionic acid, and butyric acid, with 1-octanol in an emulsified regime is a promising technological approach.[2] The solvent is a mixture of the reactant 1-octanol, the diluent *n*-undecane, and the catalyst 4-dodecylbenzenesulfonic acid (4-DBSA). Due to esterification, acetic acid, which is almost insoluble in the solvent, is transformed to octyl acetate, which shows higher solubility in the solvent phase. The concept relies on the Brønsted-acid catalytic activity and surfactant capability of 4-DBSA.[3−6] Emulsification caused by this anionic surfactant generates a quasi-homogeneous reaction regime. Such a regime provides negligible mass transfer control of the reaction combined with the advantages of quasi-homogeneous catalysis of the biphasic esterification reaction.[2,7,8] Acetic acid esterified to octyl acetate with 1-octanol with a conversion up to 54% and an overall acid separation efficiency of 57% underlines the applicability of the proposed concept.[2] However, the deployment of 4-DBSA is highly limited, as increased concentrations cause the formation of stable emulsions. Splitting of stable emulsions cannot be performed by a simple centrifugation step. The ambivalence of emulsification providing the intensifying part of the process concept yet causing the huge obstacle of formation of stable emulsions inspired the search

Received: August 9, 2019
Revised: September 10, 2019
Published: October 12, 2019

DOI: 10.1021/acssuschemeng.9b04667
ACS Sustainable Chem. Eng. 2019, 7, 18547−18553



a) 4-DBSA
b) catalyst paste after mixing
c) catalyst paste after drying
d) catalyst paste cut for dissolution

Figure 1. Preparation steps of the nickel-metallosurfactant catalyst $Ni(DBSA)_2$: (a) 4-DBSA before admixture of $Ni(OH)_2$; (b) catalyst paste right after mixing of 4-DBSA and $Ni(OH)_2$; (c) catalyst paste after 3 days storage at ambient conditions; and (d) cut catalyst paste prepared for dissolution in the solvent phase.

for a more convenient catalyst. This preferably water-insoluble catalyst is sought to show catalytic activity at the interface in biphasic esterification without the formation of stable emulsions, while maintaining a high mass transfer area through reduced interfacial tension. The concept of combined extraction/transesterification was also successfully applied by Likozar et al.[7−9] for utilizing high-molecular-weight fatty acids as biofuels. Likozar et al. developed a model capable of describing the superposition of extraction and reaction and implemented the process in a continuous tubular reactor.

Transition-metal ions catalyze esterification reactions as shown by Liu et al.[10] for noble metals like palladium and rhodium, or by Weires et al.[11] for nickel. With the surfactant catalyst 4-dodecylbenzenesulfonic acid as a basis, the most obvious approach was to make use of its ion-exchange capability, as already applied in transition-metal extraction and to, thus, control the surfactant properties with transition-metal ions. Exemplarily, transition-metal extraction has been published by Samper et al.[12] and Ferella et al.[13] Samper et al. used sodium dodecyl sulfate and linear alkylbenzene sulfonate to perform micellar-enhanced ultrafiltration to remove divalent heavy-metal ions like Zn^{2+}, Ni^{2+}, and Pb^{2+} from aqueous effluent. The metal ions are fixed to the anionic surfactant in micelles and then separated from the effluent via ultrafiltration. Ferella et al. used dodecylbenzenesulfonic acid (anionic) in comparison to dodecylamine (cationic) for the separation of Pb^{2+} and As^- in a similar approach. Both used the surfactants at concentrations below their respective critical micelle concentration (CMC) and reported an effective separation for the use of anionic surfactants. The chemical interaction between metal ions and the surfactant molecules leads to an immobilization of the resulting compounds. This immobilization allows selective positioning of these compounds. In the present case, the metal ions fixed to surfactant molecules may either be soluble in the solvent phase or in the aqueous phase and therefore be immobilized in the respective phase.[14] The thus produced substances are called metal−surfactant complexes or metallosurfactants.

The self-assembling capability of the metallosurfactant molecules in micelles or other nanostructures allows application in various fields such as preparation of nanoparticles, in medicine, and in catalysis.[15−17] Most effort has been made in the development of water-soluble metallosurfactants for systems where the respective reactants are dissolved either in the aqueous or in the organic phase and reaction takes place at the interphase.[17−19]

In the present work, the reactants for esterification are dissolved in different phases (carboxylic acid mainly in the aqueous phase; alcohol in the solvent phase). Based on the emulsification process concept,[2] 1-octanol was chosen as the alcohol for esterification and acetic acid as model carboxylic acid. Acetic acid was used at 1 mol L^{-1} to mirror the harsh reaction conditions for esterification due to a high water excess. Together with the reactant 1-octanol, the ester octyl acetate forms the solvent phase, meeting the aim of removing and upgrading the low-molecular-weight carboxylic acid from the aqueous phase. It is desirable to keep the catalyst in the solvent phase to avoid contamination of the aqueous phase and to enable recycling of the catalyst with the solvent phase. Therefore, a metallosurfactant catalyst based on 4-dodecylbenzenesulfonic acid and nickel ions was developed. This catalyst is capable of catalyzing biphasic esterification at low temperatures, which are essential in aqueous effluent treatment to minimize the energy demand. The combination of two nontoxic components allows the suppression of emulsification and therefore energy-efficient phase separation after reactive extraction.

■ EXPERIMENTAL METHODS

Materials. 4-Dodecylbenzenesulfonic acid (>95%, mixture of isomers, 4-DBSA, Sigma-Aldrich), nickel(II) hydroxide ($Ni(OH)_2$, Sigma-Aldrich), sulfuric acid (96%, H_2SO_4, Carl Roth), *n*-undecane (>99%, Sigma-Aldrich), 1-octanol (>98%, Sigma-Aldrich), and acetic acid (>99%, ChemLab) were used as supplied without further purification.

Preparation of Metallosurfactant Catalyst. The metallosurfactant catalyst was synthesized by adding nickel(II) hydroxide powder to liquid 4-dodecylbenzenesulfonic acid (4-DBSA) in a ceramic mortar. Different stoichiometric ratios of nickel to 4-DBSA were used corresponding to the possible oxidation states of nickel (+2, +4). After thorough mixing, the obtained paste was dried at ambient conditions for three days. The dried paste was then admixed to a solvent and heated to 90 °C with constant stirring until it was fully dissolved. For solvent selection, mixtures of *n*-undecane with Cyanex 923 or di-(2-ethylhexyl)phosphoric acid (DEHPA) together with 1-octanol as well as pure *n*-undecane and pure 1-octanol were tested. Figure 1 displays the catalyst preparation steps from pure 4-DBSA (a) to admixing nickel(II) hydroxide (b), drying (c), and cutting (d) for dissolution in the solvent phase. In a separating funnel, the catalyst solution was rinsed with deionized water to wash out unreacted nickel and 4-DBSA. Additionally, the solution was saturated with water to reduce loss of aqueous phase due to co-extraction of water during kinetic experiments.

Alternatively, the transition metals iron(II) chloride hexahydrate, iron(III) chloride tetrahydrate, and nickel(II) sulfate hexahydrate were tested but not further used due to undesired dissolution behavior (e.g., iron(III) chloride), instability of the produced metallosurfactant (e.g., iron(II) chloride), and incapability to prevent the formation of emulsions. Additional information can be found in the Supporting Information (Table S1 and Figure S1).

Biphasic Esterification in Batch Experiments. Kinetic performance of the synthesized metallosurfactant catalysts was evaluated for the biphasic esterification of acetic acid as a model compound in the aqueous phase (deionized water) and 1-octanol as the reactant in the solvent phase. This biphasic esterification was performed in a batch setup consisting of a 500 mL three-neck flask with a condenser atop. The latter was operated at 2.5 °C to reduce losses through evaporation. A magnetic stirrer (Heidolph MR Hei-Standard) with a heating plate stirred and heated the reaction mass with a total volume of 300 mL. Temperature of the reaction mass was controlled with a temperature sensor (Heidolph EKT 3001). Sulfuric acid was chosen as a standard mineral acid catalyst for carboxylic acid catalysis.[20] Further, 4-DBSA served as a benchmark for surfactant catalysis. For catalyst load, a low level and a high level were chosen, equivalent to 5 and 28 wt % of $Ni(DBSA)_2$, respectively. The high level represents the maximum catalyst load in pure 1-octanol due to its solubility characteristics. A phase ratio (solvent to aqueous feed) of 1, initial acetic acid concentration of 1 mol L^{-1}, a reaction time of 3 h, and a reaction temperature of 60 °C were kept constant for all kinetic investigations. A stirrer speed of 500 rpm was chosen to ensure thorough mixing of the two phases.

The catalyst was dissolved in the solvent and filled into the three-neck flask together with deionized water. This biphasic mixture was then heated up to the desired reaction temperature. Acetic acid was added with a syringe to the aqueous phase, initiating the reaction after the reaction temperature was reached. For sampling, every 30 min, the stirrer was stopped and after phase separation, samples were taken from both phases (0.2 mL each). Sampling from emulsion was done from the center of the reaction broth (1 mL) immediately after stopping the stirrer. The thus obtained emulsion sample was centrifuged for 10 min to obtain clear samples of both phases for gas chromatography (GC) analysis. At the end of each experiment, phases were separated either by gravitational settling in a separating funnel or in a benchtop centrifuge (Heraeus Labofuge 400) at rcf 2383 for 30 min in case of emulsification. The overall mass balance error was below 1.8%.

■ ANALYSIS TECHNIQUES

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Catalyst solutions were analyzed for nickel and sulfur content in an inductively coupled plasma optical emission spectroscope (ICP-OES) performed by BIOENERGY 2020+ GmbH. Solvent samples were prepared via acid digestion.

Infrared (IR) Spectroscopy. As nickel excludes NMR analysis due to its paramagnetic properties, structure characterization was performed using IR spectroscopy. A Bruker Alpha II spectrometer was used with a Platinum ATR. A spectral range of 4000−400 cm^{-1} was analyzed with a spectral resolution of 2 cm^{-1}.

Spinning Drop Tensiometry. Interfacial tension between solvent/catalyst mixtures and deionized water was measured with a Dataphysics spinning drop video tensiometer SVT20. The measuring chamber with the rotating capillary was temperature controlled to ensure accurate results. For the calculation of the interfacial tension σ, three different models were applied, depending on the drop shape: Vonnegut (VG), Laplace−Young (LY), and Cayias−Schechter−Wade (CSW).

Gas Chromatography. Samples of liquid phases were analyzed in Shimadzu GC2010plus equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) in parallel operation. A Zebron ZB WAXplus column with 60 m length, 0.32 mm inner diameter, and a film thickness of 0.5 μm was used. The gas chromatograph was operated in split mode (split ratio 120) with helium as the carrier gas. Injection via AOC 20i/s autosampler was done at 250 °C; the detectors were operated at 270 °C. The oven program started with a hold at 40 °C for 6.5 min and a temperature plateau at 60 °C for 2.5 min. This was followed by another temperature plateau at 120 °C held for 2 min and a final increase to 200 °C without a hold time. The heating rate in between the temperature plateaus was 20 °C min^{-1}. The samples were precooled to 5 °C in the autosampler and injected undiluted. The relative standard error of the measurements was in the order of 1.3% for the analysis with FID and 2.5% for TCD.

■ RESULTS AND DISCUSSION

Catalyst Selection and Characterization. 1-Octanol exhibited outstanding performance as a solvent with respect to extraction efficiency, catalyst load and stability, and phase separation behavior compared to the other tested solvents (*n*-undecane, Cyanex 923, DEHPA, 1-octanol, and mixtures thereof; further details in the Supporting Information). Extraction efficiency for metallosurfactant experiments with 1-octanol as solvent was above 53%. Metallosurfactant catalysts with nickel are best suited for the biphasic esterification of all investigated transition-metal ions (Fe(III), Fe(II), and Ni(II)), as the complexes offer high stability in the solvent phase coupled with almost no tendency to emulsify. Only the nickel-metallosurfactant with a stoichiometric ratio (4-DBSA to nickel) of 2 exhibits appropriate stability and catalytic performance together with the desired prevention of emulsification.

The nickel-metallosurfactant catalyst $Ni(DBSA)_2$ dissolved in 1-octanol was analyzed via ICP-OES and IR spectroscopy. The former confirmed a stoichiometric ratio of nickel to sulfur in the catalyst solution of 2 even after rinsing with deionized water. Figure 2 displays the IR spectra of 4-DBSA, 1-octanol, and two concentrations of $Ni(DBSA)_2$ dissolved in 1-octanol including the bands involved in the bonding of nickel and 4-DBSA. In the 4-DBSA spectrum, these bands show up at 573, 831, 905, 1004, and 1034 cm^{-1}. The band at 573 cm^{-1} is assigned to the bending and the bands at 1004 and 1034 cm^{-1}

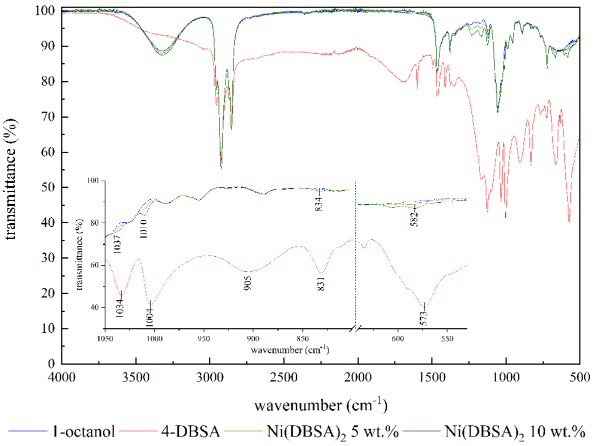


Figure 2. IR spectra of 4-dodecylbenzenesulfonic acid (red), 1-octanol (blue), 5 wt % $Ni(DBSA)_2$ in 1-octanol (light green), and 10 wt % $Ni(DBSA)_2$ in 1-octanol (dark green). Inset: focused areas of wavenumbers 1050−800 and 650−500 cm^{-1}.

DOI: 10.1021/acssuschemeng.9b04667
ACS Sustainable Chem. Eng. 2019, 7, 18547−18553

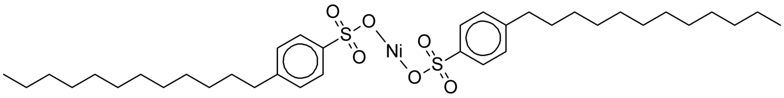


Figure 3. Proposed structure of the nickel-metallosurfactant $Ni(DBSA)_2$ with a divalent nickel ion and two 4-DBSA molecules.

to the symmetric stretching of the sulfonic acid group. The out-of-phase bending of the OH group in the sulfonic acid group is represented by bands at 831 and 905 cm^{-1}.[21] Resulting from the ion-exchange bonding of two sulfonic acid groups to a single nickel ion, the sulfonic acid group bands are slightly shifted to 582, 834, 1010, and 1037 cm^{-1}. The band at 905 cm^{-1} disappears completely, indicating a bonding between SO_3^- and the nickel ion, suggesting a structure as displayed in Figure 3.

Kinetic Performance of $Ni(DBSA)_2$ in Biphasic Esterification. The kinetic performance of $Ni(DBSA)_2$ was evaluated based on the octyl acetate yield and compared to that of sulfuric acid and 4-dodecylbenzenesulfonic acid as catalysts. Octyl acetate was only detected in the solvent phase by GC analysis as described in the analysis techniques section. Table 1 summarizes the excess of water in the reaction system, the excess of 1-octanol to acetic acid, and the total amount of catalyst used in equivalent to 5 wt % (low level) and 28 wt % (high level) of $Ni(DBSA)_2$. The basis for the calculation of catalyst load of sulfuric acid and 4-DBSA is their H^+-ion equivalent and for $Ni(DBSA)_2$ the amount of nickel determined by ICP-OES. Selection of the amount of nickel as the basis for the metallosurfactant calculation was performed with the assumption that the catalytic activity of the metallosurfactant is based on the Brønsted acid/base interaction.

Table 1. Summary of Initial Molar Excess of Water and 1-octanol and Total Amount of Catalyst with Low Level and High Level Equivalent to 5 and 28 wt % of $Ni(DBSA)_2$, Respectively

		molar excess of water to acetic acid	molar excess of 1-octanol to acetic acid	total amount of catalyst $[cat_i]_T$
$Ni(DBSA)_2$	low	51.7	6.1	0.0070 mol_{Ni}[a]
	high	51.8	4.3	0.0323 mol_{Ni}[a]
sulfuric acid	low	52.0	6.4	0.0084 mol_{H^+}[b]
	high	52.1	6.4	0.0397 mol_{H^+}[b]
4-DBSA	low	52.5	6.4	0.0089 mol_{H^+}[b]
	high	51.7	6.4	0.0395 mol_{H^+}[b]
uncatalyzed	-	52.2	6.4	-

[a] Basis for the calculation is the amount of nickel from ICP-OES analysis with 3260 $kg_{Ni}\ kg^{-1}_{5wt\%\ solution}$ for low level and 16 300 $kg_{Ni}\ kg^{-1}_{28wt\%\ solution}$ for high level. [b] Basis for the calculation is the number of H^+-ion equivalents: for sulfuric acid 0.019588 equiv $g^{-1}_{H_2SO_4,96\%}$ and for 4-DBSA 0.003154 equiv $g^{-1}_{4\text{-}DBSA,95\%}$.

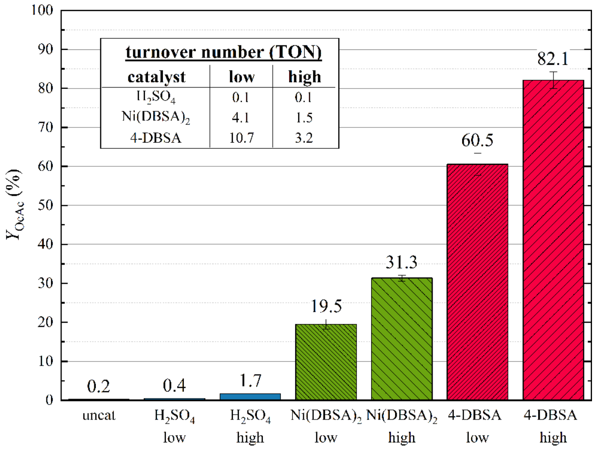


Figure 4. Octyl acetate yield Y_{OcAc} and turnover number (TON) for low and high levels of different catalysts. Catalysts used: H_2SO_4 (blue bars), $Ni(DBSA)_2$ (green bars), and 4-dodecylbenzenesulfonic acid (red bars) at 60 °C, 1-octanol as solvent phase, acetic acid concentration of 1 mol L^{-1}, phase ratio 1, stirrer speed 500 rpm, and error bars determined from three parallel experiments.

Figure 4 compares the octyl acetate yield achieved by the different catalysts with the uncatalyzed reaction. Sulfuric acid is widely used in the esterification of carboxylic acids, as it is highly efficient for concentrated reaction systems. In contrast, sulfuric acid is nearly inactive in the present system with a molar excess of water beyond 52 (see Table 1). Addition of sulfuric acid to the aqueous phase improves the extraction efficiency of acetic acid, as more undissociated and therefore extractable acetic acid is available. However, the achievable yield of octyl acetate for sulfuric acid catalysis is in the same order of magnitude as the uncatalyzed reference with 0.4% for the low level and 1.7% for the high level catalyst load. Location of the catalyst within the biphasic reaction system explains this effect. In contrast to the self-assembling (metallo)surfactant molecules, sulfuric acid is preferably present in the aqueous bulk phase and not at the interface, where the reaction takes place. Performance of 4-DBSA on the other hand is the upper benchmark in this case. The strong acidic properties and the emulsification induced by its surfactant ability allow yields between 60.5% (low level) and 82.1% (high level). The latter seems to be the maximum achievable yield from the interpretation of the octyl acetate concentration curve. The difference in the catalytic performance is also displayed by the difference in the turnover number (TON). The TON was calculated as the ratio of the amount of octyl acetate produced (n_{OcAc}) to the amount of catalyst used (n_{CAT}) according to eq 1.

$$\mathrm{TON} = \frac{n_{OcAc}}{n_{CAT}} \tag{1}$$

For the given reaction conditions, the TON for low level of 4-DBSA with 10.7 is 2 orders of magnitude higher than the TON of sulfuric acid with 0.1. Regardless of its catalytic activity, 4-DBSA faces the problem of the formation of stable emulsions in the used load range. Emulsions formed by both levels of catalyst load cannot be split solely by gravitational force. Centrifugation or other means of emulsion splitting needs to be applied, increasing the complexity of the process and preventing the use of standard equipment (e.g., stirred extraction columns).

The nickel-metallosurfactant $Ni(DBSA)_2$ clearly exhibits catalytic activity, as confirmed by 19.5% octyl acetate yield for the low level and 31.3% for the high level catalyst load. Yields are below that of low level 4-DBSA catalysis (60.5%), but clearly above the uncatalyzed reaction (0.2%) and the high level of sulfuric acid catalysis (1.7%). TON for Ni(DBSA)$_2$ of 4.1 and 1.5 for low and high level catalyst load, respectively, lies between sulfuric acid and 4-DBSA. It should be noted that the ratio between TON of Ni(DBSA)$_2$ and 4-DBSA is better for the high catalyst load, as TON highly decreases from low to high level of 4-DBSA.

The advantage of Ni(DBSA)$_2$ compared to the other catalysts lies in the complete prevention of emulsification, at the same time allowing intensive phase contact as a consequence of low interfacial tension. Adjustment of interfacial tension through the nickel-metallosurfactant enables a quasi-homogeneous state during reaction, with phase separation behavior comparable with the surfactant-free system. Interfacial tension of pure 1-octanol as well as of low and high metallosurfactant load in 1-octanol in water was measured with spinning drop video tensiometry. The measured interfacial tension σ_i for 25 and 60 °C is shown in Figure 5. A reduction of the interfacial tension between solvent phase and deionized water between 34 and 44% for low metallosurfactant load and between 70 and 75% for high metallosurfactant load was observed. While measurement with 4-DBSA containing solvent was not possible due to immediate emulsification in the measurement capillary, the high metallosurfactant load with a σ_i of 2.1 mN m^{-1} showed a phase separation behavior similar to that of the surfactant-free reference system. Additional information regarding spinning drop measurements can be found in the Supporting Information. The immediate emulsification can be explained by the catalyst load of 4-DBSA, which is orders of magnitude higher than the critical micelle concentration of 4-DBSA (CMC = 5.51 × 10^{-4} mol L^{-1})[22] for both levels of catalyst load. Within the investigated temperature range, no significant temperature dependency of the metallosurfactant containing solvent phases was observed.

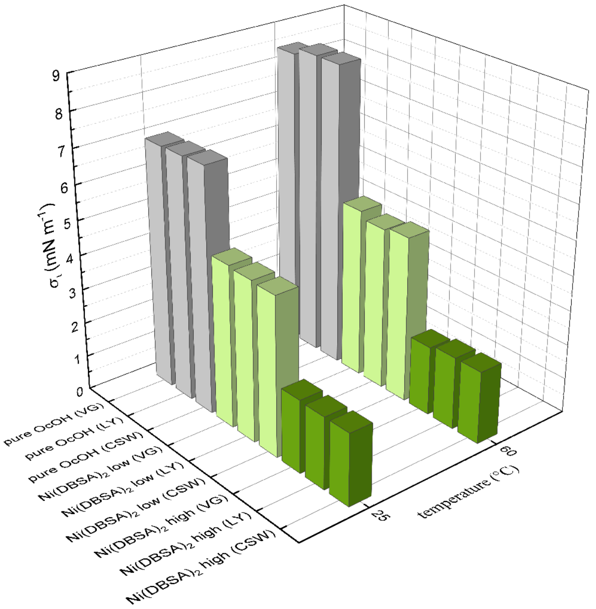


Figure 5. Interfacial tension σ_i between solvent/metallosurfactant mixtures and deionized water at 25 and 60 °C evaluated with models of Vonnegut (VG), Laplace–Young (LY), and Cayias–Schechter–Wade (CSW). Pure 1-octanol (OcOH) in gray, low level load of Ni(DBSA)$_2$ in 1-octanol in light green, and high level load of Ni(DBSA)$_2$ in 1-octanol in dark green.

Order in Catalyst. The order in catalyst was determined by applying the graphical method proposed by Burés.[23,24] Main advantage of this straightforward method is that it uses the experimentally derived reactant concentration to determine the order in catalyst without further calculations. In addition, this method equally works for experiments with a low number of data points or data with a high experimental error. Reaction profiles of the investigated catalysts at both load levels are combined with a normalized time scale. For that purpose, the product concentration (concentration of octyl acetate in the solvent phase $c_{\mathrm{OcAc,i}}$) is plotted over a time normalized by the total amount of catalyst raised to the power of γ, which represents the order in catalyst. This normalized time $t[\mathrm{cat_i}]_T^{\gamma}$ is adjusted until the reaction profiles are overlapping. Figure 6 shows the results of this method for sulfuric acid, Figure 7 for Ni(DBSA)$_2$, and Figure 8 for 4-DBSA as catalysts. Table 1 depicts the total amount of catalyst used for this analysis method.

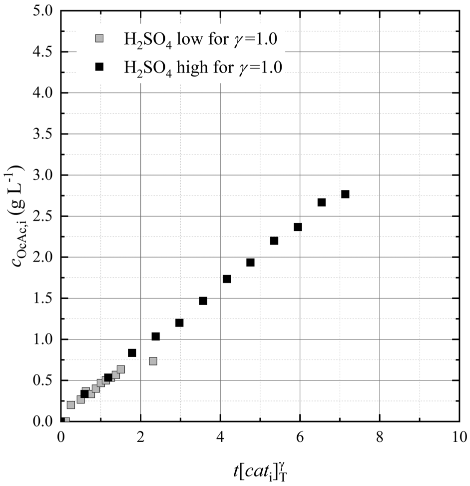


Figure 6. Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés[23,24] for catalysis with low and high level sulfuric acid load; order in catalyst γ = 1.0; reaction temperature 60 °C.

Both, sulfuric acid and 4-DBSA have an order in catalyst of γ = 1.0. This suggests that all active sites of these two catalysts are involved in catalysis. Nevertheless, the maximum concentration of octyl acetate for the sulfuric acid catalyzed experiments was at about 2.9 g L^{-1}, while in 4-DBSA catalyzed experiments, the maximum concentration was around 129 g L^{-1}. This remarkable difference is a consequence of the catalyst location in the system. While 4-DBSA molecules are located at the interface and therefore available for catalysis, sulfuric acid (and its H$^+$ ions) are distributed mainly in the aqueous phase. An estimated partition coefficient[25] log K_{OW} of −2.2 supports this assumption. It follows, that the active sites of sulfuric acid are not available at the place of reaction (at the interface) in a sufficient quantity. In contrast to sulfuric acid, the nickel-metallosurfactant is located at the interphase as 4-DBSA. Despite a reduced catalytic activity indicated by an order in catalyst of γ = 0.4, the maximum concentration of octyl acetate was at 59 g L^{-1}.

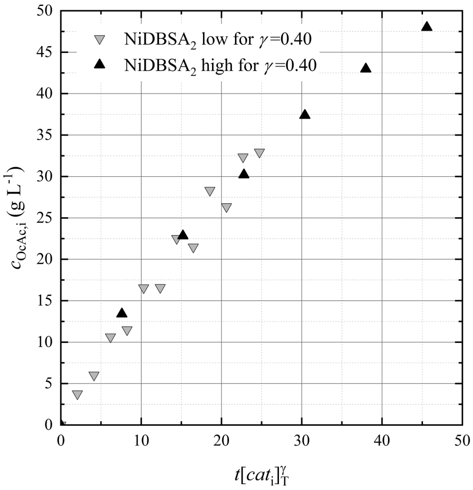


Figure 7. Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés[23,24] for catalysis with low and high level Ni(DBSA)$_2$ load; order in catalyst γ = 0.4; reaction temperature 60 °C.

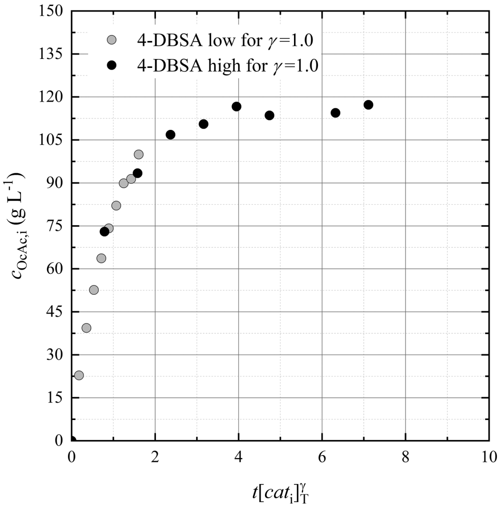


Figure 8. Octyl acetate reaction profiles from biphasic esterification with normalized time scale according to Burés[23,24] for catalysis with low and high level 4-DBSA load; order in catalyst γ = 1.0; reaction temperature 60 °C.

■ CONCLUSIONS

A metallosurfactant based on the anionic surfactant 4-dodecylbenzenesulfonic acid and divalent nickel (Ni(DBSA)$_2$) is suitable for the interfacial catalysis of biphasic esterification of low-molecular-weight carboxylic acids with 1-octanol. Although the catalytic performance is below that of 4-dodecylbenzenesulfonic acid, the metallosurfactant shows excellent characteristics, as it does not induce emulsification. With this catalyst, an octyl acetate yield of up to 31.3% was obtained, compared to 0.2% yield in the uncatalyzed reference experiment. Even a reduction of the interfacial tension of around 75% to 2.1 mN m^{-1} due to the metallosurfactant load did not result in emulsification nor hindered the phase separation. 1-Octanol as a solvent for Ni(DBSA)$_2$ prevents the metallosurfactant from precipitating during reaction and shows satisfying extraction performance for carboxylic acids extraction. Utilizing 1-octanol as a reactive solvent provides sufficient excess for the esterification of the carboxylic acid and driving force for the extraction of carboxylic acid. Biphasic esterification enhanced by interfacial catalysis with Ni(DBSA)$_2$ allows the utilization of dilute low-molecular-weight carboxylic acids for holistic use of biomass feedstock.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b04667.

> Table with investigated solvent mixtures, metal ions, and reason for exclusion; pictures of metallosurfactant mixtures displaying undesired solution behavior or instability; and pictures of spinning drop video tensiometry (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the contribution of Tanja Weiß in the experimental work and the advice of Ao.Univ.-Prof. Mag. Dr.rer.nat. Robert Schennach from the Institute of Solid State Physics at Graz University of Technology in IR spectra interpretation.

■ ABBREVIATIONS

4-DBSA,4-dodecylbenzenesulfonic acid; CMC,critical micelle concentration; DEHPA,di-(2-ethylhexyl)phosphoric acid; FID,flame ionization detector; GC,gas chromatography; ICP-OES,inductively coupled plasma optical emission spectroscopy; TCD,thermal conductivity detector; TON,turnover number; *c*,concentration; cat,amount of catalyst; i,component/phase/catalyst i; OcAc,octyl acetate; *t*,time; *T*,total; *Y*,yield; γ,order in catalyst; σ,interfacial tension

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DOI: 10.1021/acssuschemeng.9b04667
ACS Sustainable Chem. Eng. 2019, 7, 18547−18553

8. Solvent regeneration *via* transesterification in a (dis-)continuous benchtop reactive distillation setup

8.1. Introduction

The solvents from the esterification step, laden with octyl esters, residual carboxylic acids and co-extracted water, need sufficient regeneration to close the solvent cycle. Figure 8.1 displays exemplarily the vapor-liquid equilibrium (VLE) of 1-octanol and octyl acetate. With an azeotropic point close to pure 1-octanol and a low relative volatility simple atmospheric distillation is not suitable to achieve efficient solvent regeneration. In comparison, the VLE of methyl acetate/1-octanol and methyl acetate/octyl acetate show nearly ideal separation behavior. Therefore, transesterification of octyl acetate to methyl acetate provides an option for shifting the VLE towards ideal behavior.

An additional benefit of transesterification is the impact on the overall temperature level for distillative regeneration. Octyl acetate has a boiling point at 211 °C, while methyl acetate already boils at 56 °C. Aim of every solvent regeneration is high regeneration efficiency, which is in this case equivalent to high conversion of the octyl esters and high separation efficiency of the low-boiling components from the solvent. Reactive distillation supports transesterification by constantly removing the low-boiling esters and thus, shifting the equilibrium reaction towards the product side.

To demonstrate applicability of this solvent regeneration concept, batch experiments in a benchtop reactive distillation setup were performed with various solvent compositions and methanol excess. Both catalysts used in the esterification step of the overall process concept (4-DBSA and $Ni(DBSA)_2$) were tested for their performance in transesterification. To evaluate the concept in continuous operation, the benchtop setup was modified. The goal of this investigation was to validate the concept and to provide basic data for future process optimization.

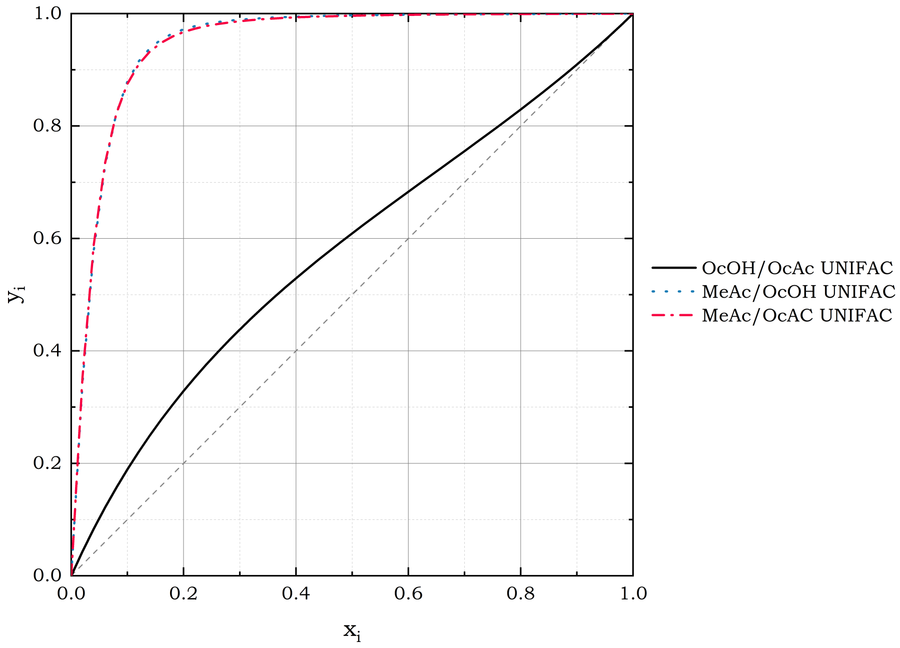

Figure 8.1.: Isobaric vapor-liquid equilibria of 1-octanol/octyl acetate, methyl acetate/1-octanol and methyl acetate/octyl acetate calculated with UNIFAC at 1.013 bar; index i represents the low-boiling component of the respective binary mixture.

8.2. Material and analytical methods

8.2.1. Chemicals

Octyl acetate (>98 %, CAS: 112-14-1; Sigma-Aldrich), methanol (>99 %, CAS: 67-56-1; Carl Roth), 1-octanol (>98 %, CAS: 111-87-5; Sigma-Aldrich), and acetic acid (>99 %, CAS: 64-19-7; Sigma-Aldrich) were used as reactants for the transesterification experiments. *n*-Undecane (>99 %, CAS: 1120-21-4; Sigma-Aldrich) served as an inert diluent for the solvent mixtures. For accelerating the transesterification reaction, the catalysts 4-dodecylbenzenesulfonic acid (>95 %, mixture of isomers; CAS: 121-65-3; Sigma-Aldrich; 4-DBSA) and the metallosurfactant Ni(DBSA)$_2$ were used. Latter catalyst was prepared according to the synthesis instructions reported in chapter 7. All commercially available chemicals were used as supplied by the manufacturer.

Discontinuous reactive distillation was performed with four different feed mixtures as listed in Table 8.1. While the feed mixtures *A/discont.*, *B/discont.* and *C/discont.* represent synthetic laden solvents, the fourth mixture (*D/discont.*) is a real laden solvent from a reactive LLX experiment with the catalyst Ni(DBSA)$_2$.

Table 8.1.: Feed composition (synthetic laden solvent) for the discontinuous transesterification experiments

feed	octyl acetate in wt%	acetic acid in wt%	1-octanol in wt%	*n*-undecane in wt%	catalyst in wt%
A/discont.	15.1	0.0	24.5	59.0	1.4 [a]
B/discont.	15.2	0.0	80.5	0.0	4.2 [b]
C/discont.	14.2	2.0	25.6	56.8	1.3 [a]
D/discont.	8.0	0.6	86.8	0.0	4.6 [b]

[a] 4-DBSA used as catalyst with 3.1536 mEq $g^{-1}{}_{4\text{-DBSA},95\,\%}$

[b] $Ni(DBSA)_2$ used as catalyst at 3260 mg_{Ni} $kg^{-1}{}_{5\text{ wt\% solution}}$

For the continuous reactive distillation experiments, three different solvent mixtures were prepared. Their respective composition is given in Table 8.2.

Table 8.2.: Feed composition (synthetic laden solvent) for the continuous transesterification experiments

feed	octyl acetate in wt%	acetic acid in wt%	1-octanol in wt%	*n*-undecane in wt%	4-DBSA in wt%
A/cont.	20.5	0.0	77.0	0.0	2.5
B/cont.	20.5	0.0	32.0	45.0	2.5
C/cont.	20.2	2.0	31.5	43.8	2.5

8.2.2. Analytical methods

Gas chromatography

All samples were analyzed with a gas chromatograph, Shimadzu GC-2010 Plus, equipped with a flame ionization detector (FID). The column used was a Zebron ZB-WAXplus column with a length of 60 m, an inner diameter of 0.32 mm and a film thickness of 0.5 µm. Helium was used as carrier gas and the samples were injected with a 5 µl syringe through an AOC 20i/s autosampler. Dimethyl sulfoxide (DMSO) served as rinsing solvent for the syringe. The injector was operated in split mode with a split ratio of 120 at 250 °C, while the FID was operated at 270 °C. A linear velocity of 30.0 cm s^{-1} was set in 'linear velocity' flow control mode. Samples were precooled to 5 °C in the autosampler with a LAUDA thermostat RE 104 and injected without dilution. The temperature program with a total run time of 19 min is given in Table 8.3.

Table 8.3.: Temperature program used with the ZB WaxPlus column in Shimadzu GC-2010 Plus; total program time: 19 min

heating rate in °C min^{-1}	temperature in °C	hold time in min
-	40	6.5
20	60	2.5
20	120	2.0
20	200	0.0

Karl-Fischer (KF) titration

Esterification of residual acetic acid results in formation of water. Samples from these experiments were therefore analyzed with volumetric Karl-Fischer titration to determine the water content. KF titration was performed with SI Analytics TitroLine® 7500 KF equipped with a KF1100 double platinum electrode. Apura® Titrant 5 and Aquastar™ Solvent supplied by Merck KGaA were used for the two-component KF titration.

8.3. (Dis-)Continuous benchtop reactive distillation setup

A benchtop reactive distillation setup, suitable for discontinuous and continuous operation, was set up to proof the concept of solvent regeneration from reactive extraction (Chapter 6 and Chapter 7) by transesterification in reactive distillation.

Figure 8.2 displays a scheme of the experimental setup used for reactive distillation experiments. The core of the experimental setup consists of a four-neck flask heated and stirred with a magnetic stirrer (Heidolph 3003) as reboiler and a 30 cm Vigreux column for intensive phase contact and a column head with reflux splitter. Column head and top product funnel were cooled with a thermostat to 2 °C with isopropanol as coolant. The magnetic reflux splitter was set to a reflux ratio of 1:10 for all experiments. Temperature was recorded at the top of the column head (coolant temperature), at the middle of the column head (top temperature), at the bottom of the column head (middle temperature; only in discontinuous operation) and in the four-neck flask (bottom temperature). In continuous operation, the middle temperature probe socket was used for feed influx. Feed (laden solvent), methanol and bottom product were pumped with a

Ismatec® Reglo ICC three-channel peristaltic pump. Methanol was added directly to the four-neck flask and the bottom product was withdrawn *via* the fourth probe socket. Ice was used to cool the bottom product vessel. The used tubing from Ismatec® is listed in Table 8.4. In discontinuous operation, the tubing pump system was removed and the corresponding probe sockets of the four-neck flask were sealed with a glass plug.

Table 8.4.: Tubing types used in the continuous reactive distillation setup

stream	tubing type - pump tube	tubing type - connection tubes
feed	Tygon® F4040-A	PharMed® BPT
methanol	Tygon® F4040-A	Norprene® A-60-G
bottom product	Tygon® F4040-A	PharMed® BPT

8.3.1. Discontinuous operation: experimental plan and procedure

Experimental plan

The reactive distillation in discontinuous operation was used to prove the applicability of solvent regeneration *via* transesterification. To meet the targets of high conversion of octyl acetate to methyl acetate and high separation efficiency of the low boiling components (methyl acetate, methanol and acetic acid), the molar methanol excess was varied. Performance of the catalysts 4-DBSA and $Ni(DBSA)_2$ in catalyzing the transesterification was determined. Pure 1-octanol was used as solvent in experiments with the catalyst $Ni(DBSA)_2$ because of the higher solubility of the metallosurfactant catalyst in pure 1-octanol (Chapter 7). In case of experiments with the catalyst 4-DBSA, the solvent was made up of a mixture of 1-octanol and *n*-undecane analogous to the investigation of reactive extraction with emulsion (Chapter 6). In a first attempt, the overall process concept was tested by consecutively performing discontinuous reactive liquid-liquid extraction (dRLLX) and discontinuous reactive distillation (dRD). Therefore, an dRLLX experiment was done for a reaction time of 4 h at a reaction temperature of 60 °C, a phase ratio of 1 and initial acetic acid concentration of 1 mol l^{-1} in the reactor described in Chapter 6. A 5 wt% solution of $Ni(DBSA)_2$ in 1-octanol was used as the catalyst-doped solvent for the dRLLX experiment. The resulting laden solvent was then transferred to the benchtop reactive distillation setup. In all dRD experiments the reflux ratio was kept constant at 1:10.

The feed mixtures (synthetic mixtures and experimentally laden solvents) are given in Table 8.1 and the experimental plan is summarized in Table 8.5.

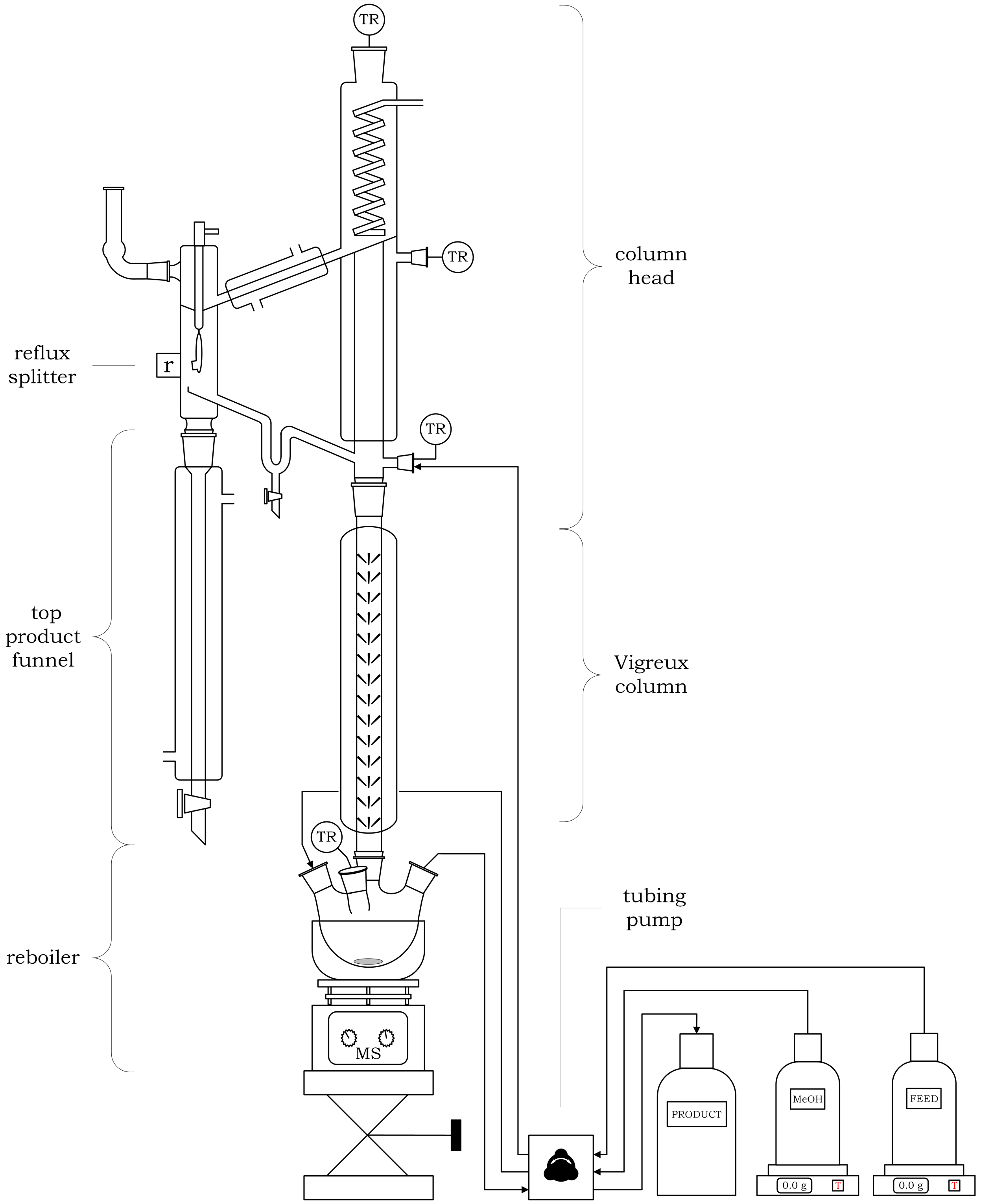

Figure 8.2.: Schema of the (dis-)continuous benchtop reactive distillation setup with a 500 ml four-neck flask as reboiler, a 30 cm Vigreux column and a three-channel peristaltic pump.

Table 8.5.: Experimental plan for discontinuous reactive distillation

experiment	methanol excess[a]	feed	catalyst
20 M, 4-DBSA	20:1	*A/discont.*	4-DBSA
3 M, 4-DBSA	3:1	*A/discont.*	4-DBSA
1.5 M, 4-DBSA	1.5:1	*A/discont.*	4-DBSA
1 M, 4-DBSA	1:1	*A/discont.*	4-DBSA
1.5 M, $Ni(DBSA)_2$	1.5:1	*B/discont.*	$Ni(DBSA)_2$
1.5 M, HAc, 4-DBSA	1.5:1	*C/discont.*[b]	4-DBSA
3.5 M, HAc, $Ni(DBSA)_2$, exp	1.5:1	*D/discont.*[b]	$Ni(DBSA)_2$

[a] molar excess, based on initial amount of octyl acetate
[b] experiments with residual acetic acid

Experimental procedure

Discontinuous experiments were started by filling the respective feed into the 500 ml four-neck flask together with the required amount of methanol. The amount of initial reaction mass (feed plus methanol) was chosen with 250 g. The reaction mass was then heated and constantly stirred until it started boiling. Heating power was reduced upon boiling to avoid overheating. For the heating period, the setup was operated at infinite reflux. As soon as the siphon in the column head was filled with top product, the reflux splitter was set to a reflux ratio of 1:10. Starting from this time, the top product was removed from the product funnel every hour. The samples were weighed and subsequently analyzed with gas chromatography and (in case of experiments with acetic acid) Karl-Fischer titration.

As soon as no more top product was obtained, the experiment was stopped. Heating was turned off, the remaining reaction mass and the top product in the siphon was weighed. Final samples of the remaining reaction mass and top product were taken and analyzed.

8.3.2. Continuous operation: experimental plan and procedure

Experimental plan

Following the proof of concept in discontinuous operation, the reactive distillation with transesterification was performed in continuous operation. The scale was the same as in discontinuous operation to ensure comparability. Two solvents were investigated: 1-octanol and a mixture of 1-octanol/*n*-undecane. In continuous operation only 4-DBSA was used as a catalyst, due to its significantly higher catalytic activity. In the continuous operation experiments (experimental plan in Table 8.6) the molar excess of methanol to octyl acetate was varied for 1-octanol as the solvent. Experiments with *n*-undecane were performed with 1.5-fold (1.5 M) and 3-fold (3 M) molar excess of methanol to octyl acetate. The 3 M experiments were done with and without residual acetic acid in the synthetic laden solvent. The corresponding feed compositions are given in Table 8.2.

The continuous reactive distillation was tested with the experiments listed in Table 8.6 to evaluate steady-state operation and solvent regeneration performance. Further, insensitivity of the continuous operation to possible formation of a second phase was evaluated, as water is co-extracted and/or formed during esterification of the residual acetic acid.

Table 8.6.: Experimental plan for continuous reactive distillation

experiment	methanol excess[a]	feed	residual acetic acid
OcOH/ 1.5 M	1.5:1	*A/cont.*	no
OcOH/ 3 M	3:1	*A/cont.*	no
OcOH/ 6 M	6:1	*A/cont.*	no
Und/ 1.5 M	1.5:1	*B/cont.*	no
Und/ 3 M	3:1	*B/cont.*	no
Und/ 3 M HAc	3:1	*C/cont.*	2 wt%

[a] molar excess, based on initial amount of octyl acetate

Experimental procedure

Continuous reactive distillation with transesterification was investigated in 48 h experiments. At the beginning of the experiment, the reaction mass, a mixture of respective feed and methanol, was filled into the four-neck flask, as done in the discontinuous experiments. Also heating up was done the same way at infinite reflux. Meanwhile, the tubes for feed and methanol supply were filled and the scales were tared. Masses of the feed and methanol supply flasks were recorded continuously. The reflux ratio was set to 1:10 as the siphon was full with top product. As soon as the bottom and top temperature were constant, the tubing pump was started. While the supply flows of feed and methanol were adjusted to achieve the desired methanol excess, the bottom product flow from the four-neck flask to the ice-cooled sample vessel was adjusted to maintain the fluid level in the four-neck flask. Heating was constantly monitored and adapted when necessary to avoid overheating.

Starting with setting the reflux ratio to 1:10, samples of the top and bottom product were taken every hour. These samples were weighed and analyzed with gas chromatography and Karl-Fischer titration. At the end of each day (after 9 h), the experiment was stopped by setting the reflux ratio to infinity and switching off the heating. All tubes were emptied into the respective supply flask or sample vessel and masses were determined. The reaction mass remained in the setup overnight. The top product from the siphon as well as the remaining reaction mass in the four-neck flask were only removed, weighed and analyzed at the end of the second day (after 9 h).

8.4. Results of (dis-)continuous reactive distillation experiments

8.4.1. Discontinuous reactive distillation: conversion and product composition

The concept of solvent regeneration *via* reactive distillation with transesterification was proven in discontinuous operation. The conversion of octyl acetate and acetic acid for the performed experiments is compiled in Figure 8.3 and the corresponding experimental time is given in Table 8.7. Highest conversion of 95.7 % was achieved with 20-fold excess of methanol. As could be expected, the conversion drops with lower excess of methanol; to 75.6 % for 3 M, 63.0 % for 1.5 M and 36.2 % for equimolar use of methanol. While the experiment with equimolar amount of octyl acetate and methanol was already stopped after 4 h, as no more top product accrued, 6 h where necessary for 20-fold excess of methanol. The longest experimental time was needed for 3-fold and 1.5-fold excess.

Directly compared, the presence of 2 wt% residual acetic acid reduces the octyl acetate conversion to 40.5 %, which is a relative reduction of 35.7 %. This is caused by an effective reduction of the methanol excess from 1.5 to 1.06 as a consequence of the present acetic acid. Acetic acid is directly esterified in the reaction mass to methyl acetate and water. Therefore, octyl acetate conversion is close to the one with equimolar use of methanol. Nevertheless, acetic acid could nearly be completely converted (95.2 %) and no second phase was formed. The used solvent mixture of 1-octanol/*n*-undecane is capable of keeping the formed water of the esterification reaction in solution, which prevents the formation of a second phase.

4-DBSA has shown high potential in catalyzing the transesterification. Compared to this catalyst, $Ni(DBSA)_2$ shows a lower activity, as only 40.9 % of the octyl acetate were converted to methyl acetate. The catalyst seems to be stable at elevated temperature and remains dissolved in the solvent phase. While avoidance of emulsification in the RLLX-stage is a major benefit, the drawback of lower activity needs to be compensated by higher methanol excess.

Table 8.7.: Experimental time of discontinuous reactive distillation experiments

experiment	experimental time
20 M, 4-DBSA	6.0 h
3 M, 4-DBSA	7.5 h
1.5 M, 4-DBSA	7.5 h
1 M, 4-DBSA	4.0 h
1.5 M, Ni(DBSA)$_2$	4.0 h
1.5 M, HAc, 4-DBSA	6.0 h
3.5 M, HAc, Ni(DBSA)$_2$, exp	6.0 h

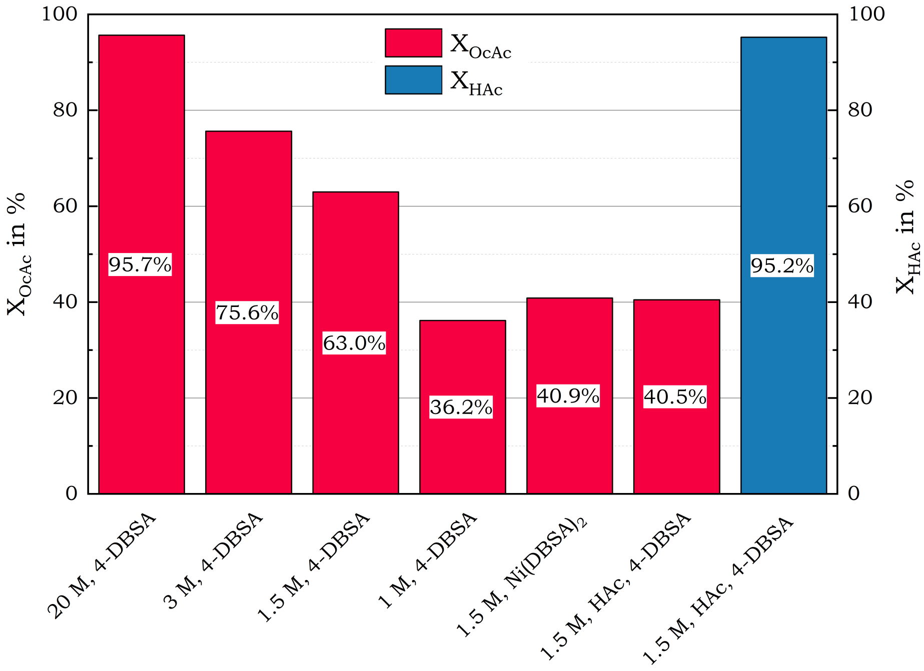

Figure 8.3.: Octyl acetate and acetic acid conversion in discontinuous reactive distillation for varying molar excess of methanol, different catalysts and residual acetic acid; reflux ratio 1:10.

While a 20-fold excess of methanol nearly yields 96 % octyl acetate conversion, the unreacted methanol remains a problem. The regenerated solvent contains 31.3 wt% volatile components (1.1 wt% methyl acetate and 30.2 wt% methanol). Further, the top product only contains about 40 wt% methyl acetate. All top products, except for the one from the residual acetic acid experiment, only consisted of methyl acetate and methanol. The concentration profile of methyl acetate and methanol in the top product of selected experiments is displayed in Figure 8.4. In contrast, the experiment with 1.5-fold excess of methanol produced a top product approaching the azeotropic composition of methyl acetate/methanol which is indicated by the grey bar in Figure 8.4. The upper and lower value of the azeotropic composition were taken from SpringerMaterials online database with 79.12 wt% [115] and 86.03 wt% [116] methyl acetate, respectively.

A vapor-liquid equilibrium of this binary mixture at 1.013 bar is shown in Figure 8.5 based on data from Dechema Chemistry Data Series. The experiment with 1.5-fold excess of methanol to octyl acetate and 2 wt% acetic acid yielded a nearly azeotropic mixture of methyl acetate and methanol, with traces of water (<0.5 wt%). Additionally, the first top product occurs earlier in the experiment with residual acetic acid than in the experiment without acetic acid and reaches the azeotropic composition earlier. This is due to the fact that esterification is faster than transesterification and therefore a sufficient amount of methyl acetate is formed earlier.

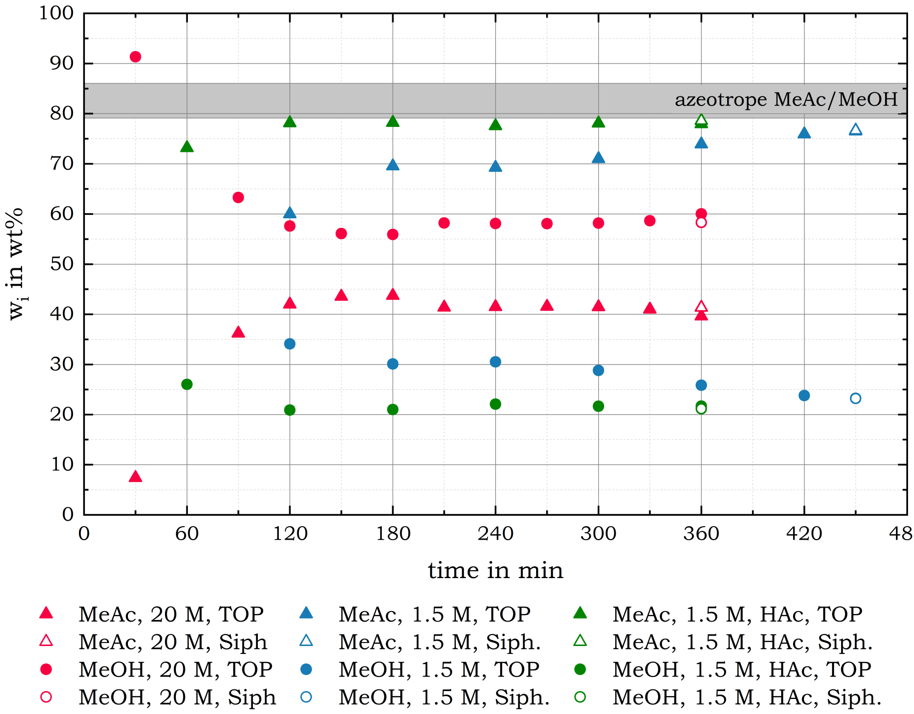

Figure 8.4.: Concentration profile of methyl acetate (MeAc) and methanol (MeOH) in top product (TOP) including the siphon content during discontinuous reactive distillation. Index i represents MeAc and MeOH, respectively; azeotrope area: lower and upper value taken from SpringerMaterials online database [115, 116]; experiments: 20 M, 4-DBSA (20 M), 1.5 M, 4-DBSA (1.5 M) and 1.5 M, HAc, 4-DBSA (1.5 M, HAc); reflux ratio 1:10.

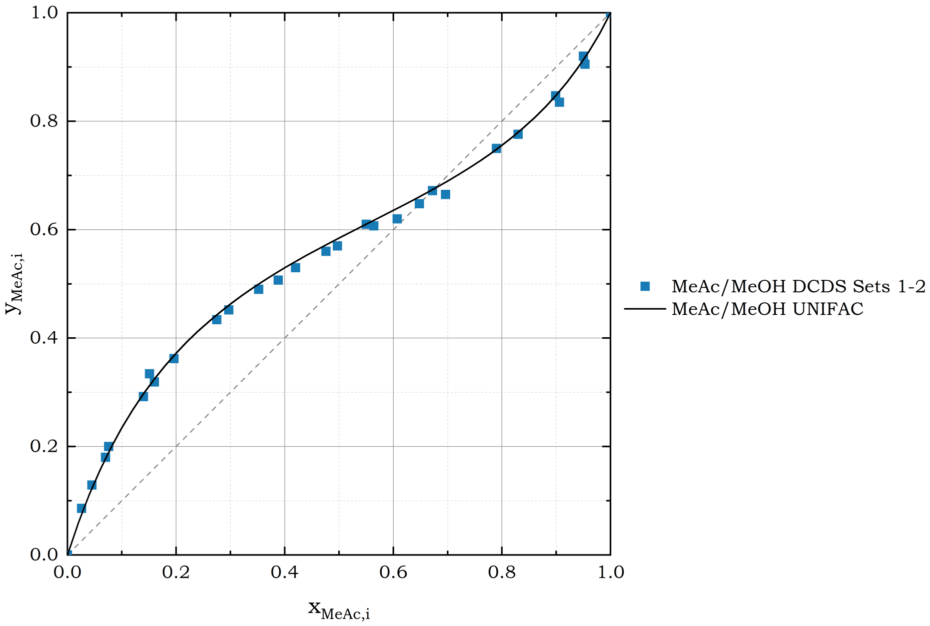

Figure 8.5.: Isobaric vapor-liquid equilibrium of methyl acetate/methanol from Dechema Chemistry Data Series (DCDS) and calculated with UNIFAC at 1.013 bar; Data sets are shown in Appendix C; index i represents the experimental data and the UNIFAC derived values, respectively.

8.4.2. Proof of concept for the overall process in discontinuous operation

The overall process concept with reactive extraction in an emulsified regime and subsequent reactive distillation for solvent regeneration was successfully tested in discontinuous operation. $Ni(DBSA)_2$ enabled an acetic acid conversion of 32.54 % in the discontinuous RLLX stage within 4 h. The yield of octyl acetate of 32.37 % determined *via* GC analysis and component balance confirms this result. 1-Octanol allows a separation efficiency (SE) of acetic acid from the aqueous phase of 56.65 %, which is higher than with *n*-undecane as a solvent due to increased physical extraction. Due to the reduced surfactant properties of $Ni(DBSA)_2$ complete phase separation is achieved by gravitational settling in a separation funnel. The thus generated laden solvent containing 14.15 g l^{-1} acetic acid and 35.21 g l^{-1} octyl acetate was then transferred to the discontinuous reactive distillation for regeneration. The results of both discontinuous stages are compiled in the scheme in Figure 8.6.

In the discontinuous reactive distillation a 3.5-fold excess of methanol was used, which yielded an octyl acetate conversion of 19.19 % in 6 h. At the same time 54.96 % of the acetic acid in the laden solvent were converted. A major drawback of 1-octanol as a solvent is in this case the low load capacity for water. As a consequence a second phase was formed in the four-neck flask during

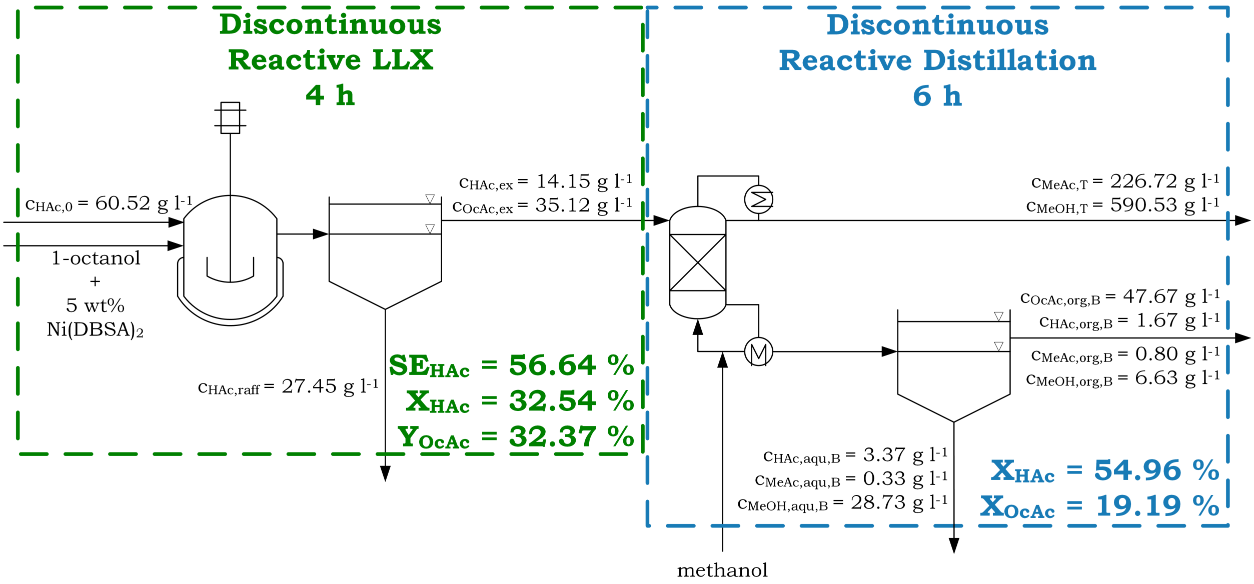

Figure 8.6.: Scheme of the overall process in discontinuous operation with Ni(DBSA)$_2$ as catalyst. Parameters of RLLX: phase ratio 1, 1-octanol as solvent, 5 wt% Ni(DBSA)$_2$, initial acetic acid concentration 1 mol l^{-1}, reaction temperature 60 °C. Parameters of discontinuous RD: 3.5 molar excess of methanol based on octyl acetate in the feed, reflux ratio 1:10, Ni(DBSA)$_2$ as catalyst.

reactive distillation. In total, this second phase made up only 0.6 wt% of the final reaction mass. This aqueous phase extracted methanol and acetic acid from the laden solvent, additionally hindering the transesterification. This must be considered in future solvent selection. Despite formation of an aqueous phase, no emulsification occurred and the aqueous phase could simply be removed *via* gravitational settling.

8.4.3. Regeneration performance in continuous operation

Figure 8.7 compares octyl acetate conversion for varying methanol excess and different solvents as well as the influence of residual acetic acid on the conversion. All bars in the graph represent the conversion in steady state. For 1-octanol as the solvent, a significant increase of the conversion could be achieved by increasing the excess of methanol. Thereby, the conversion of octyl acetate could be increased by a factor of 1.78 by quadrupling the methanol excess from 1.5 M to 6 M. Due to a much lower excess of 1-octanol by using *n*-undecane as a main solvent, the necessary excess of methanol to achieve the same conversion could be halved. While the octyl acetate conversion decreases upon presence of residual acetic acid (2 wt% in feed), a nearly 97 % conversion of acetic acid was reached in continuous operation. The effective excess of methanol in the experiment of residual acetic acid was 2.3 to both reactants (octyl acetate and residual acid).

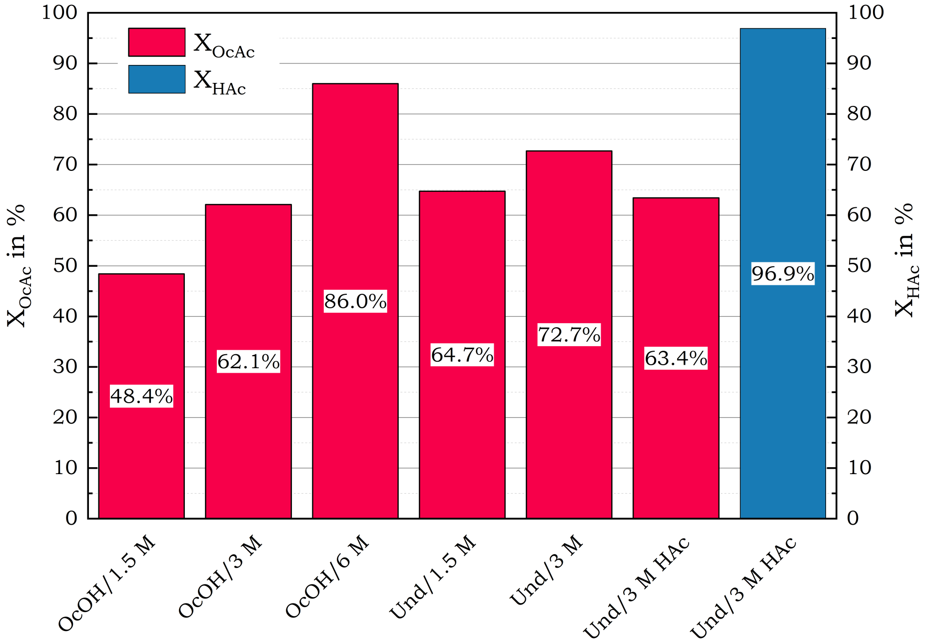

Figure 8.7.: Octyl acetate and acetic acid conversion compared for varying methanol excess (1.5 M to 6 M), different solvent types and residual acetic acid in steady-state reactive distillation.

All calculations of conversion and regeneration performance were based on the high boiling components, as loss of volatile components through the column head in the experimental setup is misleading. In Figure 8.8 the experimental *versus* the calculated yield of methyl acetate is compared for all continuous experiments. The experiment with 6-fold methanol excess stands out, with a relative error of about 38 %. This error was caused by the high amount of methanol, additionally dragging methyl acetate to the vapor phase according to the vapor-liquid equilibrium (Figure 8.5).

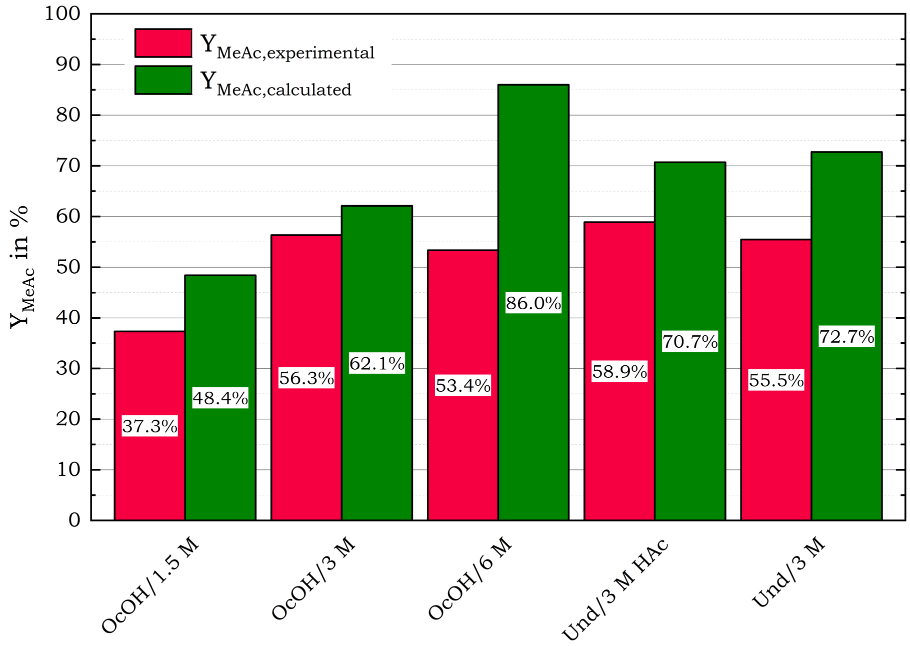

Figure 8.8.: Experimentally determined *vs.* calculated methyl acetate yield for varying methanol excess (1.5 M to 6 M), different solvent types and residual acetic acid in steady-state reactive distillation.

8.4.4. Composition of the regenerated solvent

As the main purpose of the solvent regeneration is a regenerated solvent free of octyl acetate and low boiling components, the consequences of excess methanol and initial solvent selection need evaluation.

Impact of methanol excess. The composition of laden solvent (feed) and regenerated solvents for 1-octanol as solvent is compared in the radar diagram in Figure 8.9. First and foremost, the decrease of octyl acetate with increased methanol excess is clearly visible (see also section 8.4.3). The reduction of octyl acetate in case of 6 M is from 20.5 wt% to about 4 wt%. On the other hand the methanol content increases to above 7 wt%. Methyl acetate content is in all cases below 0.8 wt% and therefore one order of magnitude below methanol.

Solvent selection effects. The effect of the main solvent on the composition of the regenerated solvent is compared in Figure 8.10 for 1-octanol and 1-octanol/*n*-undecane as main solvent. For the latter, the reduction of octyl acetate is higher than for 1-octanol. In this case about 72 % of the octyl acetate were regenerated to 1-octanol. The solvent with *n*-undecane has a lower affinity to methanol, resulting in a lower residual amount of methanol in the regenerated solvent. The residual methyl acetate content shows no significant change with the selected solvent.

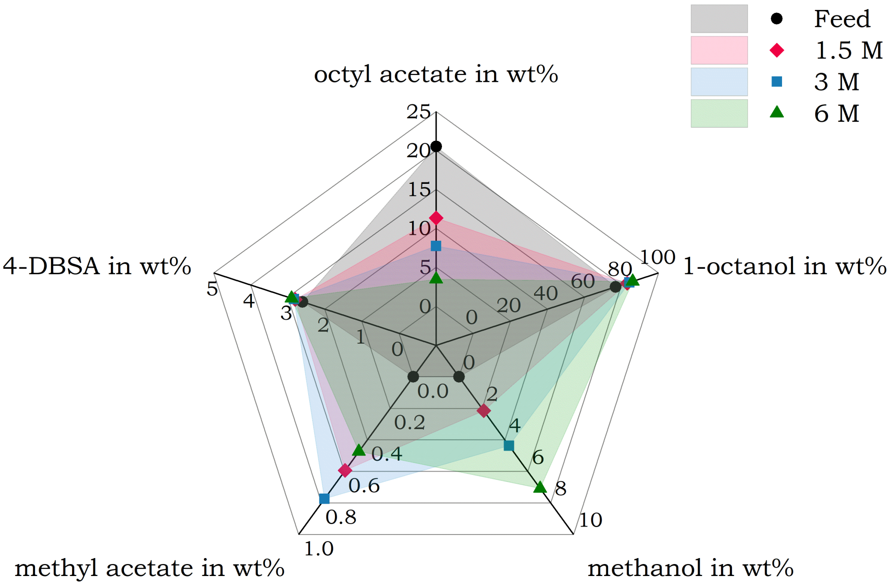

Figure 8.9.: Composition of regenerated solvent (1-octanol without n-undecane) in dependence of methanol excess in transesterification; black circles: feed (laden solvent), red diamonds: 1.5-fold MeOH-excess, blue squares: 3-fold MeOH-excess, green triangles: 6-fold MeOH-excess.

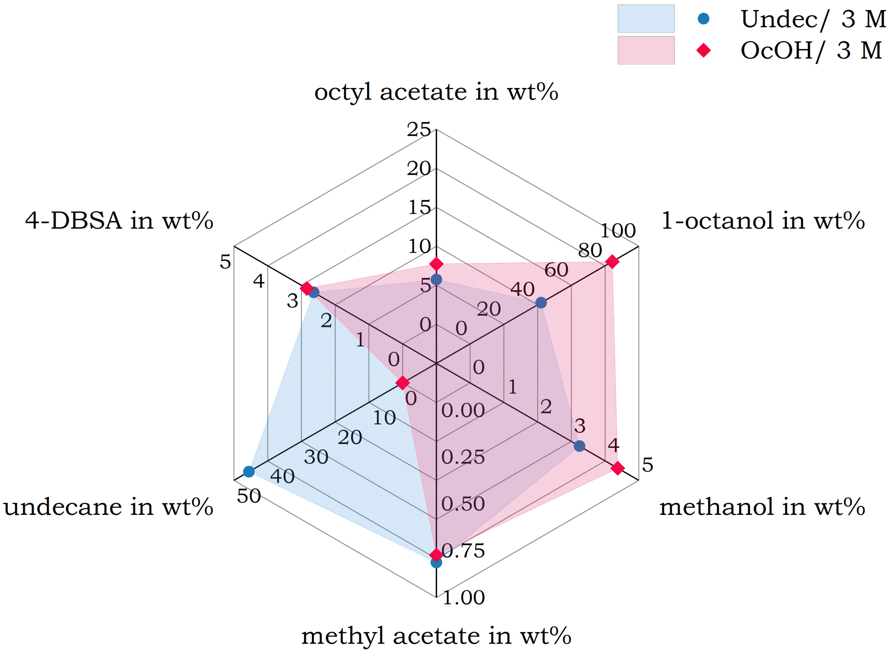

Figure 8.10.: Composition of regenerated solvent in dependence of solvent selection; blue circles: 1-octanol/n-undecane as solvent with 3-fold molar MeOH-excess, red diamonds: 1-octanol as solvent with 3-fold molar MeOH-excess.

Residual acetic acid influence The radar diagram in Figure 8.11 compares the laden solvent in case of 2 wt% residual acetic acid (Feed HAc) and the regenerated solvent with 3-fold methanol excess. Most important is the nearly complete removal of acetic acid and the uptake of the thus formed water. The resulting 0.8 wt% of water stay fully dissolved in the solvent and do not form a second phase. In the corresponding experiment without acetic acid (Figure 8.10), the methanol content of the regenerated solvent is only slightly higher. The content of methyl acetate increased, as it forms an azeotrope with water.

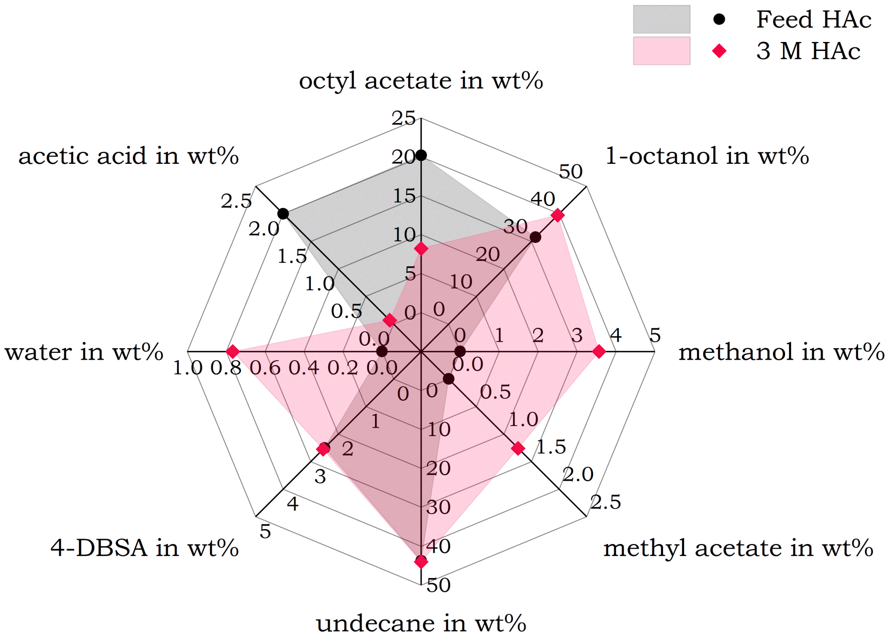

Figure 8.11.: Composition of regenerated solvent in dependence of residual acetic acid; black circles: feed (laden solvent), red diamonds: regenerated solvent with 2 wt% acetic acid and 3-fold molar MeOH-excess.

8.4.5. Evaluation of the energy demand

The specific energy demand based on the amount of converted substance (octyl acetate and acetic acid) in steady state operation of the reactive distillation experiments is displayed in Figure 8.12 for all experiments. As shown in the diagram, the energy demand increases with methanol excess by 5 to 10 % for 1-octanol as the main solvent. *n*-Undecane with residual acetic acid at a methanol excess of 3 demands 5.4 % less energy than without acetic acid. Compared to 1-octanol at the same methanol excess, *n*-undecane demands about 25 % less energy. These values highly depend on the conversion of constituents, as a higher amount of converted substance lowers the specific energy demand. In contrast, a high methanol excess drastically increases the energy demand, as the excess methanol is evaporated and circulated in the reactive distillation. Therefore, the experiment with 6-fold excess of methanol has the highest specific energy demand, although yielding the highest conversion.

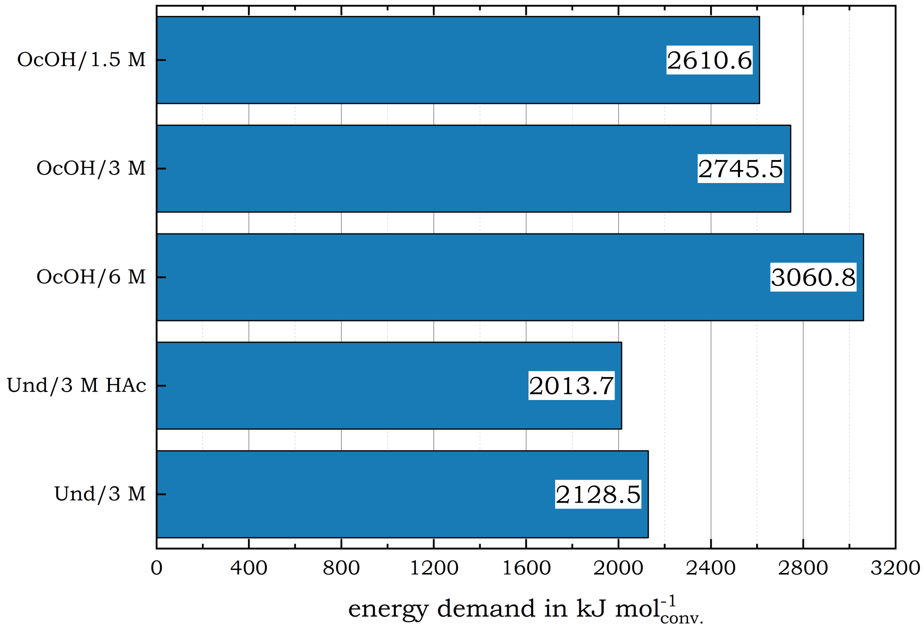

Figure 8.12.: Specific energy demand based on the amount of substance converted in steady-state; amount of substance converted: sum of converted octyl acetate and acetic acid.

8.5. Summary of main findings

The regeneration concept for an octyl acetate laden solvent from reactive liquid-liquid extraction with 1-octanol as reactant was proven *via* transesterification in reactive distillation. Discontinuous operation of the benchtop reactive distillation step showed promising results with yields up to 95.7 % for 4-DBSA as catalyst. The regeneration performance highly depends on the provided methanol excess and it is insensible to residual acetic acid and water formed by esterification of acetic acid. This was confirmed in continuous operation, where in steady-state operation with a 6-fold methanol excess 86.0 % of octyl acetate was converted. Acetic acid does not cause problems in continuous operation, confirmed by 96.0 % conversion. Methanol excess is the key parameter in the investigated process, as an optimum between conversion and enrichment of the regenerated solvent with low boiling components (methanol, methyl acetate). As the low boiling components would be extracted to the aqueous phase in the RLLX-stage, they need to be removed. Removal is only a matter of energy input according to the vapor-liquid equilibrium in Figure 8.1 and can be performed in a stripper.

Regarding the solvent selection, sole 1-octanol is beneficial for acetic acid extraction in the RLLX-stage, but limits the transesterification reaction due to Le Chatelier's principle. Additionally, 1-octanol has a lower capacity for taking up water, which may cause formation of a second phase in reactive distillation. *n*-Undecane is a better choice, in terms of reactive distillation. Further investigation of alternative solvents is recommended.

The overall process concept could be proven in discontinuous operation. As a catalyst, the metallosurfactant $Ni(DBSA)_2$ was used in this proof of concept and shows activity in both, esterification and transesterification. Nevertheless, its catalytic activity is lower than the activity of 4-DBSA acid. This lower activity is subject to a future optimization, as phase separation is much better for $Ni(DBSA)_2$.

The top product consists exclusively of methanol, methyl acetate and water. The latter only for residual acetic acid in the laden solvent. Especially the formation of an azeotrope by methyl acetate and methanol (Figure 8.5) requires appropriate purification technologies. In this context, membrane based technologies, like pervaporation, show good performance. [117, 118]

Part III.

Conclusions and future activity

9. Conclusions

In line with the scope of this thesis, a process concept for valorization of low-molecular-weight carboxylic acids (LMCAs) from dilute aqueous streams was developed and tested. The technical and economic problem of low acid concentration and high water excess in valorization of LMCAs was tackled by applying reactive separation technologies involving two reactions: esterification and transesterification. In Figure 9.1 the reaction pathway/reaction cycle of the proposed concept is shown exemplarily for acetic acid isolation. In a first step, the LMCAs are esterified with 1-octanol in an emulsified regime. After phase separation, the laden solvent phase is regenerated *via* transesterification the high-boiling esters to their respective low-boiling methyl esters in a reactive distillation step.

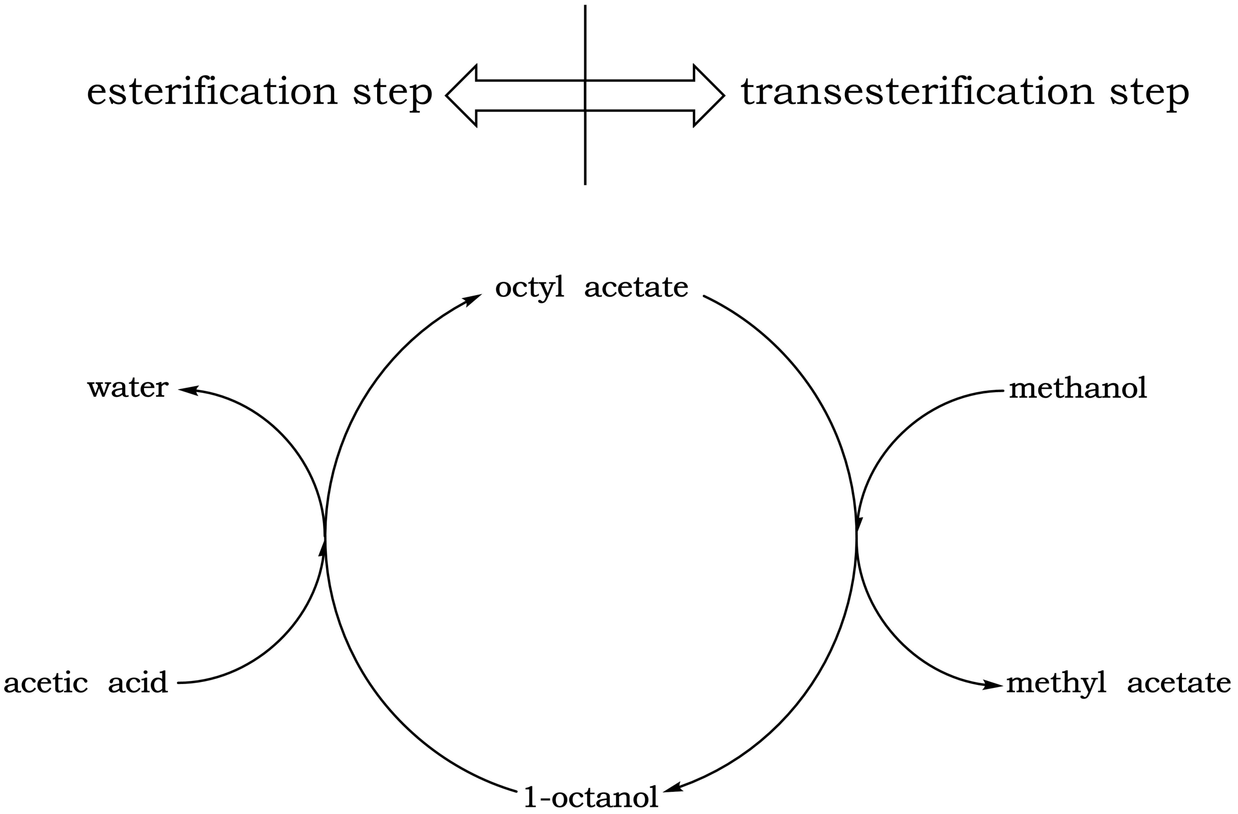

Figure 9.1.: Reaction cycle of low-molecular-weight carboxylic acid and 1-octanol in the proposed reactive separation process concept, exemplarily shown for acetic acid; esterification step: acetic acid is esterified with 1-octanol to water and octyl acetate; transesterification step: octyl acetate is transesterified with methanol to methyl acetate and 1-octanol.

Three aspects of the proposed concept were investigated:

- the feasibility of emulsion-enhanced biphasic esterification
- the emulsion-control through development of a metallosurfactant catalyst, and
- the solvent regeneration and product isolation through reactive distillation with transesterification.

The esterification step in an emulsified regime was proven feasible with conversion of LMCAs far beyond the respective equilibrium conversion in the corresponding aqueous feed. In this step, 4-dodecylbenzenesulfonic acid (4-DBSA) showed high performance in catalysis and emulsification, yet opening the challenge of emulsion splitting. The high mass transfer area in quasi-homogeneous state provided by the Brønsted-acid-surfactant catalyst 4-DBSA has proven to be advantageous for high conversion.

The results of emulsion handling suggested modifying the catalyst to control its surfactant properties. A new catalyst was developed, and it did prove suitable for the task of providing a quasi-homogeneous state without formation of stable emulsions. The ion-exchange properties of 4-DBSA allowed combination with the transition metal nickel to form the new metallosurfactant catalyst $Ni(DBSA)_2$. Successful emulsion splitting was achieved, as the interfacial tension increased compared to the catalyst of 4-DBSA, and formation of stable emulsions was suppressed, although correction of surfactant properties was exchanged against reduced catalytic activity of $Ni(DBSA)_2$.

Both catalysts were proven active in esterification and transesterification. The latter catalyst system was integrated in a continuously operated benchtop reactive distillation setup for solvent regeneration. Regeneration of synthetic solvent mixtures and experimentally laden solvent through transesterification of the octyl ester to its respective methyl ester was proven feasible. Co-extracted water and residual carboxylic acid did not cause problems in continuous operation.

The overall process concept was proven feasible for valorization of low-molecular-weight carboxylic acids with the benefit of producing value-added biobased chemicals. Optimization and further process design my be subject of future investigations.

10. Future activity

Future investigations on improvement and optimization of the proposed process concept should include the transfer of the technology concept to a wider range of biobased carboxylic acids and alternative solvents. Especially for the use of the metallosurfactant catalysts, a solvent with higher catalyst load capacity would be beneficial to increase the maximum catalyst amount in the reaction system. Apart from 1-octanol, investigation of other high-boiling alcohols (aliphatic and branched) could broaden the product range and applicability of the process. Like for any conceptual process, testing with effluents from real processes (fermentation broths, pulping effluents) is necessary to test its robustness to impurities and other interferants.

Simulation of the process is crucial for evaluation of the economic feasibility and performance. Therefore, the development of a rigorous kinetic model capable of describing and predicting the superposition of chemical reaction, mass transfer and phase equilibrium is recommended.

Regarding the solvent regeneration, a structured optimization of the process conditions is proposed by applying Design of Experiments. Additionally, product purification, e.g, with membrane processes like pervaporation, should be considered to reduce methanol consumption and provide high quality products.

Further insight into interfacial catalysis with the metallosurfactant $Ni(DBSA)_2$ is recommended. Investigations of the processes at the interphase of solvent and aqueous phase during esterification in presence of $Ni(DBSA)_2$ were recently performed *via* small-angle x-ray scattering (SAXS) at the ELETTRA synchrotron in Trieste. The results of these measurements, financially supported and enabled by the CERIC-ERIC Consortium, need to be interpreted.

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Appendix

Appendix A.

Publications and (co-)supervised theses

A.1. Publications

A.1.1. Articles

2019

Toth, A., Schnedl, S., Painer, D., Siebenhofer, M. and Lux, S. *Interfacial Catalysis in Biphasic Carboxylic Acid Esterification with a Nickel-Based Metallosurfactant* in ACS Sustainable Chemistry and Engineering 7, 2019, 18547-18553, DOI: 10.1021/acssuschemeng.9b04667.

2018

Toth, A., Lux, S. and Siebenhofer, M., *Utilization of Low Molecular Weight Carboxylic Acids from Dilute Aqueous Feed* in CEET konkret, 2018, 18-19, DOI: 10.3217/978-3-85125-650-5.

Toth, A., Lux, S., Painer, D. and Siebenhofer, M., *Intensification of esterification through emulsification: isolation of dilute low molecular weight carboxylic acids* in Reaction Chemistry and Engineering 3, 2018, 905-911, DOI: 10.1039/C8RE00194D.

2017

Toth, A. and Lux, S., *DoE based Process Parameter Screening of Esterification in Emulsified Systems* in CEET konkret, 2017, 10-11, DOI: 10.3217/978-3-85125-580-5.

Painer, D., Lux, S., Grafschafter, A., **Toth, A.** and Siebenhofer, M., *Isolation of Carboxylic Acids from Biobased Feedstock* in Chemie Ingenieur Technik 89, 1-2, 2017, 161-171, DOI: 10.1002/cite.201600090.

2016

Toth, A. and Lux, S., *Application of Heuristic Process Development for Isolation of Dilute Carboxylic Acids from Biobased Effluents* in CEET konkret, 2016, 16-17, DOI: 10.3217/978-3-85125-503-4.

A.1.2. Conference proceedings

2019

Toth, A., Lux, S., Painer, D. and Siebenhofer, M., *Utilization of Dilute Carboxylic Acids by Reactive Separations* in Conference Proceedings of 15th Minisymposium VT, 2018.

2018

Toth, A., Lux, S. and Siebenhofer, M., *Emulsion-based Isolation of Dilute Carboxylic Acids* in Conference Proceedings of 8th International Thai Institute of Chemical Engineering Conference (ITIChE), 2018.

Toth, A., Lux, S. and Siebenhofer, M., *Utilization of Biorefinery Side Products by Reactive Separation* in Conference Proceedings of ProcessNet Annual Meeting, 2018, DOI: 10.1002/cite.201855090.

Toth, A., Painer, D., Lux, S. and Siebenhofer, M., *Process Parameter Evaluation for Esterification in Emulsions* in Conference Proceedings of 14th Minisymposium VT, 2018.

2017

Toth, A., Lux, S. and Siebenhofer, M., *Intensified Process Concept for Isolation of Carboxylic Acids from Aqueous Effluents* in Conference Proceedings of 7th International Thai Institute of Chemical Engineering Conference (ITIChE), 2017.

Toth, A., Lux, S. and Siebenhofer, M., *Esterification in Emulsified Biphasic Systems* in Conference Proceedings of 13th Minisymposium VT, 2017.

2016

Toth, A., Painer, D., Lux, S. and Siebenhofer, M., *Herausforderungen in der Technologie- und Verfahrensentwicklung und Lösungsalgorithmen* in Conference Proceedings of 12th Minisymposium VT, 2016, DOI: 10.3217/978-3-85125-456-3.

A.1.3. Presentations

2019

Toth, A., Schnedl. S., Lux, S., Painer, D., and Siebenhofer, M., *Esterification of Dilute Aqueous Carboxylic Acids with Metallosurfactant Type Catalysts* at AIChE Annual Meeting 2019, Orlando, FL, USA.

Toth, A., Schnedl. S., Lux, S., Painer, D., and Siebenhofer, M., *Biphasic catalysis for esterification of dilute aqueous carboxylic acids* at 46th International Conference of the Slovak Society of Chemical Engineering (SSChE), Tatranske Matliare, Slovakia.

Toth, A., Schnedl, S., Painer, D., Lux, S. and Siebenhofer, M., *Katalysierte Ver- und Umesterung zur Nutzbarmachung von Carbonsäuren* at 45th Tieftemperatur-Thermodynamik-Kolloquium (TTTK), 2019, Canazei, Italy.

2018

Toth, A., Lux, S. and Siebenhofer, M., *Emulsion-based Isolation of Dilute Carboxylic Acids* at 8th International Thai Institute of Chemical Engineering Conference (ITIChE), 2018, Bangkok, Thailand.

Toth, A., Painer, D., Lux, S. and Siebenhofer, M., *Process Concept for Isolation of Low Molecular Weight Carboxylic Acids from Dilute Aqueous Feed* at AIChE Annual Meeting 2018, Pittsburgh, PA, USA.

Toth, A., Lux, S. and Siebenhofer, M., *Acetic Acid Esterification in Biphasic Emulsified Systems* at ACHEMA Conference, 2018, Frankfurt, Germany.

Toth, A., Lux, S. and Siebenhofer, M., *Isolation of Dilute Carboxylic Acids from Biobased Effluents through Reactive Extraction with Emulsification* at FP 1306 COST Action, 2018, Thessaloniki, Greece.

Toth, A., Lux, S. and Siebenhofer, M., *Veresterung in O/W-Emulsionen* at 44th Tieftemperatur-Thermodynamik-Kolloquium (TTTK), 2018, Heiligenblut, Austria.

2017

Toth, A., Painer, D., Macher-Ambrosch, R., Lux, S. and Siebenhofer, M., *Intensification of Acetic Acid Esterification in Dilute Aqueous Solution through Liquid-Liquid Extraction and Emulsification* at 21st International Solvent Extraction Conference (ISEC), Miyazaki, Japan.

Toth, A., Painer, D., Macher-Ambrosch, R., Lux, S. and Siebenhofer, M., *Intensification of Carboxylic Acid Isolation Processes by Emulsification* at AIChE Annual Meeting 2017, Minneapolis, MN, USA.

Toth, A., Lux, S. and Siebenhofer, M., *Intensified Process Concept for Isolation of Carboxylic Acids from Aqueous Effluents* at 7th International Thai Institute of Chemical Engineering Conference (ITIChE), 2017, Bangkok, Thailand.

Toth, A., Lux, S. and Siebenhofer, M., *Reaktionen in emulgierten Systemen* at 43rd Tieftemperatur-Thermodynamik-Kolloquium (TTTK), 2017, Canazei, Italy.

2016

Toth, A., Macher-Ambrosch, R., Painer, D., Lux, S. and Siebenhofer, M., *Intensified Liquid-Liquid Extraction with Chemical Reaction By Emulsification* at AIChE Annual Meeting 2016, San Francisco, CA, USA.

Toth, A., Painer, D., Macher-Ambrosch, R., Lux, S. and Siebenhofer, M., *Isolation of Carboxylic Acids from Dilute Aqueous Solutions – Intensifying Approach By Conversion in Emulsified Reactive Solvents* at AIChE Annual Meeting 2016, San Francisco, CA, USA.

Toth, A., Painer, D., Lux, S. and Siebenhofer, M., *Die Verfahrensentwicklung am Beispiel des binären Systems Wasser/Essigsäure* at 42nd Tieftemperatur-Thermodynamik-Kolloquium (TTTK), 2016, Canazei, Italy.

2015

Lux, S., **Toth, A.** and Siebenhofer, M., *Recovery of Carboxylic Acids from Waste Water - Process Intensification By Reactive Extraction with Esterification* at AIChE Annual Meeting 2015, Salt Lake City, UT, USA.

A.1.4. Posters

2019

Toth, A., Lux, S., Painer, D. and Siebenhofer, M., *Reactive Separation Concept for Valorizing Low-Molecular-Weight Carboxylic Acids from Aqueous Media* at 12th European Congress of Chemical Engineering (ECCE), 2017, Florence, Italy.

Toth, A., Lux, S., Painer, D. and Siebenhofer, M., *Solvent Regeneration via Transesterification in Reactive Distillation* at DECHEMA Jahrestreffen Reaktionstechnik, 2019, Würzburg, Germany.

Toth, A., Lux, S., Painer, D. and Siebenhofer, M., *Utilization of Dilute Carboxylic Acids by Reactive Separations* at 15th Minisymposium VT, 2019, Leoben, Austria.

2018

Toth, A., Lux, S. and Siebenhofer, M., *Nickel-based catalysts for biphasic esterification* at 20th Symposium on Separation Science and Technology for Energy Applications (SST), 2018, Gatlinburg, TN, USA.

Toth, A., Lux, S. and Siebenhofer, M., *Utilization of Biorefinery Side Products by Reactive Separation* at ProcessNet Annual Meeting, 2018, Aachen, Germany.

Toth, A., Lux, S. and Siebenhofer, M., *DoE based Parameter Screening for Biphasic Esterification* at DECHEMA Jahrestreffen Reaktionstechnik, 2018, Würzburg, Germany.

Toth, A., Lux, S. and Siebenhofer, M., *Process Parameter Evaluation for Esterification in Emulsions* at 14th Minisymposium VT, 2018, Linz, Austria.

Toth, A., Lux, S. and Siebenhofer, M., *Reactive Solvents and Applications* at DECHEMA Jahrestreffen Extraktion, 2018, Frankfurt, Germany.

Toth, A., Lux, S. and Siebenhofer, M., *Acetic Acid Isolation with Reactive Solvents in Emulsified Regimes* at DECHEMA Jahrestreffen Fluidverfahrenstechnik, 2018, München, Germany.

2017

Toth, A., Lux, S. and Siebenhofer, M., *Acetic Acid Esterification in Emulsified Systems* at 10th World Congress of Chemical Engineering (WCCE), 2017, Barcelona, Spain.

Toth, A., Lux, S. and Siebenhofer, M., *Esterification of Carboxylic Acids in Dilute Aqueous Effluents* at DECHEMA Jahrestreffen Reaktionstechnik, 2017, Würzburg, Germany.

Toth, A., Lux, S. and Siebenhofer, M., *Esterification in Emulsified Biphasic Systems* at 13th Minisymposium VT, 2017, Innsbruck, Austria.

2016

Toth, A., Painer, D., Macher-Ambrosch, R., Lux, S. and Siebenhofer, M., *Intensification of Liquid-Liquid Extraction with Chemical Reaction through Emulsification* at 19th Symposium on Separation Science and Technology for Energy Applications (SST), 2016, Gatlinburg, TN, USA.

Toth, A., Painer, D., Lux, S. and Siebenhofer, M., *Herausforderungen in der Technologie- und Verfahrensentwicklung und Lösungsalgorithmen* at 12th Minisymposium VT, 2016, Graz, Austria.

A.2. (Co-)Supervised theses

A.2.1. Bachelor theses

Koweindl, L., *Entwicklung einer Analysevorschrift zur Konzentrationsbestimmung von 4-Dodecylbenzolsulfonsäure mit UV/VIS Spektrometrie*, in progress.

Donauer, M., *Reaktionskinetik der Umesterung von Octylacetat mit Methanol und Ethanol*, 2019.

Greil, R., *Kinetikuntersuchung der Veresterung von Essigsäure mit n-Octanol in Tetrahydrofuran*, 2019.

Christopharo M., *Katalysierte Veresterung von niedermolekularen Carbonsäuren in Emulsionen*, 2019.

Grosinger, D,. *Veresterungsreaktionen in emulgierten Systemen*, 2017.

Gschiel, M., *Veresterung von stark verdünnter Essigsäure in zwei Phasen*, 2017.

Kotzmaier, V., *Elektrostatische Emulsionsspaltung*, 2017.

A.2.2. Project reports

Schnedl, S., *Heterogene Katalyse in zweiphasigen Systemen*, 2019.

Tschurtschenthaler, M., *Kontinuierliche Reaktivdestillation zur Regenerierung von 1-Octanol aus Octylacetat*, 2019.

Stachel, A., *DoE basiertes Parameterscreening für Essigsäureveresterung im emulgierten System*, 2017.

A.2.3. Master theses

Paster, G., *Kinetikmodellierung der Veresterung von Essigsäure in Emulsionen*, in progress.

Schnedl, S., *Grenzflächenkatalyse in der zweiphasigen Veresterung von Essigsäure*, in progress.

Appendix B.

Supporting Information for the article in ACS Sus. Chem. Eng. (Chapter 7)

The supporting information for the article in chapter 7 is available free of charge *via* DOI: 10.1021/acssuschemeng.sc9b04667_si_001.

Interfacial catalysis in biphasic carboxylic acid esterification with a nickel-based metallosurfactant

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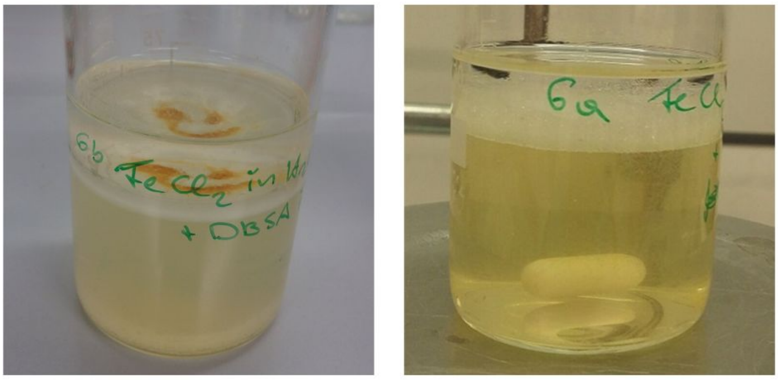
Number of pages: 4

Number of tables: 1

Number of figures: 2

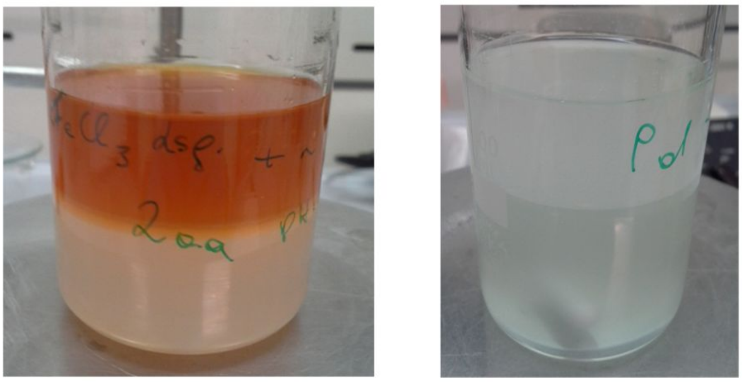
Table S1: Investigated metal ions, solvent mixtures and reasons for exclusion

metal ion	metal salt	solvent mixtures	reasons for exclusion
Fe(II)	$FeCl_2 \cdot 4\ H_2O$	*n*-undecane *n*-undecane/Cyanex®923 *n*-undecane/DEHPA *n*-undecane/1-octanol	- negligible catalytic activity - instability of complex, due to oxidation of Fe(II) to Fe(III) - preferably water soluble metallosurfactants
Fe(III)	$FeCl_3 \cdot 6\ H_2O$	*n*-undecane *n*-undecane/Cyanex®923 *n*-undecane/DEHPA *n*-undecane/1-octanol	- negligible catalytic activity - formation of emulsions/turbidities - corrosive
Ni(II)	$NiSO_4 \cdot 6\ H_2O$ $Ni(OH)_2$	*n*-undecane *n*-undecane/Cyanex®923 *n*-undecane/DEHPA	- water solubility of metallosurfactants from $NiSO_4$ - low solubility of $Ni(OH)_2$ metallosurfactants in solvents without 1-octanol



a) oxidation of Fe(II) to Fe(III)

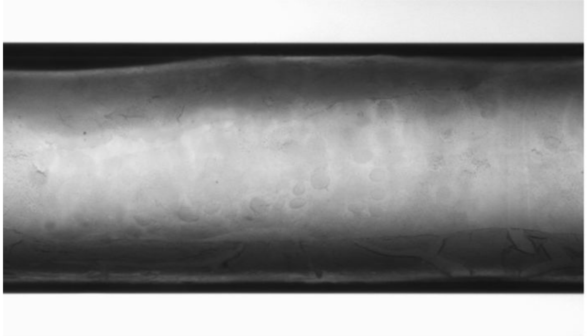
b) high water solubility of Fe(II)



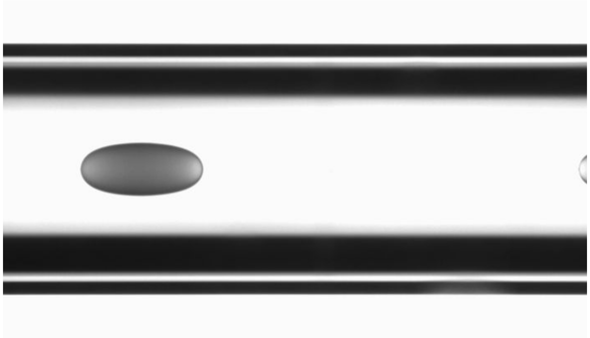
c) low solubility of $FeCl_3$ with emulsification

d) low solubility of $NiSO_4$ with emulsification

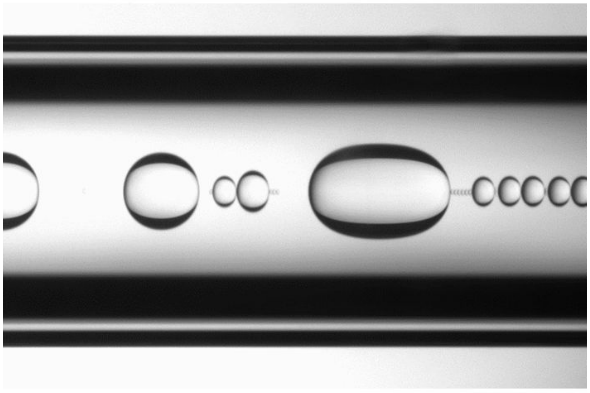
Figure S1: Metallosurfactant solution behavior in biphasic environment: a) Fe(II) oxidizes over time to Fe(III) visible as rust-colored precipitate; b) Fe(II) metallosurfactants exhibit high water solubility, undesired for the investigated application; c) Fe(III) metallosurfactants tend to form a fine precipitate with low solubility in solvent phase and cause emulsification/turbidity at the interface and the aqueous phase; d) metallosurfactants prepared from $NiSO_4$ show unfavorable solubility in both phases.



a) complete emulsification of 4-DBSA/solvent mixture



b) formation of drops with internal emulsification



c) well shaped, stable drops without emulsification

Figure S2: Pictures of drops in the measurement capillary of the spinning drop video tensiometer with deionized water as continuous phase: a) 4-dodecylbenzenesulfonic acid (4-DBSA) lowers the interfacial tension by an order of magnitude where measurement is impossible due to complete emulsification; b) unrinsed Ni(DBSA)$_2$/1-octanol solution forms well shaped drops, but residual 4-DBSA induces internal emulsification preventing reproducible measurement; c) rinsed Ni(DBSA)$_2$/1-octanol solution forms well shaped, stable drops without emulsification

Appendix C.

Vapor-liquid equilibrium data sets

C.1. Vapor-liquid equilibrium data for Figure 2.1

The vapor-liquid data from Figure 2.1 are experimental values taken from:

J. Gmehling, U. Onken, W. Arlt, *Vapor-Liquid Equilibrium Data Collection: Aqueous-organic systems*, Chemistry data series, Vol. I, Part 1, Dechema, Frankfurt am Main **1977**; ISBN: 3-921567-01-7.

C.1.1. Binary system water/formic acid

Table C.1.: Isobaric vapor-liquid equilibrium data for water/formic acid at 1.013 bar from Dechema Chemistry Data Series

Set 1		Set 2		Set 3	
x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}
0	0	0.0405	0.0245	0.0520	0.0280
0.3241	0.2816	0.1550	0.1020	0.0990	0.0480
0.3793	0.3594	0.2180	0.1620	0.1570	0.0920
0.4533	0.4639	0.3210	0.2790	0.2060	0.1530
0.5215	0.5606	0.4090	0.4020	0.2080	0.1470
0.5759	0.6359	0.4110	0.4050	0.3260	0.2670
0.6163	0.6955	0.4640	0.4820	0.4270	0.4270
0.6878	0.7813	0.5220	0.5670	0.4330	0.4480
0.7315	0.8094	0.6320	0.7180	0.5880	0.6680
0.7700	0.8616	0.7400	0.8360	0.6300	0.7320
0.7890	0.8769	0.8290	0.9070	0.7190	0.8260
0.8359	0.9119	0.9000	0.9510	0.7770	0.8760
0.8696	0.9325		0.8440	0.9180	
0.8950	0.9503		0.9080	0.9530	
0.9359	0.9697		0.9530	0.9800	
0.9697	0.9860				
1	1				

Set 1: Chalov N.V., Aleksandrova O.A., Sbornik Trudov Vses.Nauch.-Issled. Inst. Gidroliz.I Sulfitno-Spirt.Prom., 6, 149 (**1958**).
Set 2: Ito T., Yoshida F., J.Chem.Eng.Data, 8, 315 (**1963**).
Set 3: Plewes A.C., Pei D.C., Code R.K., Can.J.Chem.Eng., 37, 121 (**1959**).

C.1.2. Binary system water/acetic acid

Table C.2.: Isobaric vapor-liquid equilibrium data for water/acetic acid at 1.013 bar from Dechema Chemistry Data Series

Set 1		Set 2		Set 3	
x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}
0	0	0.0355	0.0705	0.0220	0.0580
0.1881	0.3063	0.0850	0.1570	0.0540	0.1230
0.3084	0.4467	0.1440	0.2400	0.0860	0.1680
0.4498	0.5973	0.2210	0.3390	0.0990	0.1830
0.5195	0.6580	0.2610	0.3840	0.1010	0.1880
0.5824	0.7112	0.3400	0.4670	0.1890	0.2980
0.6750	0.7970	0.3900	0.5150	0.3030	0.4330
0.7261	0.8239	0.4800	0.6050	0.4130	0.5450
0.7951	0.8671	0.6130	0.7220	0.5220	0.6490
0.8556	0.9042	0.7080	0.7990	0.6240	0.7350
0.8787	0.9186	0.8030	0.8640	0.6960	0.7920
0.9134	0.9409	0.9170	0.9340	0.7780	0.8510
0.9578	0.9708			0.8760	0.9140
1	1			0.9230	0.9440
				0.9450	0.9600
				0.9850	0.9890

Set 1: Brusset H., Kaiser L., Hocquel J. Chim.Ind., Genie Chim., 99, 207 (**1968**).
Set 2: Garner F.H., Ellis S.R.M., Pearce C.J., Chem.Eng.Sci., 3, 48 (**1954**).
Set 3: Ito T., Yoshida F., J.Chem.Eng.Data, 8, 315 (**1963**).

C.1.3. Binary system water/propionic acid

Table C.3.: Isobaric vapor-liquid equilibrium data for water/propionic acid at 1.013 bar from Dechema Chemistry Data Series

Set 1		Set 2	
x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}
0.0200	0.1000	0	0
0.0500	0.2200	0.0330	0.1070
0.1000	0.3700	0.0400	0.1530
0.2000	0.5450	0.0550	0.1950
0.3000	0.6600	0.0780	0.2940
0.4000	0.7490	0.1170	0.4200
0.5000	0.8050	0.1530	0.5120
0.6000	0.8440	0.2260	0.6050
0.7000	0.8750	0.2630	0.6410
0.8000	0.9030	0.4540	0.7720
0.9000	0.9320	0.5250	0.8010
0.9500	0.9480	0.5850	0.8310
0.9800	0.9730	0.6140	0.8430
		0.6440	0.8540
		0.7670	0.8910
		0.7860	0.8960
		0.8270	0.9070
		0.8770	0.9210
		0.8850	0.9230
		0.9110	0.9310
		0.9250	0.9370
		0.9500	0.9490
		0.9570	0.9550
		0.9710	0.9670
		0.9810	0.9760
		1	1

Set 1: Othmer D.F., Ind.Eng.Chem., 35, 614 (**1943**).

Set 2: Rivenq F., Bull.Soc.Chim.Fr., 1392 (**1961**).

C.1.4. Binary system water/butyric acid

Table C.4.: Isobaric vapor-liquid equilibrium data for water/butyric acid at 1.013 bar from Dechema Chemistry Data Series

Set 1		Set 2	
x_{H_2O}	y_{H_2O}	x_{H_2O}	y_{H_2O}
0	0	0	0
0.1480	0.7340	0.0140	0.1250
0.2000	0.8100	0.0410	0.4060
0.3310	0.8790	0.0520	0.5040
0.5620	0.9190	0.0650	0.5220
0.7000	0.9380	0.1250	0.7280
0.8000	0.9420	0.2100	0.8180
0.9000	0.9490	0.2900	0.8600
0.9790	0.9680	0.3300	0.8770
1	1	0.3370	0.8750
		0.3660	0.8820
		0.4600	0.9050
		0.4980	0.9120
		0.5270	0.9160
		0.6150	0.9290
		0.6640	0.9350
		0.6890	0.9400
		0.7970	0.9460
		0.8350	0.9480
		0.8410	0.9490
		0.8920	0.9520
		0.9370	0.9550
		0.9570	0.9580
		0.9590	0.9580
		0.9630	0.9590
		0.9720	0.9640
		0.9800	0.9690
		1	1

Set 1: Aristovich V.Yu., Levin A.I., Morachevsky A.G., Tr.Vses.Nauchn.Issled. Inst.Neftekhim.Protsessov, 5, 84 (**1962**).

Set 2: Rivenq F., Bull.Soc.Chim.Fr., 1192 (**1962**).

C.2. Vapor-liquid equilibrium data for Figure 8.1

The vapor-liquid data from Figure 8.1 were calculated with UNIFAC at 1.013 bar, using published UNIFAC-parameters from http://www.ddbst.com/published-parameters-unifac.html.

Table C.5.: Isobaric vapor-liquid equilibrium data for 1-octanol/octyl acetate, methyl acetate/1-octanol and methyl acetate/octyl acetate at 1.013 bar calculated with UNIFAC

OcOH/OcAc		MeAc/OcOH		MeAc/OcAc	
x_{OcOH}	y_{OcOH}	x_{MeAc}	y_{MeAc}	x_{MeAc}	y_{MeAc}
0	0	0	0	0	0
0.0200	0.0432	0.0200	0.3436	0.0200	0.3534
0.0400	0.0835	0.0400	0.5786	0.0400	0.5882
0.0600	0.1210	0.0600	0.7289	0.0600	0.7333
0.0800	0.1562	0.0800	0.8218	0.0800	0.8212
0.1000	0.1892	0.1000	0.8791	0.1000	0.8753
0.1200	0.2203	0.1200	0.9151	0.1200	0.9097
0.1400	0.2497	0.1400	0.9383	0.1400	0.9325
0.1600	0.2774	0.1600	0.9538	0.1600	0.9481
0.1800	0.3037	0.1800	0.9645	0.1800	0.9591
0.2000	0.3288	0.2000	0.9721	0.2000	0.9672
0.2200	0.3526	0.2200	0.9777	0.2200	0.9732
0.2400	0.3754	0.2400	0.9818	0.2400	0.9779
0.2600	0.3972	0.2600	0.9849	0.2600	0.9815
0.2800	0.4181	0.2800	0.9874	0.2800	0.9843
0.3000	0.4382	0.3000	0.9893	0.3000	0.9866
0.3200	0.4576	0.3200	0.9908	0.3200	0.9885
0.3400	0.4764	0.3400	0.9921	0.3400	0.9900
0.3600	0.4945	0.3600	0.9931	0.3600	0.9913
0.3800	0.5121	0.3800	0.9940	0.3800	0.9924
0.4000	0.5293	0.4000	0.9947	0.4000	0.9933
0.4200	0.5459	0.4200	0.9953	0.4200	0.9941
0.4400	0.5622	0.4400	0.9958	0.4400	0.9948
0.4600	0.5782	0.4600	0.9962	0.4600	0.9954
0.4800	0.5938	0.4800	0.9966	0.4800	0.9959
0.5000	0.6092	0.5000	0.9969	0.5000	0.9963
0.5200	0.6243	0.5200	0.9972	0.5200	0.9967
0.5400	0.6393	0.5400	0.9975	0.5400	0.9970
0.5600	0.6540	0.5600	0.9977	0.5600	0.9973

0.5800	0.6687	0.5800	0.9979	0.5800	0.9976
0.6000	0.6832	0.6000	0.9981	0.6000	0.9979
0.6200	0.6977	0.6200	0.9983	0.6200	0.9981
0.6400	0.7121	0.6400	0.9984	0.6400	0.9983
0.6600	0.7265	0.6600	0.9985	0.6600	0.9984
0.6800	0.7410	0.6800	0.9987	0.6800	0.9986
0.7000	0.7554	0.7000	0.9988	0.7000	0.9987
0.7200	0.7700	0.7200	0.9989	0.7200	0.9989
0.7400	0.7846	0.7400	0.9990	0.7400	0.9990
0.7600	0.7994	0.7600	0.9991	0.7600	0.9991
0.7800	0.8144	0.7800	0.9992	0.7800	0.9992
0.8000	0.8295	0.8000	0.9992	0.8000	0.9993
0.8200	0.8449	0.8200	0.9993	0.8200	0.9994
0.8400	0.8606	0.8400	0.9994	0.8400	0.9995
0.8600	0.8765	0.8600	0.9995	0.8600	0.9996
0.8800	0.8928	0.8800	0.9995	0.8800	0.9996
0.9000	0.9095	0.9000	0.9996	0.9000	0.9997
0.9200	0.9265	0.9200	0.9997	0.9200	0.9998
0.9400	0.9441	0.9400	0.9998	0.9400	0.9998
0.9600	0.9622	0.9600	0.9998	0.9600	0.9999
0.9800	0.9808	0.9800	0.9999	0.9800	0.9999
1	1	1	1	1	1

C.3. Vapor-liquid equilibrium data for Figure 8.5

The vapor-liquid data from Figure 8.5 were calculated with UNIFAC at 1.013 bar, using published UNIFAC-parameters from http://www.ddbst.com/published-parameters-unifac.html. The experimental values were taken from:

J. Gmehling, U. Onken, W. Arlt, *Vapor-Liquid Equilibrium Data Collection: Organic hydroxy compounds: Alcohols*, Chemistry data series, Vol. I, Part 2a, Dechema, Frankfurt am Main **1977**; ISBN: 3-921567-09-2.

Table C.6.: Isobaric vapor-liquid equilibrium data for methyl acetate/methanol at 1.013 bar from Dechema Chemistry Data Series and calculated with UNIFAC

Set 1		Set 2		UNIFAC	
x_{MeAc}	y_{MeAc}	x_{MeAc}	y_{MeAc}	x_{MeAc}	y_{MeAc}
0	0	0.0260	0.0860	0	0
0.0700	0.1800	0.0450	0.1290	0.1109	0.0400
0.1510	0.3340	0.0760	0.2000	0.1978	0.0800
0.2750	0.4340	0.1400	0.2920	0.2675	0.1200
0.3520	0.4900	0.1600	0.3190	0.3246	0.1600
0.4200	0.5300	0.1960	0.3620	0.3721	0.2000
0.4970	0.5700	0.2970	0.4520	0.4125	0.2400
0.5500	0.6100	0.3880	0.5070	0.4473	0.2800
0.6070	0.6200	0.4760	0.5600	0.4778	0.3200
0.6480	0.6480	0.5640	0.6070	0.5051	0.3600
0.6960	0.6650	0.6720	0.6720	0.5299	0.4000
0.7900	0.7500	0.8300	0.7760	0.5527	0.4400
0.9060	0.8350	0.8990	0.8470	0.5743	0.4800
0.9500	0.9200	0.9530	0.9050	0.5950	0.5200
1	1			0.6153	0.5600
				0.6357	0.6000
				0.6565	0.6400
				0.6783	0.6800
				0.7017	0.7200
				0.7272	0.7600
				0.7557	0.8000
				0.7883	0.8400
				0.8264	0.8800
				0.8721	0.9200
				0.9284	0.9600
				1	1

Set 1: Balashov M.I., Grishunin A.V., Serafimov L.A., Zh.Fiz.Khim., 41, 1210 (**1967**).

Set 2: Nagata I., J.Chem.Eng.Data, 14, 418 (**1969**).