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**Modern tools for process intensification:
REACTIVE SEPARATIONS**

DOCTORAL THESIS

to achieve the university degree of
Doktorin der technischen Wissenschaften

submitted to

Graz University of Technology

Supervisor

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Graz, May 2017

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Modern tools for process intensification: REACTIVE SEPARATIONS

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Acknowledgements

First of all I want to thank my "Doktorvater" Matthäus Siebenhofer for supervising my PhD-thesis in the field of reactive separations. The guidance was full of impressive ideas, always with an open door for questions or discussions and completely without jumpiness regarding my perfect timing. I absolutely appreciated the numerous possibilities to present and defend my research work at scientific conferences.

My special thanks are directed to my co-supervisor Susanne Lux for the fruitful discussions, the motivating and encouraging suggestions as well as her social engagement. Her enthusiasm for teaching and research activities are definitely catching. It was a pleasure for me to work in this amazing research group.

I am very grateful to Prof. Gatterer for reviewing and assessing my PhD-thesis.

Of course many thanks are directed to all students, who were doing their bachelor and master thesis or projects within my research. I really enjoyed working together with so many national and international students. Without them, it would not have been possible for me to perform all the experiments, data processing and simulations.

Furthermore, I'm thankful for the support and practical advices in the technical center and experiment execution from our laboratory team.

Especially I want to thank my office colleagues Robert, Annika, Andreas and Peter for the cheerful working environment.

My biggest thanks are directed to my family. My parents Roswitha and Peter always strengthened me in my plans and ambitions, enabled my education and shared the excitement for my studies. My sister Angi and her family inspired and encouraged me in all ups and downs and provided a perfect balance for me.

Abstract

Renewable resources for chemical and fuel production gain increasing interest in research and industry. However, biorefineries have to handle multicomponent mixtures with high water content. Efficient downstream processing and complete utilization of the biomass are often the key facts for competitiveness. Aqueous mixtures of low molecular weight carboxylic acids are commonly produced as byproducts during pulping, fermentation or pyrolysis. Isolation of carboxylic acids from biobased broths may be challenging, due to their tendency to form azeotropes. State of the art separation of acetic acid and formic acid from effluents covers liquid-liquid extraction followed by several distillation steps for solvent regeneration and product isolation.

Task of this PhD-Thesis was the process intensification of solvent regeneration and product isolation for economic recycling of formic acid and acetic acid. Therefore the approach of changing the properties of the carboxylic acids via chemical reaction integrated in a distillation step for continuous product removal was investigated. The carboxylic acids were esterified with methanol to produce the low-boiling methyl esters. These methyl esters can be removed easily via the distillate to force the reaction equilibrium towards complete conversion. The significant change in boiling point and enthalpy of evaporation through esterification reduces the energy demand in downstream processing. Compared to the acid-water mixture, the methyl esters have a beneficial vapor-liquid equilibrium behavior for final separation via distillation, simplifying the process concept.

Single and multi-acid esterification experiments of formic acid, acetic acid and propionic acid with methanol were performed without catalyst, to investigate intramolecular catalysis and acid interaction. Based on single acid kinetic data, a model was developed incorporating the catalytic activity of the carboxylic acids via acid dissociation. This kinetic model is able to predict reaction kinetics in multi-acid esterification with deviation from experimental results of max. 1.7 %.

Subsequently, batch and continuous reactive distillation were proven for separation of the ternary mixture formic acid, acetic acid and water. Experiments have shown a high conversion of formic acid (99 %) due to higher reaction rate, while conversion of acetic acid in continuous reactive distillation was limited to 71 %. The distillate solely contained the methyl esters and the excess of methanol.

Finally, reactive distillation for solvent regeneration (70 wt.% Cyanex[®]923 in *n*-undecane) from liquid-liquid extraction of acetic acid and formic acid was verified. Uncatalyzed batch reactive distillation of the laden solvent has shown 97 % conversion of formic acid and 28 % conversion of acetic acid. By admixture of 5 wt.% 4-dodecylbenzenesulfonic acid to the solvent, methyl ester yields could be highly enhanced to 100 % and 88 % of methyl formate and methyl acetate, respectively. Adduct formation of Cyanex[®]923 with acids enables the circulation of the acidic catalyst with the solvent phase between extraction and reactive distillation.

Kurzfassung

Nachwachsende Rohstoffe für die Chemikalien- oder Treibstoffherzeugung erhalten zunehmendes Interesse in Forschung und Industrie. Allerdings müssen Bioraffinerien Multikomponentengemische mit hohem Wassergehalt verarbeiten. Effizientes Downstreamprocessing und vollständige Nutzung der Biomasse sind oft Schlüsselfaktoren für die Wettbewerbsfähigkeit. Wässrige Gemische von niedermolekularen Carbonsäuren entstehen als Nebenprodukte beim Holzaufschluss, in der Fermentation oder in der Pyrolyse. Die Neigung dieser Gemische zur Azeotropbildung verhindert die wirtschaftliche Nutzung der Nebenprodukte. Stand der Technik zur Abtrennung von Ameisen- und Essigsäure aus Abwässern ist Extraktion, gefolgt von mehreren Destillationsschritten für die Lösungsmittelregenerierung und Produktauftrennung.

Problemstellung dieser Dissertation war die Prozessintensivierung der Lösungsmittelregenerierung und Produktauftrennung für eine ökonomische Rückgewinnung von Essig- und Ameisensäure. Durch Kombination von chemischer Reaktion und Destillation wurden die Substanzeigenschaften verändert und das Reaktionsgleichgewicht beeinflusst. Die Carbonsäuren wurden mit Methanol zu den niedrigsiedenden Methylestern verestert und kontinuierlich über das Destillat abgezogen. Durch die Verringerung der Siedepunkte und Verdampfungsenthalpien wird der Energiebedarf reduziert. Weiters haben die Methylester ein günstiges Dampf-Flüssig Gleichgewicht für die Auftrennung durch Destillation, wodurch sich das Prozesskonzept vereinfacht.

Zu Beginn wurden Einzel- und Multisäurenveresterungen von Ameisen-, Essig- und Propionsäure mit Methanol ohne Katalysator durchgeführt, um den Einfluss von intramolekularen Katalyse und Säureinteraktionen zu untersuchen. Basierend auf der Einzelsäurenveresterung wurde ein Kinetikmodell entwickelt, welches die katalytische Aktivität der Carbonsäuren durch Säuredissoziation beinhaltet. Dieses Kinetikmodell berechnet die Reaktionskinetik der Multisäurenveresterung mit Abweichung vom experimentellen Ergebnis von max. 1.7 %.

Anschließend wurde die Reaktivdestillation zur Auftrennung von Ameisensäure, Essigsäure und Wasser im Batch- und kontinuierlichen Betrieb geprüft. Die Experimente ergaben einen Umsatz von 99 % der Ameisensäure aufgrund der höheren Reaktionsgeschwindigkeit. Im Gegensatz dazu war der Essigsäureumsatz in der kontinuierlichen Reaktivdestillation mit 71 % limitiert. Das Destillat bestand aus den Methylestern und dem überschüssigen Methanol.

Abschließend wurde die Reaktivdestillation auf die Lösungsmittelregenerierung (70 wt.% Cyanex[®]923 in *n*-Undecan) der Säureextraktion übertragen. Unkatalysierte Batch-Reaktivdestillation ergab 97 % Ameisensäure- und 28 % Essigsäureumsatz. Die Zugabe von 5 wt.% 4-Dodecylbenzolsulfonsäure als Katalysator zum Lösungsmittel führte zur Erhöhung der Ausbeuten auf 100 % Methylformiat und 88 % Methylacetat. Durch die Adduktbildung von Cyanex[®]923 mit Säuren ist es möglich den sauren Katalysator in der Lösungsmittelphase zu halten und in den Extraktion- und Reaktivdestillationskreislauf einzubinden.

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Introduction

Biomass is the upcoming feedstock material for chemicals and fuels, not only due to the lack of fossil sources but even more due to CO₂ regulations for reducing the anthropogenic greenhouse effect. The pulp and paper industry is one of the oldest biorefineries, but just focused on fiber production. Increasing interest in biobased chemicals aims at the byproducts of pulping, mainly lignin, furfural, carboxylic and hydroxycarboxylic acids. Commonly, these byproducts are used for energy production due to problems in isolation. Before incineration of the black liquor, which contains byproducts and solvent from pulping, the water content must be reduced. During water evaporation the volatile carboxylic acids acetic acid and formic acid are removed with the water from the black liquor. Isolation of the carboxylic acids formic acid and acetic acid from aqueous effluents is challenging due to azeotrope formation. For the recovery of these low molecular weight carboxylic acids a process was patented in 1981, which is still applied. As shown in Figure 1.1 the removal of the acids from the effluent is a simple task, performed via reactive liquid-liquid extraction. Solvents and apparatus design are well investigated and optimized for this process. In contrast, the solvent regeneration and product isolation is incorporated with extensive technical equipment and high energy demand for several distillations. Solvent regeneration consists of a recuperator (D1) with removal of 65 wt.% of the aqueous phase followed by vacuum distillation (D2), where a heterogeneous azeotrope is withdrawn at the top of the distillation column. Next a distillation (D3) for impurity removal like SO₂ and methanol is installed and an entrainer distillation (D4) for dewatering. A mixture of acetic acid, formic acid and furfural is obtained as bottom product, which needs further isolation steps.[1] This downstream processing must be intensified for economic isolation of the byproducts from aqueous solutions.

In general, process intensification has obtained growing attention in research for improving process efficiency, reducing energy demand, simplifying process concepts, increasing process safety and enhancing product quality. In process intensification the development of strategies for new processes like the theory of inventive problem solving (TIPS) is a very helpful tool. TIPS offers 40 principles and combinations thereof for overcoming physical contradictions to solve problems. It was found that approximately 80 % of all patents are based on these 40 principles.[2] Exemplarily, for separation of azeotropes the principles of intermediary, parameter change or phase transition could be combined. Precisely, the substance properties may be changed by chemical conversion combined with distillation for continuous product isolation. In the example of aqueous acetic acid/formic acid mixtures the carboxylic acids are removed with an intermediary in liquid-liquid extraction and converted to their low-boiling methyl esters via esterification with methanol, which are separated in distillation.

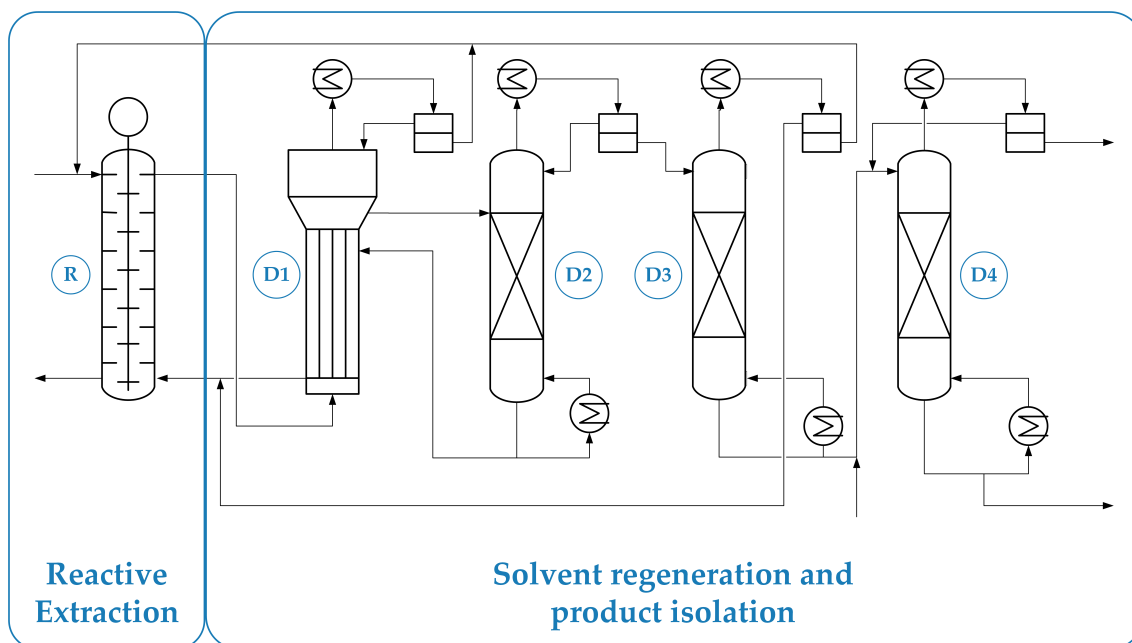


Figure 1.1: Recovery of low molecular weight carboxylic acids via reactive extraction and solvent regeneration. Adapted from [1]

The following chapters discuss the approach of changing properties via chemical reaction combined with changing the physical state through distillation for process intensification in solvent regeneration.

Chapter 2 gives an overview of different sources of aqueous mixtures of low molecular weight carboxylic acids in biobased processes. Furthermore feasible intervention points for process intensification via reactive separations in downstream processing are discussed. For reactive separations the knowledge of reaction rates, interaction in acid mixtures and temperature dependency is essential. Chapter 3 covers the investigation of kinetics of formic acid, acetic acid and propionic acid esterification with methanol and presents a kinetic model for prediction of simultaneous multi-acid esterification. Chapter 4 and 5 illustrate the separation feasibility of acetic acid, formic acid and water via reactive distillation with methanol as esterifying agent. Chapter 4 focuses on the separation of the crude distillate after extraction and distillation (D2 in Figure 1.1) for solvent recovery. Acetic acid, formic acid and water were fed to batch and continuous reactive distillation processes, investigating the influence of methanol in excess. Chapter 5 discusses the feasibility of reactive distillation incorporated directly as solvent regeneration. In batch reactive distillation experiments the influence of a strongly acidic homogeneous catalyst was studied for accelerating carboxylic acid esterification. For avoiding catalyst isolation, the cycling of the catalyst with the solvent phase between extraction and reactive distillation was proven. In chapter 6 a summary of the main findings is given and future directions for this project are presented.

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Isolation of Carboxylic Acids from Biobased Feedstock

Isolation of Carboxylic Acids from Biobased Feedstock

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DOI: 10.1002/cite.201600090

Isolation of low concentrated constituents from side streams of biobased processes has recently received increased technical and economical attention. For energy efficient acid isolation reactive extraction is proposed in literature. The crucial step for efficient process application is the solvent regeneration. Alternatively to conventional reactive extraction, physical extraction with chemical conversion simplifies the technical demand. For continuous operation of heterogeneous catalyzed esterification with physical extraction the Taylor-Couette disc contactor has proven to be applicable.

Keywords: Chemical reaction, Reactive extraction, Solvent recovery, Three-phase extractor

Received: June 30, 2016; *accepted:* November 29, 2016

1 Introduction

Implementation of bulk products from biobased resources in the chemical industry is expected to help delaying the greenhouse problem. In the past the main product, e.g., cellulose from pulping, was target of economic optimization, while several byproducts just had to contribute to cover the energy demand of production sites. In the pulping industry nearly 50 % of the processed wood is finally used for steam production, with a significant loss of valuable basic bulk products. To suffice the needs of greenhouse gas emission reduction it is essential to make also use of the byproducts from biobased processes. But there is a major obstacle to be resolved. The byproducts are often highly dilute aqueous multicomponent mixtures and isolation may end up in costly and energy intensive downstream processing. Consequently, such side streams are rather considered as a costly burden than a valuable source for bulk chemicals.

Low molecular weight carboxylic acids like formic acid (FA), acetic acid (AA) and propionic acid (PA) are important bulk chemicals in the food industry, as commodity chemicals in the textile industry, for the manufacture of pharmaceuticals, and many more. Black liquor from the pulping process typically contains lignin, aliphatic carboxylic acids, and other organics and inorganics. This is a potential source for valuable byproducts based on renewable raw material [1]. In the pulping process AA is formed by deacetylation of acetyl groups from the hemicelluloses in the initial phase of delignification, while FA is constantly formed during the peeling reaction [2]. For heat production from black liquor, the dilute black liquor (15 %) has to be concentrated to about 70–75 % by multi-stage evaporators [3]. The main amount of volatile fatty acids is collected in the condensate of black liquor evaporators. Recovery of these valuable byproducts from the black liquor condensate

is important in order to reduce the biochemical oxygen demand in the wastewater treatment plant and for further chemical production. Depending on the type of wood and process, the ratio between acids over the raw material varies from 14 % for hardwood up to 46 % for straw [4]. The main acids produced are FA, AA, lactic acid, and glucoisosaccharinic acid. Kraft pulping of birch wood decomposes about 19 % of the wood into (hydroxy-) carboxylic acids, whereof 12 % and 29 % from birch are decomposed to FA and AA respectively [4]. For a typical pulping plant capacity of 200 000 t a⁻¹ birch, this figures result in production of acidic byproducts of around 75 000 t a⁻¹, corresponding to a FA production of 9000 t a⁻¹ and an AA production of 22 000 t a⁻¹ [4].

Further, biobased pyrolysis oil (bio-oil) is a complex mixture containing carboxylic acids, mainly AA and FA, with a content up to 11 wt %. Depending on the feedstock, the AA concentration varies between 3.5 wt % in pine, 4.6 wt % in hardwood, and up to 7.4 wt % in straw bio-oil. FA concentrations lie between 1 wt % in hardwood, 2 wt % in straw, and 2.5 wt % in pine bio-oil. Separation of acids improves the product quality and additionally generates valuable byproducts.

A similar composition of carboxylic acids was reported for forest residues bio-oil, with concentration of FA being 1.5 wt % and 3.8 wt % of AA [5].

The isolation of pure AA and FA from aqueous solutions is difficult because of the complex vapor-liquid equilibrium

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(Fig. 1). In addition to a binary high boiling azeotrope of FA and water, this mixture also exhibits a ternary saddle point azeotrope. Therefore alternative separation processes for distillation are necessary to recover these valuable constituents from aqueous feed in an economical way.

This paper discusses alternative technologies for isolation of carboxylic acids from aqueous side streams of biobased processes. Reactive extraction by adduct formation between acid and extractant for carboxylic acid removal from aqueous streams is extensively reported in the literature [8–25]. Information for solvent regeneration is limited though. Chemical conversion of carboxylic acids by esterification combined with physical extraction of the reaction product is a newer approach. In Fig. 2 the conventional reactive extraction process with solvent regeneration (black line) is shown. Feasible positions for admixture of alcohols for combined reaction-separation processes by esterification of acids are marked with grey arrows. A new apparatus design based on CFD optimization of a rotating disc contactor, which is perfectly suited for application in liquid-liquid extraction of valuable byproducts from biobased process effluents, is presented. Due to the simple design this extractor offers access to three-phase contact (e.g., aqueous phase-solvent phase-heterogeneous catalyst).

2 Reactive Extraction

Liquid-liquid extraction is an appropriate technology for separation of constituents from dilute effluents. In reactive extraction the physical extraction is overlaid by a chemical reaction enhancing the extraction efficiency.

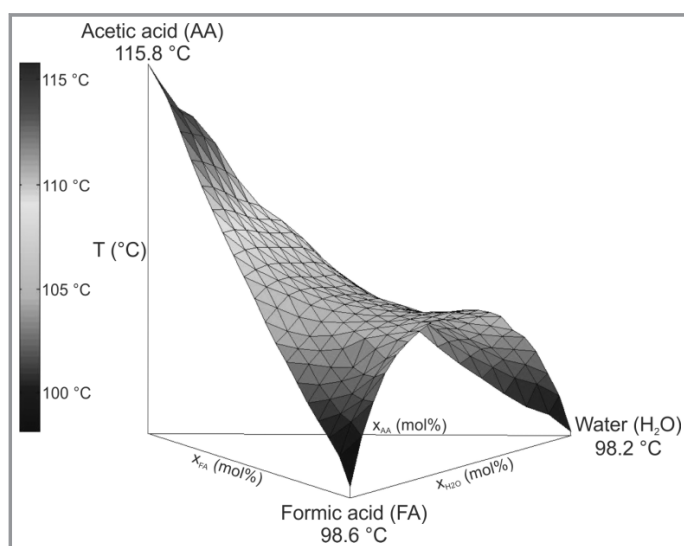


Figure 1. Boiling point surface of FA/AA/water at 95 kPa. Binary high boiling azeotrope of FA/water: 105.6 °C; ternary saddle point azeotrope: 105.2 °C [6].

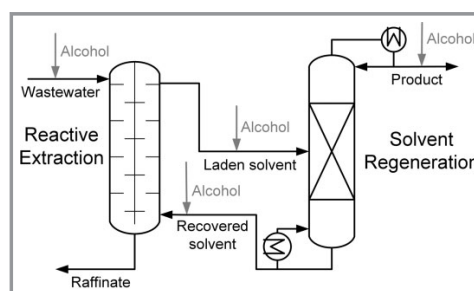


Figure 2. Process concept for reactive carboxylic acid recovery with potential positions for admixing alcohols for esterification.

2.1 Reactive Extraction by Adduct Formation

For low molecular weight carboxylic acids a variety of extractants has been investigated. Several papers have been published for carboxylic acid extraction, giving a detailed overview on extractants and diluents [7–12]. Simultaneous extraction of several carboxylic acids as well as selective extraction of carboxylic acids from multicomponent mixture is discussed in this paper.

The general reaction equation for reactive extraction of acid A_{aq} with a solvent B_{org} is given in Eq. (1) with the corresponding equilibrium constant K for an adduct with a molar ratio of acid to extractant of n according to Eq. (2). The distribution coefficient D gives the ratio of the acid concentration in the solvent and the aqueous phase at equilibrium (Eq. (3)). The selectivity S is the ratio of the distribution coefficients of the desired component over the undesired component (Eq. (4)). The extraction efficiency (degree of extraction or extraction yield) η , quantifying the ratio of the mass of the target acid in the extract phase to the mass of this acid in the feed phase, is shown in Eq. (5).



$$K = \frac{c_{A_nB_{org}}}{c_{A_{aq}}^n c_{B_{org}}} \quad (2)$$

$$D = \frac{c_{A_{org,eq}}}{c_{A_{aq,eq}}} \quad (3)$$

$$S = \frac{D_A}{D_{water}} \quad (4)$$

$$\eta_{E,A} = \frac{m_{A_{org,eq}}}{m_{A_{feed}}} 100 \% \quad (5)$$

Kertes and King [7] already distinguished three categories of extractants for acid extraction: (1) carbon-bonded oxygen donor extractants, (2) phosphorus-bonded oxygen donor

extractants and (3) high molecular weight aliphatic amine extractants. The extraction process with extractants of the first two categories includes solvation of the acids by donor bonds, while in the third category acid extraction occurs by proton transfer or by ion pair formation. The carbon-bonded oxygen donor extractants, e.g., alcohols, ethers or ketones, form weak hydrogen bonds between the acid hydrogen (proton) and the oxygen donor which are not considered as specific solvation. This group of solvents has a higher solubility in water and distribution coefficients are low, varying from 0.14 to 1.68 [13]. Phosphorus-bonded oxygen donor extractants are stronger Lewis bases than the extractants of group (1), providing more specific solvation and higher distribution coefficients. Aliphatic amines (Brønsted bases) are at least as strong as or stronger bases than phosphorus-bonded oxygen donor extractants. [7] Preferably tertiary amines are used because primary amines have a high solubility in water and secondary amines may irreversibly form amides with acids at elevated temperature [13].

Inert and modifying diluents have an important effect on reactive extraction with amines because solubility of amine salts is very low and density and viscosity are unfavorable for liquid-liquid extraction. Modifiers improve the solubility of amine-acid salts in the solvent phase and may alter stoichiometry in the solvent phase while inert diluents alter the physical properties and water solubility of the solvent phase [14].

Solvation decreases in the series alcohol > nitrobenzene > proton-donating halogenated hydrocarbon > ketone > halogenated aromatic hydrocarbon > benzene > alkyl aromatic hydrocarbon > aliphatic hydrocarbon [15].

Tab. 1 summarizes the best available extractants found in literature for extraction of low molecular weight carboxylic acids from highly dilute aqueous effluents.

Rasrendra et al. [22] performed liquid-liquid extraction experiments for separation of carboxylic acids from an aqueous pyrolysis oil phase. The aqueous phase contained acids (3.33 wt % AA, 0.56 wt % FA, and 0.18 wt % glycolic acid), aldehydes, sugars, ketones, phenolics, and furans. The extraction was performed with trioctylamine (TOA), Alamine[®]300, Alamine[®]304-1, and Alamine[®]336. 2-Ethylhexanol was selected as the best diluent. An extractant mixture of 40 wt % TOA, Alamine[®]300, and Alamine[®]336 in 2-ethylhexanol gave similar extraction efficiencies of 84 % for AA and 92 % for FA. Co-extraction of ketones and phenolics beside the carboxylic acids was observed; sugars and aldehydes preferably remained in the aqueous phase. Mahfud et al. [23] investigated the recovery of AA directly from bio-oil and from the aqueous phase of thermally treated bio-oil with TOA in octane. Experiments with pure bio-oil containing 6.2 wt % AA, 0.4 wt % PA, and 0.04 wt % butyric acid (BA) showed low extraction efficiencies (2.7 – 5.8 %) for different concentrations of TOA in dodecane or petrol ether. High solubility of TOA was observed in the bio-oil phase. When processing the aqueous layer of thermally treated bio-oil containing 6.22 wt % AA and 0.07 wt % PA no losses of TOA were observed and an extraction efficiency of 75 % was obtained with TOA in toluene.

Simultaneous reactive extraction for the recovery of FA, AA, and furfural from aqueous acid hydrolysis process streams was studied by Demesa et al. [24]. The solvents 2-methyltetrahydrofuran (2-MTHF) and Alamine[®]336 diluted in toluene were compared for different initial acid

Table 1. Literature data of best available extractants for various carboxylic acids.

Acid	Extractant	$c_{A, aq}$ [kmol m ⁻³]	c_{org} [kmol m ⁻³]	Initial concentrations for given D [kmol m ⁻³] ($V_{org}/V_{aq} = 1:1$)	D	T [°C]	Lit.
<i>Organophosphorous compounds</i>							
FA	Cyanex [®] 923	0.019 – 0.353	0.251 – 2.514	$c_{org,0} = 2.263$, $c_{A, aq,0} = 0.087$	8.69 ^{a)}	25	[16]
AA	Cyanex [®] 923	0.017 – 0.334	0.251 – 2.514	$c_{org,0} = 2.514$, $c_{A, aq,0} = 0.168$	6.5 ^{a)}	25	[16]
PA	Cyanex [®] 923	0.018 – 0.854	0.251 – 2.514	$c_{org,0} = 2.514$, $c_{A, aq,0} = 0.2412$	23.36 ^{a)}	25	[16]
BA	TBP	0.025 – 0.25	0.368 – 2.94	$c_{org,0} = 2.94$, $c_{A,0} = 0.081$	21.06	20	[17]
<i>Amine</i>							
FA	Amberlite [®] LA-2	2.173	0.371 – 1.859	$c_{org,0} = 1.859$ in isoamylalcohol	19.89	25	[18]
AA	Tri- <i>n</i> -butylamine, Tri- <i>n</i> -pentylamine, THA, TOA	0.833	0.833	$c_{org,0} = 0.833$ THA in 1-butanol, $c_{A,0} = 0.833$ ($m_{org}/m_{aq} = 1$)	15.00	40	[19]
PA	TOA	0.05 – 0.4	0.229 – 2.059	$c_{org,0} = 0.686$ in oleyl alcohol, $c_{A,0} = 0.05$	10.11	32	[20]
BA	TOA	0.026 – 0.25	0.226 – 1.13	$c_{org,0} = 1.13$ in 1-decanol/dodecane, $c_{A,0} = 0.084$	34.3	20	[21]

^{a)} Calculated distribution coefficients from given data; mixture density was approximated by ideal mixing.

and furfural concentrations (1–8 wt %). Best results were obtained with an initial concentration of 3 wt % for all solutes. The extraction of FA performed better with Alamine[®]336 ($D_{\text{Alamine}^{\text{®}}336} = 5.63$, $D_{2\text{-MTHF}} = 1.27$ at 45 °C) but furfural extraction was better with 2-MTHF ($D_{\text{Alamine}^{\text{®}}336} = 3.34$, $D_{2\text{-MTHF}} = 6.56$ at 45 °C). AA extraction gave similar distribution coefficients for both extractants ($D_{\text{Alamine}^{\text{®}}336} = 1.77$, $D_{2\text{-MTHF}} = 1.41$ at 45 °C). The effect of operation temperature on the extraction behavior was different; the distribution coefficients for furfural increased, and decreased for FA and AA with increasing temperature between 25 to 45 °C.

The selective extraction of FA and AA from aqueous succinic acid with TOA diluted in *n*-heptane, butyl acetate, or dichloromethane with or without the modifier 1-octanol was investigated by Caşcaval et al. [25]. The extraction efficiency increased for all acids with increasing TOA concentration in the diluent; with dichloromethane performing best. For FA and AA this effect was significant at lower TOA concentrations, because FA and AA form 2:2 and 1:1 complexes with TOA. For comparison succinic acid forms 1:2 complexes with TOA and needs higher amounts of TOA for extraction. Additionally, TOA tends to form adducts with the stronger FA followed by the weaker acids. In [25] selectivity was defined as the yield of AA plus the yield of FA over the yield of succinic acid. The best results were obtained by adding 1-octanol (20 vol % of diluent) to the solvent phase; the selectivity reached 148 when 50 g L⁻¹ TOA extractant were applied.

In general sufficient extraction efficiency for carboxylic acid extraction at low aqueous feed concentration was observed. Extraction efficiency increased with increasing extractant concentration, decreased with increasing feed concentration and decreased with increasing temperature. Literature reports, that TOA gives the highest distribution coefficient for carboxylic acid extraction because of the high Brønsted basicity, followed by the Lewis base trialkylphosphine oxides (TRPO). The extraction efficiency for different acids is dependent on the hydrophobicity and the acidity of the acids. Longer-chain carboxylic acids are more hydrophobic and with higher acidity the association power between acid and extractant increases.

2.2 Reactive Extraction via Chemical Conversion

Different to reactive extraction by adduct formation, the reactive extraction via chemical reaction utilizes chemical conversion of the carboxylic acid into derivatives. Due to different solubility the reaction product is transferred into the solvent phase by physical extraction enhancing conversion of the acid. Al-Saadi et al. [26] used *n*-butanol to esterify concentrated AA solutions in presence of sulfuric acid as a homogeneous catalyst. For combination with a physical extraction step they used *n*-heptane as solvent. Due to the fact that their experiments were carried out in a highly con-

centrated system the results are not applicable for processing dilute effluents from biobased feedstock.

Bianchi et al. [27] investigated the esterification of highly dilute AA effluents of 6 wt % with 6 wt % *n*-butanol in batch experiments with Amberlyst[®]200 as a heterogeneous catalyst. The experimental setup consisted of a stirred three-necked flask as reactor with complete condensation of the evaporated phase. For the evaluation of their experiments, Bianchi et al. defined a process efficiency given in Eq. (6).

$$E = \frac{n_{\text{AA,aq,in}} - n_{\text{AA,aq,out}}}{n_{\text{AA,aq,in}}} 100 \% \quad (6)$$

Esterification was carried out at 99 °C for 6 h, resulting in a process efficiency of 3.4 %. This confirms the unfavorable equilibrium limit of the esterification step due to the high excess of water in the system. In further experiments Bianchi et al. used 2-ethyl-1-hexanol as an alcohol and increased the amount of alcohol above maximum solubility, resulting in the formation of a second phase. This second phase was found to have beneficial effects on the reaction equilibrium. Due to the very low solubility of the ester in water, the alcohol acts as a solvent for the product. For the use of sulfuric acid as a homogeneous catalyst, a process efficiency of about 60 % was achieved after 3 h at 99 °C.

The same experimental setup was used for different heterogeneous catalysts (e.g., Amberlyst[®]200, Amberlyst[®]15) which all had significantly lower process efficiencies of less than 45 %. The decrease in process efficiency was assumed to be a result of the reaction taking place at the interface of the two phases or within the solvent phase. Ragaini et al. [28] confirmed this assumption in experiments with 2-ethyl-1-hexanol and Amberlyst[®]15 as a heterogeneous catalyst.

In our research we have performed extraction experiments with the solute AA in a setup comparable to Bianchi et al. [30] with *n*-octanol as the solvent phase as well as alcohol for esterification. 4-dodecylbenzenesulfonic acid (4-DBSA) was used as a liquid catalyst. Compared to the mentioned process efficiency of about 60 % for homogeneous and of 45 % for heterogeneous catalysis [30], a process efficiency of 42 % after 3 h for an operation temperature of as low as 50 °C was achieved. The catalyst loading was 10 wt % 4-DBSA based on the alcohol. Esterification of dilute AA (approx. 70 g L⁻¹) with equimolar amount of ethanol (EtOH) in the presence of Amberlyst[®]15 as a heterogeneous catalyst at 50 °C was performed too. To utilize the benefits of reaction with simultaneous physical extraction, the solvent *n*-undecane in a volumetric ratio of 1:2 based on the aqueous feed was used. This approach yielded a process efficiency of 13.5 %. The reaction progress is illustrated in Fig. 3a for the aqueous phase and in Fig. 3b for the solvent phase.

The concentration profile of EtOH in the aqueous phase shows a steady descent when performing AA esterification. The step within the first 15 min may be explained by the

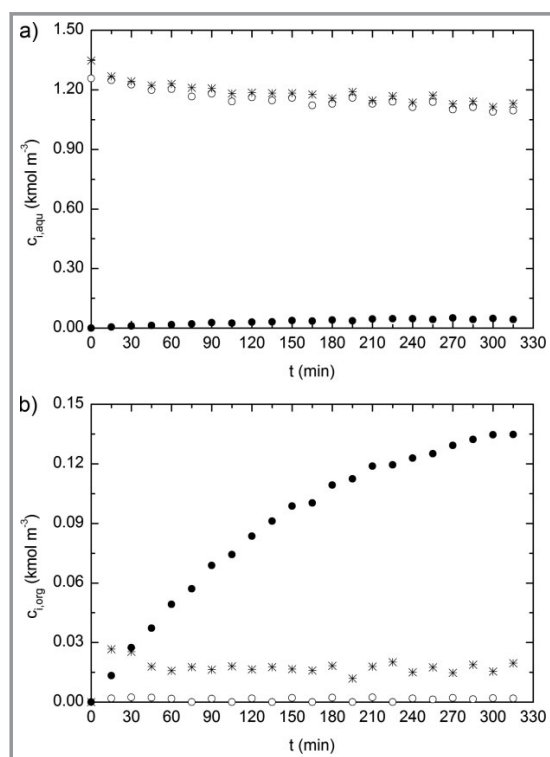


Figure 3. Concentration trend of AA (○) esterification with EtOH (*) to ethyl acetate (●) (molar ratio of AA/EtOH = 1:1) with simultaneous physical extraction ($V_{org}/V_{aq} = 1:2$) at 50 °C for a) aqueous phase and b) solvent phase (*n*-undecane) catalyzed by 10 wt % Amberlyst® 15.

partitioning of EtOH between the two phases. It is obvious that the insignificant amount of AA as well as EtOH transferred into the solvent phase is nearly constant during the whole experiment. Ethyl acetate as the desired product is extracted to a significant extent, leading to a steady depletion of the educts in the aqueous phase.

Esterification in a three-phase system demands high solubility of the alcohol in the aqueous phase and high solubility of the corresponding ester in the solvent phase. These technological boundaries enable the use of a heterogeneous catalyst (e.g., Amberlyst® 15) in the aqueous feed. The use of a solvent which is not actively taking part in the esterification reaction (e.g., alkanes like *n*-undecane) provides the benefit of shifting the reaction equilibrium to the product side with negligible solubility of the solvent phase in water. Thereby esterification of AA becomes feasible even in highly dilute systems.

The implementation of three-phase esterification in a continuous process needs accomplishment of specific requirements to the reaction-extraction setup. The setup has to provide continuous contact between the two liquid phases to maintain a maximum gradient for the extraction, and it has to provide sufficient contact of the heterogeneous

solid catalyst particles with the aqueous phase containing the reactants. An apparatus capable of meeting these requirements was investigated.

3 Industrial Scale Reactors for Continuous Reactive Extraction

Dating back to a patent from 1952 the rotating disc contactor (RDC) was established in liquid-liquid extraction [29]. The RDC has spread rapidly in industry for extraction processes due to the simple and robust construction of internals. Rotating discs, fixed on a central shaft, provide smooth energy input for droplet dissipation. In the shell-side area of the column, stator rings with a vertical offset are installed. The stator rings subdivide the column into compartments. The compartment design shall minimize axial back-mixing. Due to the condition of continuity, two toroidal vortices are formed in each compartment, causing turbulences in the continuous phase which act on the dispersed phase and increase the residence time of the dispersed phase in the column. As a result of smooth energy input by rotating discs the RDC is suitable for highly viscous media or components which are sensitive to shear stress. The RDC provides a broad variation of energy input leading to high operational flexibility. Nevertheless the RDC is not very suitable for separations of constituents in biobased processes due to the stator rings which provide dead zones for crud accumulation. Accumulation of crud may finally cause sudden breakdown and operation failure when interacting with the liquid-liquid dispersion.

Even though the RDC design is well established in industrial scale, the design of internals suffers from some uncertainties regarding the optimum ratio of the shaft diameter to the shell diameter [30]. To prevent loss of active cross section area, the shaft diameter is sized as small as possible [31]. Due to this design weakness, the dispersed phase inclines to form a stable coalescence layer at the shaft because of formation of hydrodynamic dead zones at the shaft. Addressing this construction limit the RDC design was modified and simplified. As a result the Taylor-Couette disc contactor (TCDC) was developed [32, 33].

Especially for applications in biobased processes the TCDC may offer advantageous operation features. From the hydrodynamic point of view, the TCDC is a hybrid of a classical RDC and a Taylor-Couette reactor. The TCDC is based on RDC design, but without stator rings and an increased shaft diameter. Due to missing stator rings, dead zones for crud accumulation are avoided, maintenance and cleaning is facilitated and investment costs are reduced. Increased shaft diameter improves the classical RDC design by preventing hydrodynamic dead zones and tie-in a similar flow pattern compared to banded two-phase flow in Taylor-Couette reactors. The flow pattern in the single compartment is induced by centrifugal force, counteracted by friction of the continuous phase. Furthermore, enlarged rotor

discs of the TCDC form dynamic compartments during operation, stabilizing the flow pattern and inhibiting high axial dispersion [32,33]. For application in chemical reactions the hydraulic flow pattern of banded two-phase flow exhibits small droplet size, providing large mass transfer area, and narrow residence time distribution. Compared with the Taylor-Couette reactor the TCDC provides much higher throughput, and in case of two phase flow the TCDC can be operated in co-current as well as counter-current mode. These operation features give access to many applications in mass transfer as well as chemical reactions conducted in multiphase systems.

3.1 Hydrodynamic Investigation of Three-phase Flow

By combining continuous physical extraction with chemical reaction, accelerated by heterogeneous catalysis, the hydrodynamic characteristic of three-phase flow has to be accurately investigated. Therefore several experiments in a TCDC were carried out to determine the flow profiles in presence of a third solid phase. The extractor used in this work has the following design specifications: $H_{\text{active}} = 0.4$ m, $d_{\text{column}} = 0.05$ m, $d_{\text{shaft}} = 0.02$ m, $d_{\text{rotor}} = 0.035$ m, and $H_{\text{compartment}} = 0.025$ m.

Amberlyst[®]15 was added to the continuous phase at the top of the column. ShellSol-T was used as dispersed phase entering at the bottom. First experimental investigations were carried out without the presence of the dispersed phase. Results have shown, that for a critical rotor tip velocity of $v_c \sim 0.45$ m s⁻¹, the catalyst particles are trapped in the vortices due to the higher drag force of the vortices compared to the gravity of the particles. The residence time of catalyst particles in the single compartment was increased significantly. With increasing rotational speed the catalyst got increasingly concentrated at the intersection of the toroidal vortices located at half the height of the single compartment height (Fig.4a). The dispersed phase (solvent phase) is forced into the direction of the rotor discs (Fig.4b). Even by operating the reactor with particle loaded continu-

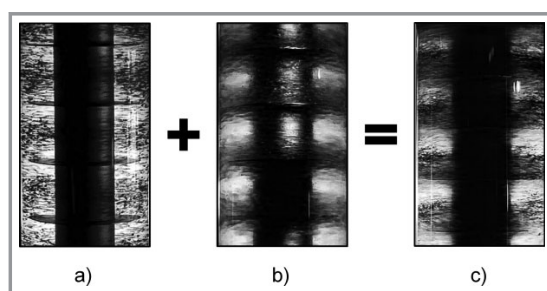


Figure 4. Flow pattern in the TCDC for rotor tip velocity of 1.7 m s⁻¹. a) Distribution of the catalyst in continuous phase, b) distribution of dispersed phase, and c) distribution of catalyst and dispersed phase in three-phase flow application.

ous phase and dispersed phase at the same time, the particles as well as the dispersed phase stay within the compartments for a reasonable residence time and do not interfere (Fig.4c). From a hydrodynamic point of view, these results imply applicability of the TCDC as a three-phase reactor for reactive extraction by chemical conversion with phase transfer of the product.

4 Solvent Regeneration

Solvent regeneration is at least as essential as the extraction step for efficient acid recovery and solvent recycle. A huge scientific effort has been done to find appropriate extractant/diluent mixtures for separation [8–25], however little information is available for solvent regeneration. The use of caustic or acidic solutions, an aqueous volatile base, temperature or diluent swing, distillation and reactive distillation are reported as possible regeneration technologies.

4.1 Re-extraction with Caustics

Usually an aqueous solution of NaOH is used as the aqueous phase for re-extraction with good regeneration results. The main drawbacks of this regeneration method are the high consumption of base and acid to isolate the carboxylic acid in its free form and producing equal amounts of solid waste.

The recovery of PA from TOA in 1-decanol or methylisobutyl ketone (MIBK) using NaOH was investigated by Keshav and Wasewar [34]. 100% recovery for both diluents with a slight molar excess of NaOH to acid was achieved for initial concentrations of PA in the organic phase of 0.334 and 0.374 kmol m⁻³.

4.2 Re-extraction with Acids

By contacting the laden solvent with an acidic aqueous solution, the stronger acid from the aqueous re-extraction phase replaces the carboxylic acid in the adduct, formed between the reactive extractant and the acid in the solvent phase. Distillation can be used for the removal of the stronger acid from the solvent phase afterwards. Re-extraction with a stronger acid leads to formation of undissociated carboxylic acids in the aqueous phase.

Yabannavar and Wang [35] applied HCl in the aqueous phase for the recovery of lactic acid from Alamine[®]336 in oleyl alcohol. For a solvent load of 28.8 kg m⁻³ lactic acid best results were obtained with 25 kg m⁻³ HCl in aqueous solution with a volumetric ratio of 1:1 between solvent and aqueous phase. The experiments led to a recovery of 83% but with 5.6 kg m⁻³ HCl remaining in the aqueous phase. A higher molar amount of HCl than lactic acid was necessary for recovery of lactic acid because all amine molecules needed to be saturated.

4.3 Re-extraction with Volatile Extractant in the Aqueous Phase

Re-extraction with a volatile aqueous base is applicable, especially when non-volatile carboxylic acids are extracted. The laden solvent is contacted with the aqueous solution of a volatile base and the carboxylic acid is re-extracted to the aqueous phase. The acid-base salt can be split by thermal treatment, the vaporous base is reabsorbed in water and the carboxylic acid is removed as bottom product [36].

Trimethylamine in aqueous phase was examined by Keshav and Wasewar [34] for PA removal from TOA in 1-decanol or MIBK. A slightly higher ratio than unity between trimethylamine and the acid enabled 100 % recovery of PA without the drawback of solid waste formation.

4.4 Temperature-swing Re-extraction

By increasing the temperature after the extraction step and by contacting the laden solvent with fresh water influences the equilibrium between solvent and aqueous phase and solvent regeneration is achieved. Due to the temperature dependency of the liquid-liquid equilibrium, higher concentration of acid in the aqueous re-extraction phase can be reached compared to the concentration in the original feed [37].

The recovery of PA from TOA in MIBK, 2-octanol or 1-decanol was investigated by two stage temperature-swing regeneration of the solvent [34]. At 90 °C re-extraction temperature and the diluent 2-octanol or 1-decanol, the highest re-extraction yield in the second stage of 35 % and that for MIBK of 88 % was reported. The authors concluded from the experimental results that active diluents lead to higher extraction but re-extraction with temperature-swing is on average.

Wisniewski and Pierzchalska [38] observed that by increasing the temperature from 20 to 70 °C the amount of extracted acids decreases (18 % FA, 15 % AA, and 11 % PA), but phase separation enhances, which is advantageous for re-extraction.

4.5 Diluent-swing Re-extraction

The composition of the laden solvent phase is changed by adding or removing a diluent to shift the aqueous solvent phase equilibrium towards the aqueous phase load. The solvent phase is then contacted with a fresh aqueous phase to re-extract the solutes. Combination with temperature-swing re-extraction may be advantageous in terms of higher product concentration in the aqueous phase [37].

Admixture of hexane, petroleum ether and toluene was investigated for solvent regeneration of TOA in 2-octanol, 1-decanol, and MIBK by Keshav and Wasewar [34]. Highest average recovery of 39.6 % was achieved with the system

TOA/MIBK by admixing hexane in a volumetric ratio of 1:1 of solvent phase to diluent.

4.6 Solvent Regeneration and Solute Isolation by Distillation

Distillation for solvent recovery is feasible for highly volatile solutes.

Golob et al. [39] performed solvent regeneration of a tri-n-octylphosphine oxide (TOPO)/kerosene mixture by continuous distillation. The solvent phase contained 2 wt % AA before and 0.18 wt % after distillation. In the distillate product 75 wt % AA and 25 wt % water from co-extraction was collected.

Ren et al. [40] investigated stripping with hot water and vacuum evaporation at 95 kPa operation pressure for tributylphosphate (TBP) recovery after low molecular weight carboxylic acid extraction. Better results were obtained by vacuum evaporation at 100 °C and at 95 kPa operation pressure, achieving 98.95 % stripping efficiency after the fourth stripping step compared to 66.57 % for re-extraction with water at 100 °C. Recovery rate of AA was 98.21 % by combining reactive extraction with TBP and vacuum evaporation for re-extraction.

Cai et al. [41] investigated two phosphate-containing extractants, TRPO and TBP, for extraction of FA and AA from aqueous solutions. For recovery of the carboxylic acids from the laden solvent distillation at a lower pressure of 3 kPa was recommended. Because of co-extraction of water, the acids are obtained in aqueous solutions with high acid concentration.

Distillative recovery at 10 kPa for carboxylic acid laden solvent was suggested by Jung et al. [19]. For extraction of AA and lactic acid the best extractant/diluent mixture was trihexylamine (THA) in 1-butanol. Because of unfavorable boiling points in the system AA/1-butanol/THA distillation is too energy intensive, but for lactic acid recovery it is feasible. Distillation of the mixture 1-butanol/water/lactic acid/THA resulted in a distillate fraction of butanol and water from co-extraction and as bottom product the amine-acid complex, which can further be treated by re-extraction with an aqueous ammonia solution, was collected.

Solvent regeneration experiments were performed by Demesa et al. [24] in a spinning band distillation setup under vacuum for FA concentrations in the solvent phase between 5 and 37 wt %. For Cyanex[®]923 regeneration a vacuum of 3.1 – 4.9 kPa and a maximum distillation temperature of 195 °C were applied because at elevated temperature thermal decomposition of FA was observed. FA removal of 75 % was achieved. N,N-dibutylformamide and Alamine[®]304 regeneration showed 85 and 88 % FA removal. Best results for FA removal were achieved with pure Alamine[®]336 with 97.6 % however for Alamine[®]336/toluene mixtures the regeneration is more complicated because of the “low” boiling point of toluene ($T_{b,atm} = 110.6$ °C). For

AA removal from Cyanex[®] 923 a temperature of 150 °C and 2.8–4.4 kPa were applied, obtaining acid removal of 16%. At higher feed concentration of AA the recovery is easier. 2-MTHF recovery is simple, distillation without high temperature or vacuum is possible because of its low boiling point of 78 °C.

For combinations of physical extraction and chemical conversion solvent regeneration can easily be achieved by distillation.

4.7 Reactive Distillation

Through chemical reactions the solute properties are changed and thermodynamic limitations like azeotropes may be overcome. The continuous removal of the reaction products forces the reaction equilibrium to the product side enabling complete conversion. For optimal process configuration the boiling point of the reaction products should be the highest and/or the lowest of the mixture, and the reaction educts shall preferably be intermediate boilers. Therefore, it is easy to keep the reaction educts in the reactive distillation column, while the products can be removed via the distillate and/or bottom product.

Tirronen et al. [42] patented a process, where reactive distillation is used for solvent regeneration in organic acid extraction. The preferred aqueous mixture contained C₁–C₅ aliphatic carboxylic acids and the preferred extractants were amines and organophosphorous based. To break the strong organic acid-extractant complex in the regeneration step, esterification of the carboxylic acid preferably with methanol (MeOH) or EtOH was performed in a reactor or reactive distillation. Admixture of homogeneous or heterogeneous catalysts to the reaction broth is possible. With the continuous removal of the reaction product, the reaction equilibrium is forced to the product side and complete separation of the acid from the laden solvent becomes feasible. If the ester is not the desired product, a hydrolysis reaction can be performed to obtain the carboxylic acid as final product.

To investigate reactive distillation in more detail, batch experiments for solvent regeneration were performed by our group for removing AA and FA from Cyanex[®] 923/*n*-undecane (70/30 vol %). The carboxylic acids were esterified with MeOH to form the low boiling esters methyl formate and methyl acetate. The esters were continuously removed via the distillate. The solvent load was varied between 1.9 and 13.7 wt % FA and 5.6 and 23.8 wt % AA. The molar ratio of MeOH to both acids was chosen between 0.58 and 2. No additional catalyst was used in the experiments. After reaction time of 90 min the reflux ratio was adjusted from infinity to 10. High concentrations of methyl formate were monitored until almost all FA was converted to methyl formate in the reboiler. Then methyl acetate concentrations in the distillate increased since AA esterification is much slower compared to FA esterification. Concurrently the MeOH concentration increased in the distillate.

Best results without a catalyst were obtained with the highest investigated solvent load and equal molar ratio of MeOH to both acids. The distillate composition is shown in Fig. 5. The molar fraction of methyl formate in the distillate was 83.9 mol% starting to decrease after 3.5 h. Methyl formate is the low boiling component in the mixture and FA esterification is the fastest step, therefore it was separated first. With ongoing distillation time, FA concentration in the reboiler decreased which led to a decrease of methyl formate concentrations in the distillate. The distillate temperature increased and the higher boiling ester methyl acetate and some MeOH were collected in the top product. These experiments enabled a methyl formate yield of 97.8% at reflux ratio 10 and a methyl acetate yield of 28.2%. For higher reflux ratio the methyl formate concentration increases while MeOH is kept in the reboiler.

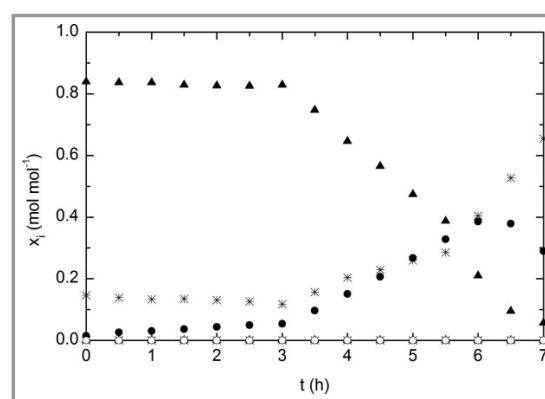


Figure 5. Distillate composition for laden Cyanex[®] 923/*n*-undecane (70/30 vol %) regeneration with reactive distillation; esterification of FA (▲) and AA (○) with MeOH (*) to methyl formate (▲), methyl acetate (●) and water (x); molar ratio of MeOH/(AA+FA) = 1, $c_{FA,0}$ = 13.7 wt %, $c_{AA,0}$ = 23.8 wt %, reflux ratio = 10, at ambient pressure.

An alternative application route for reactive distillation may be implemented for the distillate after reactive extraction and distillative solvent regeneration.

Painer et al. [6] performed continuous reactive distillation experiments with an expected product composition of liquid-liquid extraction plus solvent regeneration by distillation. The feed mixture contained 62 wt % AA, 28 wt % FA, and 10 wt % water. MeOH was used as reactant in three molar ratios, MeOH/FA = 2 and 3 and MeOH/acids = 3. The experiments were performed without catalyst. The best results were obtained with a molar ratio of MeOH/FA = 3, with 99.3% of FA and 71.5% of AA being removed from the aqueous mixture. The distillate composition was 24.4 mol % MeOH, 33.5 mol % methyl formate, and 42.1 mol % methyl acetate. No water was detected in the distillate. The distillate can be further separated by pervaporation into pure constituents. This chemical conversion produces a mixture with simple separation properties and

methyl esters with higher market values compared to their carboxylic acids.

5 Conclusions

The recovery of carboxylic acids from side streams of bio-based processes is a representative challenge for implementation of bulk products from renewable resources on the market. It is also recommended due to environmental and economical reasons. Reactive separation methods provide an appropriate separation tool for dilute, multicomponent mixtures. Reactive extraction by adduct formation enhances greatly the distribution coefficients for low molecular weight carboxylic acids compared to physical extraction. Literature reports that the best results can be obtained with amine based solvents. The drawback is the solvent regeneration step, with little information being available in literature. The most promising method is re-extraction with a volatile base in aqueous solution followed by reactive and conventional distillation. Alternatively physical extraction can be intensified by chemical conversion of the solute, e.g., esterification. Due to different solubility of the acids and the corresponding ester in the aqueous and the solvent phase, the reaction product can be continuously removed. Applicability of a continuous process of heterogeneous catalytic reaction with physical extraction of the product in the TCDC was proven.



Daniela Painer studied chemical and process engineering at Graz University of Technology and finished with the master thesis involving reactive distillation for process intensification in 2013. Currently she is doing her Ph.D. thesis dealing with combinations of chemical reactions and thermal separation processes to simplify isolation of multicomponent mixtures.



Annika Graftschafter studied chemical and process engineering at Graz University of Technology. In the year 2015 she obtained the Master of Science. Her thesis focused on hydrodynamic investigations, optimizations and simulations of liquid-liquid extractors. Presently she is doing the Ph.D. thesis at the Institute of Chemical

Engineering and Environmental Technology in the field of three-phase reactor modelling.



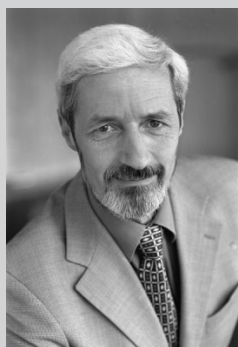
Andreas Toth studied chemical and process engineering at Graz University of Technology where his master thesis dealt with physical extraction combined with chemical reaction. He obtained his master degree in 2016 and is currently doing his Ph.D. thesis in the field of reactive separations at the Institute of Chemical Engineering

and Environmental Technology at Graz University of Technology.



Susanne Lux finished the studies in Chemical Engineering at Graz University of Technology in 2006 with her diploma thesis about reactive extraction. In 2009 she received her doctoral degree in the field of lactic acid synthesis and is currently assistant professor for chemical reaction engineering at Graz University of Technology. Her research

activities cover process intensification, heterogeneous catalysis and membrane technologies.



Matthäus Siebenhofer studied chemical engineering and received his doctoral degree in 1983 at Graz University of Technology/Austria. His doctoral thesis dealt with solvent extraction and the description of chemical reactions in the solvent phase. Currently he is Professor for chemical reaction engineering and the head of the

Institute of Chemical Engineering and Environmental Technology at Graz University of Technology.

Symbols used

<i>c</i>	[kmol m ⁻³]	concentration
<i>d</i>	[m]	column diameter
<i>D</i>	[-]	distribution coefficient
<i>E</i>	[%]	process efficiency
<i>H</i>	[m]	height
<i>K</i>	[-]	equilibrium constant
<i>m</i>	[kg]	mass
<i>n</i>	[kmol]	mole
<i>S</i>	[-]	selectivity
<i>t</i>	[s]	time
<i>v</i>	[m s ⁻¹]	rotor tip velocity
<i>x</i>	[-]	mole fraction
<i>η</i>	[%]	extraction efficiency, degree of extraction, extraction yield

Abbreviations

2-MTHF	methyltetrahydrofuran
4-DBSA	4-dodecylbenzenesulfonic acid
AA	acetic acid
Alamine [®] 304-1	tridodecylamine (> 95 %)
Alamine [®] 336	mixtures of tertiary C8 – C10 alkyl amines
Aliquat [®] 336	trioctyl methyl ammonium chloride
Amberlite [®] LA-2	N-lauryltrialkyl-methyl amine
BA	butyric acid
EtOH	ethanol
FA	formic acid
MeOH	methanol
MIBK	methyl isobutyl ketone
PA	propionic acid
RDC	rotating disc contactor
TBP	tributyl phosphate
THA	tri- <i>n</i> -hexylamine
TOA	trioctylamine (95 – 100 % Alamine [®] 300)

TOPO	trioctylphosphine oxide (Cyanex [®] 921)
TRPO	trialkylphosphine oxide (≥ 93 % Cyanex [®] 923)
TCDC	Taylor-Couette disc contactor

Subscripts

A	acid
org	solvent phase
aq	aqueous phase
feed	feed solution

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Intramolecular Catalysis of the
Esterification of Low Molecular
Weight Carboxylic Acids; single
and multi-acid esterification

Intramolecular catalysis of the esterification of low molecular weight carboxylic acids; single and multi-acid esterification¹

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KEYWORDS: intramolecular catalysis, carboxylic acids, simultaneous esterification

ABSTRACT: Downstream processing in the biorefinery is often faced with multicomponent process streams containing carboxylic acids and alcohols. Carboxylic acids may be isolated by esterification with alcohols. However, uncatalyzed esterification is generally slow at moderate temperature. In multicomponent mixtures stronger carboxylic acids may act as catalysts for esterification of weaker carboxylic acids. Single acid esterification of formic acid, acetic acid and propionic acid with methanol were investigated and a kinetic model was developed considering the intramolecular catalysis by acid dissociation. With the kinetic constants derived

¹ This chapter is intended for publication.

from single acid esterification, ester formation in multi-acid esterification was predicted and verified experimentally with standard deviation of less than 1.7 %. In multi-acid esterification, the catalytic influence of formic acid on acetic acid and propionic acid esterification was shown. Due to higher equilibrium constants transesterification from methyl formate to methyl acetate and methyl propionate is observed.

INTRODUCTION

Esters are important commodity chemicals with a wide applicability as intermediates, solvents, extractants, fragrances and flavors. Commonly, they are produced via esterification of a carboxylic acid with an alcohol.¹ Due to low reaction rate, esterification reactions are normally catalyzed by mineral acids. Esterification of low molecular weight carboxylic acids with methanol through homogenous and heterogeneous catalysis is well represented in literature (e.g. acetic acid esterification²⁻¹⁰, propionic acid esterification¹¹⁻¹³). In the context of formic acid, the autocatalytic hydrolysis of methyl formate was mainly investigated¹⁴⁻¹⁶. High purity of the reactants is in any case favored due to conversion limitation by the chemical equilibrium. Water as the byproduct shifts the equilibrium towards the reactant side and aqueous reactants thus hinder a high yield. Complete conversion of equilibrium reactions is obtained by continuous removal of a product. Exemplarily, the Eastman Kodak process for synthesis of methyl acetate combines both approaches to achieve high conversion levels. In this process glacial acetic acid and methanol are fed to a reactive distillation column with continuous methyl acetate removal via the distillate¹⁷. Continuous removal of reaction products also offers the opportunity to process dilute reactants as provided in the biorefinery. Reactive distillation was investigated for the recovery of dilute acetic acid (30 w%) via esterification with *n*-butanol and *iso*-amyl alcohol

from Saha et al.¹⁸. With the heterogeneous catalyst Indion 130 acetic acid conversions of 58 % and 51 % with *n*-butanol and *iso*-amyl alcohol were achieved, respectively. In biobased processes mixtures of several carboxylic acids may be generated, e.g. in pulping, biomass pyrolysis or fermentation. During pulping between 14-20 w% of the processed wood is converted to carboxylic acids and hydroxycarboxylic acids, depending on the process and type of wood¹⁹. Bio-oils may have an appreciable acid content, e.g. for straw oil 10.8 w%, mainly mixtures of acetic acid (7.41 w%), propionic acid (0.50 w%) and formic acid (1.85 w%)^{20,21}. In the succinic acid production via fermentation from glucose a product mixture with ethanol, lactic acid, acetic acid and formic acid as byproducts is generated²².

In bio-oil upgrading the acid content must be reduced to raise the stability of the oil. Li et al.²³ investigated simultaneous esterification of carboxylic acids and acetalization of aldehydes with methanol of bio-oil from mallee biomass with the heterogeneous catalysts Amberlyst-70. Besides acetic acid conversion of 90 % they found methyl formate and methyl propionate in the product mixture. Several catalysts and alcohols were tested for upgrading of bio-oil via esterification reducing the total acid content²⁴.

Black liquor evaporation after pulping generates a condensate with low concentration of acetic acid and formic acid. Removal of the acids from the wastewater is recommended for environmental reasons. Isolation of the high-boiling acids from water by distillation is not feasible due to the huge energy demand and the formation of a high-boiling azeotrope between formic acid and water and a ternary saddle point azeotrope. To simplify isolation, the carboxylic acids can be converted into their low-boiling esters and directly separated from water in a reactive distillation column. The azeotropes in the acidic wastewater are overcome in the course of this by changing the substance properties. Complete usage of the biobased feedstock by

implementing efficient downstream processing routines may render biobased processes economically more feasible and avoid loss of valuable bulk products because of incineration. After separation of carboxylic acids from dilute aqueous feed by solvent extraction, a state of the art unit operation, Painer et al.²⁵ suggested esterification with methanol by reactive distillation. Without additional catalysts, 99.3 % of formic acid and 71.5 % of acetic acid were converted to methyl esters and isolated in the distillate.

To the best of our knowledge almost no literature data is available for the modeling of simultaneous esterification of two or more carboxylic acids, except the esterification kinetics of succinic acid/acetic acid mixtures from fermentation broths with the heterogeneous catalyst Amberlyst 70, investigated by Orjuela et al.²⁶. An acidic catalyst suppresses intramolecular catalysis and interactions between different acids when several acids are esterified simultaneously.

The reaction kinetics of multi-acid esterification is necessary for modeling of uncatalyzed reactive distillation of two or more carboxylic acids. Likewise the reactivity and therefore stability of multi-acid mixtures with alcohols is of importance for storage in tanks, e.g. during maintenance, or at elevated temperature in heat exchangers. Due to the lack of multi-acid esterification data in literature, a kinetic model for simultaneous multi-acid esterification was developed based on single acid experiments by considering intramolecular catalytic activity and interactions between acids of different acid strength. With the resulting reaction rate constants we are able to predict multi-acid esterification with interaction of low molecular weight carboxylic acids. Temperature dependency, dilute mixtures as also equilibrium conversion and transesterification are considered.

MATERIALS AND METHODS

Chemicals

Formic acid (98-100 %, ChemLab), acetic acid (99-100 %, ChemLab), propionic acid (99.5%, Sigma Aldrich) and methanol (99.8 % ChemLab) were used without further purification. For experiments with specified initial water content aqueous formic acid (85 %, Brenntag) and deionized water were used.

Methods

For investigation of the intramolecular catalysis single acid esterification experiments were examined with different initial concentrations and temperatures. Eq. 1-3 show the stoichiometric equations for formic acid, acetic acid and propionic acid esterification with methanol, respectively. In simultaneous esterification of two or three carboxylic acids, the mutual influence of acids on the reaction rate was investigated. A detailed overview of experiments is given in Table 1 for single acid esterification and in Table 2 for simultaneous multi-acid esterification.

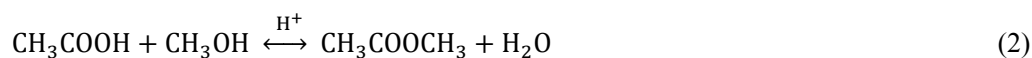


Table 1: Summary of experiments of single acid esterification (formic acid (FA), acetic acid (AA), propionic acid (PA) with different molar ratios of methanol (MeOH) to acid, at various temperatures (T) and initial water concentrations ($c_{\text{Water},0}$)).

Acid	MeOH:Acid [mol:mol]	$c_{\text{Water},0}$ [w%]	T [°C]
FA	1:1	-	30, 35, 40
FA	1:1	14	30, 35, 40
AA	1:1	-	30, 40, 50, 60, 70
AA	0.65:1	-	40, 50, 60, 70
AA	0.65:1	14	40, 50, 60, 70
PA	1:1	-	40, 60, 80
PA	0.5:1	-	30, 40
PA	2:1	-	40, 60

Table 2: Summary of experiments of multi-acid esterification (formic acid (FA), acetic acid (AA), propionic acid (PA) with different molar ratios of methanol (MeOH), at various temperatures (T) and initial water content ($c_{\text{Water},0}$)).

Acids	$c_{\text{Acid},0}$ [w%]	MeOH:Acid [mol:mol]	$c_{\text{Water},0}$ [w%]	T [°C]
FA/AA	30/60	1:1/-	10	30, 50, 60
FA/AA	30/45	1:1.2/-	25	30
FA/AA	43/57	1:1/-		30
FA/AA	43/57	1:1/1:1		30
FA/PA	50/50	1:1/1:1	-	30, 40
FA/PA	40/40	1:1/1:1	20	30, 40
FA/AA/PA	33.3/33.3/33.3	1:1/1:1/1:1	-	30

Depending on the reaction rates, the experiments were performed in a three-necked flask with continuous sampling when higher reaction rates were expected, and for low rate of reaction as also equilibrium determination experiments were performed in closed test tubes in a temperature controlled shaking bath.

Experimental setup and procedure

Short-time experiments were performed in a temperature controlled 500 cm³ three-necked flask connected to a reflux condenser to avoid loss of the volatile components. The condenser was cooled to 5 °C with a Lauda E200 cryostat. The temperature was measured in the reaction broth and controlled via a Heidolph heating plate combined with a magnetic stirrer. The stirrer speed was 500 rpm to assure provision of a homogenous mixture. The acid or acid/water mixtures were preheated prior to starting the experiments. After thermal equilibration of the acid/water mixtures, methanol of ambient temperature was admixed to start the esterification reaction. To avoid deviation of the start temperature from the selected reaction temperature, acetic acid and propionic acid were preheated to a higher temperature than the selected reaction temperature. Formic acid had to be preheated to a lower temperature due its fast initial reaction rate and the slightly exothermic behavior of the reaction. The first sample was taken after one minute of fast stirring (1000 rpm) of the reaction broth. Then the speed of stirring was reduced to 500 rpm. Samples were taken via a syringe, immediately cooled in an ice-water bath to quench the reaction, and then analyzed by gas chromatography (GC). Sampling intervals of 25 min had to be adjusted according to the analyzing time of one GC run. To check reproducibility and to obtain detailed data on reaction progress experiments were executed repeatedly with different sampling intervals.

Long-time experiments were executed to investigate slow reactions over a longer time period, and for experimental determination of the chemical equilibrium. The reaction mixture was filled in test tubes, tightly closed and shaken in a temperature controlled water bath (GLF 1083). The test tubes were used once only to avoid loss of volatile components by opening a test tube several times. Long-term experiments over 40 days were performed without loss. For determination of kinetics samples were continuously taken, whereas for equilibrium data determination samples were taken after the expected time period for equilibrium adjustment, the latter was controlled by comparison of results after different time spans.

Analysis

GC analysis (Shimadzu 2010 Plus) was performed with a Supel-QTM plot fused silica capillary column (30 m x 0.53 mm x 30 μ m). Samples were analyzed with two detectors with a split ratio of 30:1, operating at 250 °C. A thermal conductivity detector was used for water and formic acid detection with a current of 70 mA, and a flame ionization detector was used for analysis of the esters, methanol, acetic acid and propionic acid. Helium was used as carrier gas. The injection port temperature was 240 °C. The samples were stored at 5 °C in the sample tray of the auto sampler AOC-20s-i. Further details are given elsewhere²⁷.

MODELING

Modeling of kinetics was based on application of the first order contribution of each constituent to the equilibrium reaction rate. Intramolecular catalysis was included in the kinetic model by considering the conversion dependent of H⁺-concentration according to the

dissociation of carboxylic acids (Eq. 4). The catalytic activity decreased with reaction progress due to loss of acids by conversion.

$$x_{H^+} \approx \sqrt{K_{\text{Diss,Acid}} \cdot a_{\text{Acid}}} \quad (4)$$

In Eq. 5 the kinetic model is shown, where the sum of $K_{\text{Diss,Acid}} \cdot a_{\text{Acid}}$ over all acids displays the concentration of the H^+ -ions squared in the reaction mixture. Pöpken et al.² investigated acetic acid esterification and also found that the intramolecular catalytic effect of the H^+ -ions influences the reaction rates squared. The forward reaction is described with the forward reaction rate constant k_f multiplied with the activity of the reactants carboxylic acid and methanol. The reverse reaction is represented by the ratio of the forward reaction rate constant and the equilibrium constant K_T at operation temperature multiplied by the activity of the reaction products methyl ester and water. The activity coefficients were calculated by UNIFAC. For derivation of the reactant concentration c_i from activity, all constituents of the reaction mixture were considered in the overall concentration $(N/V)_{\text{total}}^3$ according to (Eq. 6). This describes the ratio of total moles of the initial feed mixture to the overall volume of constituents.

$$-r_A = -\frac{dc_A}{dt} = \left(\frac{N}{V}\right)_{\text{total}}^3 \cdot \sum_{\text{Acids}} (K_{\text{Diss,Acid}} \cdot a_{\text{Acid}}) \cdot (k_f \cdot a_{\text{Acid}} \cdot a_{\text{Alcohol}} - \frac{k_f}{K_T} \cdot a_{\text{Ester}} \cdot a_{\text{Water}}) \quad (5)$$

$$c_i = \left(\frac{N}{V}\right)_{\text{total}} \cdot x_i \quad (6)$$

The rate expression was solved with the explicit Runge-Kutta (4,5) formula²⁸. To fit the forward reaction rate constant, the error between the calculated and the experimental mole

fractions of the methyl ester was minimized (Eq. 7). The minimum search was executed with the simplex search method based on the Nelder-Mead algorithm²⁹.

$$\text{Error} = \frac{\sum n_{\text{sample}} (x_{\text{Ester,exp}} - x_{\text{Ester,calc}})^2}{n_{\text{sample}}} \quad (7)$$

With the Arrhenius equation (Eq. 8) the activation energy E_A and the frequency factor $k_{f0,i}$ were determined from the reaction rate constants $k_{f,i}$ at different temperatures.

$$k_{f,i} = k_{f0,i} \exp\left(-\frac{E_A}{R \cdot T}\right) \quad (8)$$

Single acid esterification was modeled by determining the forward reaction rate constant at different temperatures. The reverse reaction rate constant was calculated with the reaction equilibrium constant. Multi-acid esterification was modeled with the total H^+ -ion concentration of the mixture using these reaction rate constants of the esterification reactions of different single acids.

Reaction equilibrium

The standard Gibbs free energy of reaction (ΔG_R^0) was obtained with standard Gibbs free energy of formation (G_f^0) from literature^{14,30,31} and with the computer tool HSC 8.2.0 (Table 3). Methanol and water were assumed in the liquid state and carboxylic acid and corresponding methyl ester in an aqueous mixture. With Equation 9 the standard Gibbs free energy of reaction was converted to the equilibrium constant $K_{25\text{ }^\circ\text{C}}$. With the Van't Hoff equation (Eq. 10) the temperature influence on the equilibrium constant was considered. The standard enthalpies of formation (H_f^0) were also taken from literature and the standard enthalpies of reaction (ΔH_R^0) for formic acid, acetic acid and propionic acid esterification with methanol were computed (Table

3). The Gibbs free energy of formation of methyl formate was calculated from the gaseous phase¹⁴ while for methyl acetate and methyl propionate were calculated with a second-order group additivity method for condensed phase³¹. Due to the differences in literature data and data obtained with HSC, the calculated equilibrium constants were compared with equilibrium constants listed in the literature and equilibrium constants derived from experimental results (Eq. 11).

For formic acid esterification the thermodynamic equilibrium constant ($K_{25\text{ }^\circ\text{C}}=6.7$ calculated with Eq. 9) is lower compared to the literature ($K_{25\text{ }^\circ\text{C}}=29.4$ calculated with experimental results from Indu et al.³² with Eq. 11 using UNIFAC for activity coefficients). For calculation of the enthalpy of reaction, our experimental data at 30, 35 and 40 °C were extended with the results from Indu et al.³² at 25 °C resulting in $\Delta H_{R,\text{exp}}=-13.5\text{ kJ mol}^{-1}$. When comparing the reaction enthalpy of esterification with the reaction enthalpy of hydrolysis of methyl formate ($\Delta H_R=16.3\text{ kJ mol}^{-1}$)³³ the absolute value is in the same order of magnitude.

The equilibrium constant for acetic acid esterification obtained with the Gibbs free energy of reaction ($K_{25\text{ }^\circ\text{C}}=37.7$) is in good agreement with the experimental results from Pöpken et al.², who found the value 38.7 for the equilibrium constant by linear regression.

For propionic acid esterification the thermodynamic equilibrium constant ($K_{25\text{ }^\circ\text{C}}=167.7$) appears to be too high compared with literature. Ali¹³ published activity based equilibrium constants for propionic acid esterification with methanol in the range of 35.2 to 36.5 between 25 to 55 °C, respectively. The enthalpy of reaction was determined with 0.9 kJ mol^{-1} , which indicates a slightly endothermic reaction behavior while the computed enthalpy of reaction from

the literature data shows a marginally exothermic behavior. The influence of temperature on the equilibrium is negligible due to the small values of the enthalpy of reaction.

The experimental values were preferred when differences between calculated and experimental data were apparent, because of the strong influence of slight deviations in the standard Gibbs free energy of reaction on the equilibrium constant due to its exponential function. For formic acid and propionic acid esterification the equilibrium constants obtained with experimental data were used, while for acetic acid esterification the equilibrium constant based on the standard Gibbs free energy of reaction was implemented in the model.

Table 3: Standard enthalpies of formation (H_f^0) and standard Gibbs free energies of formation (G_f^0) as also standard enthalpies of reaction (ΔH_R^0) and standard Gibbs free energies of reaction (ΔG_R^0) for formic acid, acetic acid and propionic acid esterification at 25 °C.

	Formic acid esterification		Acetic acid esterification		Propionic acid esterification	
	H_f^0	G_f^0	H_f^0	G_f^0	H_f^0	G_f^0
	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]
Acid	-425 ³⁰	-361.4 ³⁰	-484.3 ³⁰	-389.9 ³⁰	-510.7 ³⁰	-381.6 ³¹
Methanol	-239.2 ³⁰	-166.6 ³⁰	-239.2 ³⁰	-166.6 ³⁰	-239.2 ³⁰	-166.6 ³⁰
Ester	-386.1 ³⁰	-295.6 ¹⁴	-445.9 ³⁰	-328.4 ³¹	-464.8 ³¹	-323.8 ³¹
Water	-285.8 ³⁰	-237.1 ³⁰	-285.8 ³⁰	-237.1 ³⁰	-285.8 ³⁰	-237.1 ³⁰
	ΔH_R^0	ΔG_R^0	ΔH_R^0	ΔG_R^0	ΔH_R^0	ΔG_R^0
	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]
Eq. 8	-7.7	-4.7	-8.2	-9	-0.7	-12.7
HSC	-11.2	-7.1	-14.8	-6.4	-13.6	-6.0

$$K_{T_0} = \exp\left(-\frac{\Delta_R G^0}{R T}\right) \quad (9)$$

$$K_T = K_{T_0} \exp\left(-\frac{\Delta_R H^0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (10)$$

$$K_T = \prod a_{i,T}^{v_i} \quad (11)$$

RESULTS AND DISCUSSION

Single acid esterification

Single acid esterification experiments were performed with formic acid, acetic acid and propionic acid to investigate the intramolecular catalytic effect of the carboxylic acid on esterification. Methanol was chosen as the esterifying agent. Different molar ratios (methanol to acid of 0.5-2), temperatures between 30 to 80 °C and with or without water present in the initial reaction mixture were investigated.

Figure 1 a), b) and c) compare the reaction kinetics at 40 °C of formic acid, acetic acid and propionic acid esterification respectively. The experimental data points are illustrated with symbols while the model is shown as a full line. Formic acid esterification (Figure 1 a)) shows the highest reaction rate. This may be attributed to the small inductive effect and negligible steric hindrance of the carboxylic acid that possesses the shortest chain length. The intramolecular catalytic effect of formic acid is pronounced because of its pK_A value of 3.75³⁰. The number of available H^+ -ions in the reaction mixture is one order of magnitude higher than for acetic acid and propionic acid and therefore formic acid esterification shows the highest reaction rate without additional catalyst. The reaction equilibrium of formic acid esterification at 40 °C was

obtained within four hours. Compared to formic acid, acetic acid esterification (Figure 1 b)) is much slower. According to the literature data the esterification of acetic acid with methanol at 40 °C takes more than 40 days to reach the equilibrium⁹. This fact is due to the lower acidity of acetic acid ($pK_A=4.756^{30}$) and the increase of its steric hindrance. With an increasing alkyl chain the positive inductive effect of the alkyl group increases and therefore the tendency for dissociation decreases. The negative charge at the carbon atom of the carboxyl group facilitates the protonation but impedes the nucleophilic attack of the alcohol which retards esterification. In acid catalyzed esterification the steric hindrance is considered as the more significant influence than the inductive effect³⁴. In uncatalyzed esterification the lack of dissociation has a more distinct effect on reaction rate. This is also observed in propionic acid esterification (Figure 1 c)). The steric hindrance due to the propyl group and the inductive effect both rise compared to acetic acid, despite the acidities being comparable ($pK_{A,Propionic\ acid}=4.87^{30}$). A decrease in reaction rate from acetic acid to propionic acid esterification is evident but not as distinct as the drop in reaction rate between formic acid and acetic acid esterification. These results suggest that the intramolecular catalytic effect based on the acidity of the carboxylic acid has the strongest influence on reaction rate. In Table 3 the frequency factors k_0 and the activation energies E_A for the forward and reverse reaction of formic acid, acetic acid and propionic acid esterification are compared. Figure 2 shows the Arrhenius plot for the forward reaction rate constants k_f . The similarity in reaction rate of acetic acid and propionic acid esterification is confirmed by the activation energy and frequency factor for the forward reaction, which are in the same range of magnitude. By comparison here, the frequency factor of formic acid esterification for the forward reaction is five orders of magnitude higher. The activation energy for propionic acid esterification is in parallel with the endothermic behavior with a decrease from forward to

reverse reaction. For formic acid and acetic acid esterification the opposite effect is observed.

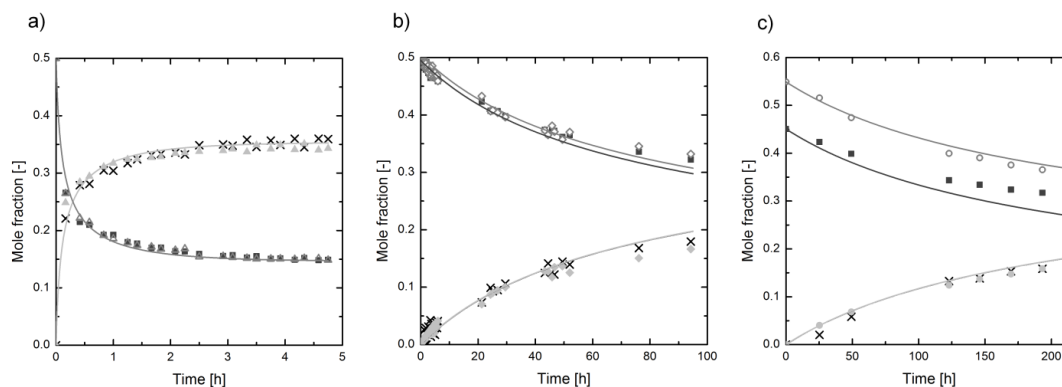


Figure 1: Esterification of carboxylic acids with methanol (■) to the corresponding methyl esters and water (x) at 40 °C; a) formic acid (Δ) to methyl formate (▲); b) acetic acid (◇) to methyl acetate (◆); c) propionic acid (○) to methyl propionate (●); kinetic model (full line).

Table 3: Frequency factor k_0 and the activation energy E_A for the forward and reverse reaction of formic acid, acetic acid and propionic acid esterification.

Acid	Forward reaction			Reverse reaction		
	k_{f0} $\text{m}^6 \text{h}^{-1} \text{mol}^{-2}$	$E_{A,f}$ kJ mol^{-1}	R^2	k_{r0} $\text{m}^6 \text{h}^{-1} \text{mol}^{-2}$	$E_{A,r}$ kJ mol^{-1}	R^2
Formic acid	$5.47 \cdot 10^{11}$	82.63	0.93	$4.39 \cdot 10^{12}$	96.17	0.95
Acetic acid	$3.15 \cdot 10^6$	60.13	0.99	$2.28 \cdot 10^6$	68.33	0.99
Propionic acid	$4.80 \cdot 10^6$	62.29	0.99	$9.22 \cdot 10^4$	61.33	0.99

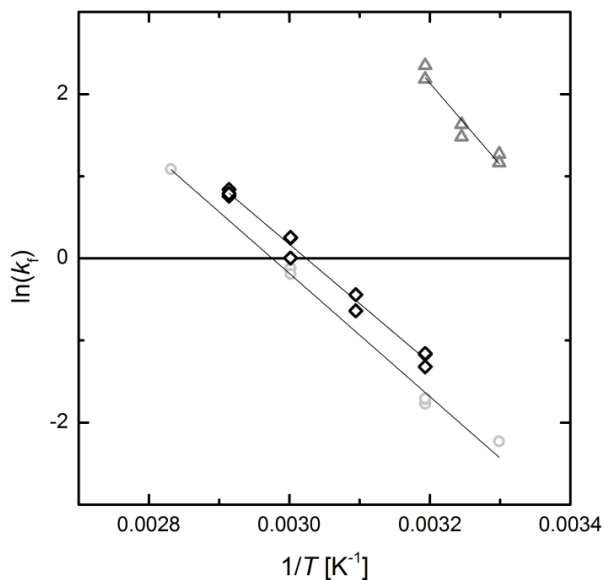


Figure 2: Arrhenius plot of the forward reaction rate constant k_f of formic acid (Δ), acetic acid (\diamond) and propionic acid (\circ) esterification with methanol.

Multi-acid esterification

First, simultaneous esterification experiments of formic acid and acetic acid esterification were performed at different temperatures (30-60 °C), molar ratios (equimolar to formic acid or to both acids), varying initial water concentration (0-25 w%) and reaction time. In Figure 3 a) the detailed reaction progress of the simultaneous esterification of acetic acid (60 w%) and formic acid (30 w%) with an initial water content (10 w%) and a molar ratio of methanol to formic acid of one at 50 °C is plotted for the first five hours. Figure 3 b) shows esterification of acetic acid (45 w%) and formic acid (30 w%) with an initial water content (25 w%) and a molar ratio of methanol to formic acid of 1.2 at 30 °C over a period of 720 hours. The difference in initial

reaction rate between formic acid and acetic acid esterification is shown in Figure 3 a). The concentration of methyl formate was almost constant after two hours with a formic acid conversion of 66.8 %. The acetic acid conversion was 9 % after two hours. The frequency factors and activation energies from single acid esterification were used for modeling. Catalytic acceleration was implemented via the total concentration of H⁺-ion from formic acid and acetic acid dissociation. The model is able to predict the concentration of all reactants during simultaneous esterification of formic acid and acetic acid with adequate precision of max. 1.6 %, at initial reaction conditions as also after 720 hours. Due to the competitive reaction of formic acid and acetic acid with methanol both reaction equilibria are influenced. The fast formic acid esterification reaches the chemical equilibrium within four hours, while acetic acid continues to react with methanol. The methanol concentration thus decreases further, which consequently influences the formic acid conversion. Accordingly, the hydrolysis reaction of methyl formate is enhanced and methyl formate serves as methanol donor. After five hours reaction time the transesterification of methyl formate with acetic acid to methyl acetate is marginally recognizable. The standard deviation between the experimental and calculated data for methyl formate and methyl acetate in short term experiments are 0.5 % and 0.3 %, respectively. The reaction period was increased to 720 hours to validate the model for predictability of transesterification. In Figure 3 b) transesterification is clearly noticeable in the depletion of methyl formate and the increase of formic acid after the initial reaction period of 35 hours. The transesterification occurs due to the higher equilibrium constant of acetic acid esterification ($K_{30\text{ }^{\circ}\text{C}}=35.6$) compared with formic acid esterification ($K_{30\text{ }^{\circ}\text{C}}=26.8$). Because of the faster reaction rate of formic acid esterification, methyl formate is generated in the initial reaction period. With ongoing reaction progress methyl formate is transesterified to methyl acetate. After

35 hours reaction time the selectivity of methanol towards methyl formate formation is 72 % and towards methyl acetate formation 28 %, respectively. After 720 hours the selectivity shifts to 29 % for methyl formate and 71 % for methyl acetate, respectively. The standard deviation for the long term experiment for methyl formate and methyl acetate are 1.2 % and 1.6 %, respectively.

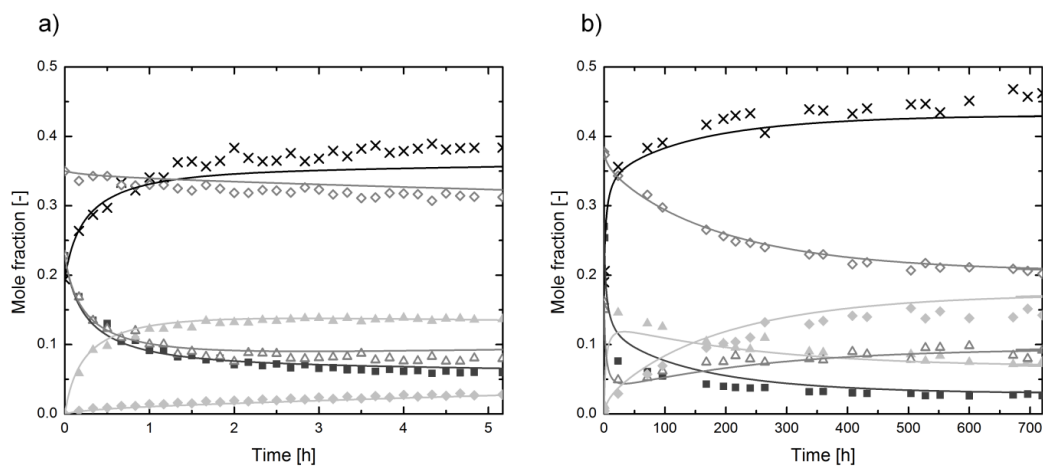


Figure 3: Simultaneous esterification of formic acid (Δ) and acetic acid (\diamond) with methanol (\blacksquare) to methyl formate (\blacktriangle), methyl acetate (\blacklozenge) and water (x); kinetic model (full line) a) molar ratio of methanol:formic acid=1 at 50 °C over 5 h; b) molar ratio of methanol:formic acid=1.2 at 30 °C over 720 h.

To test the model for different carboxylic acids, the simultaneous esterification of formic acid, acetic acid and propionic acid with methanol at 30 °C was investigated (Figure 4). For better readability the reaction profiles were split into reactants (Figure 4 a)) and reaction products (Figure 4 b)). In this ternary carboxylic acid mixture the fast formic acid esterification proceeds within the first 70 hours followed by slow transesterification to methyl acetate and methyl propionate. The similar reaction rate of acetic acid and propionic acid esterifications, as derived

from single acid esterification experiments, is also confirmed in simultaneous esterification. The model is able to predict all concentrations with a standard deviation for methyl formate of 1.7 %, for methyl acetate of 0.5 % and for methyl propionate of 0.8 % respectively.

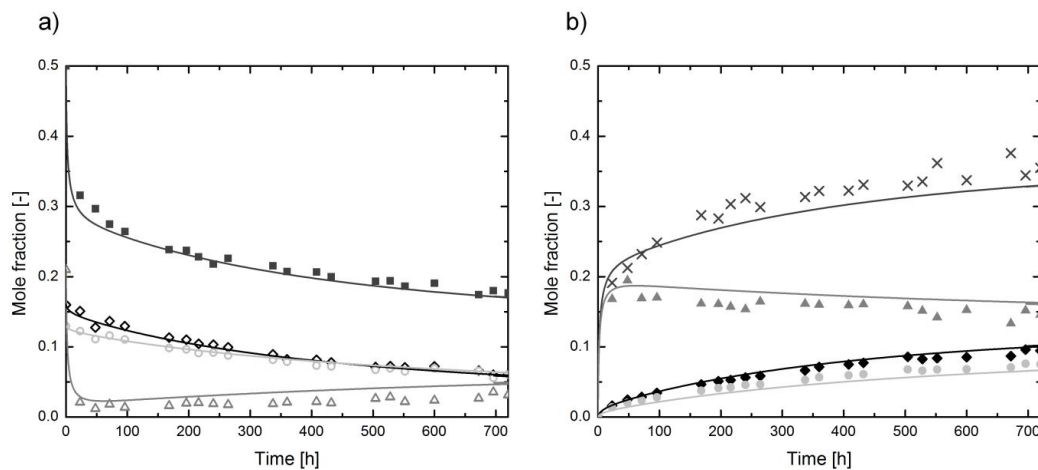


Figure 4: Simultaneous esterification of formic acid (Δ), acetic acid (\diamond) and propionic acid (\circ) with methanol (\blacksquare) to methyl formate (\blacktriangle), methyl acetate (\blacklozenge), methyl propionate (\bullet) and water (x) at 30 °C with a molar ratio of methanol:(formic acid+acetic acid+propionic acid)=1; kinetic model (full line) a) reaction educts; b) reaction products.

SUMMARY

Single acid esterification and simultaneous esterification of formic acid, acetic acid and propionic acid with methanol without a catalyst were investigated. A kinetic model for single acid esterification was developed taking the intramolecular catalytic action of the carboxylic acid into consideration. The model was successfully applied for the prediction of multi-acid esterification and transesterification. The total concentration of H^+ -ions from carboxylic acid

dissociation was implemented in the model to account for the catalyst concentration. Transesterification of methyl formate with acetic acid and propionic acid to methyl acetate and methyl propionate, as suggested by thermodynamics, was confirmed experimentally.

Multi-acid mixtures are commonly generated in several biobased processes. The knowledge and predictability of the reactivity of multicomponent mixtures and interaction between carboxylic acids and alcohols without catalysts is important for storage purposes or at increased residence times in heat exchanger. Catalyzed or uncatalyzed reactive separations open a huge toolbox for process intensification in downstream processing.

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ACKNOWLEDGEMENT

The authors acknowledge the financial support of NAWI Graz. The authors also appreciate support of Candela Campos-Dominguez, Christoph Almer, Armin Ehrenhöfer and Pei Shi Lam for executing the experiments.

ABBREVIATIONS

AA Acetic acid
FA Formic acid
GC Gas chromatograph

MeOH Methanol

PA Propionic acid

a_i	[-]	Activity of component i
c_i	[w%]	Concentration of component i
E_A	[kJ mol ⁻¹]	Activation energy
G_f^0	[kJ mol ⁻¹]	Standard Gibbs free energy of formation
ΔG_R^0	[kJ mol ⁻¹]	Standard Gibbs free energy of reaction
H_f^0	[kJ mol ⁻¹]	Standard enthalpy of formation
ΔH_R^0	[kJ mol ⁻¹]	Standard enthalpy of reaction
K	[-]	Equilibrium constant
K_{Diss}	[-]	Equilibrium constant of dissociation
k_{f0}	[m ⁶ h ⁻¹ mol ⁻²]	Frequency factor for the forward reaction
k_f	[m ⁶ h ⁻¹ mol ⁻²]	Reaction rate constant
k_{r0}	[m ⁶ h ⁻¹ mol ⁻²]	Frequency factor for the reverse reaction
R	[J mol ⁻¹ K ⁻¹]	Gas constant
$-r_A$	[mol m ⁻³ h ⁻¹]	reaction rate of the acid
T	[K]	Temperature
x_i	[-]	Mole fraction of component i
ν	[-]	stoichiometric coefficient

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Recovery of Formic Acid and
Acetic Acid from Waste Water
Using Reactive Distillation

Recovery of Formic Acid and Acetic Acid from Waste Water Using Reactive Distillation

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Processing of biobased feedstock materials may lead to formation of multicomponent azeotropic mixtures. Reactive separations provide an opportunity to circumvent azeotropes by changing the substance properties through chemical reactions. Exemplarily several effluents from black liquor processing contain aqueous mixtures of low molecular weight fatty acids such as formic acid and acetic acid. These mixtures form inseparable azeotropes. Separation of the system formic acid–acetic acid–water by esterification with methanol was investigated. Reactive distillation experiments in batch and continuous mode confirmed complete removal of formic acid in a first step. Acetic acid may then be isolated by distillation or by reactive distillation.

Keywords reactive distillation; azeotrope; esterification; acetic acid; formic acid; fatty acid

INTRODUCTION

Implementation of biobased materials, a traditional feedstock in pulping, in the chemical industry is expected to increase rapidly in near future. Product broths and side streams from processing of biobased feed are often multicomponent mixtures, rarely with appropriate concentrations of the valuable constituents, but with distinct tendency to form azeotropes (1, 2). Pulp processing for instance produces a dilute condensate effluent that contains mainly formic acid (HfO, HCOOH) and acetic acid (HAc, CH₃COOH) (3). This aqueous mixture faces both a binary high boiling azeotrope (51 mol% formic acid and 49 mol% water at T = 105.6°C and P = 950 mbar) and a ternary saddle point azeotrope (49.8 mol% formic acid, 11.2 mol% acetic acid, 39.0 mol% water at T = 105.2°C and P = 950 mbar) (4).

For separation, the literature suggests several energy-consuming processes such as azeotropic distillation (5, 6), extraction combined with distillation (7), or catalytic decomposition of formic acid prior to isolation of acetic acid (8). In case of decomposition, actually the valuable constituent formic acid is destroyed in an energy consuming process step.

Reactive distillation provides an alternative approach for separation of multicomponent azeotropic mixtures. By changing substance properties through chemical reaction with appropriate reactants, thermodynamic limitations like azeotrope formation can be avoided. So far only two patents have been published, both in the early 1970s, using reactive distillation for the separation of this ternary system (9, 10). In both proposals distillation columns with high reflux ratios were recommended. These patents show the huge potential of reactive distillation for application in multicomponent separation. Detailed process data have not been published yet.

In the last decades, reactive distillation has established in process intensification. Reactive distillation has been industrially applied in improving conversions of equilibrium reactions or in waste water treatment (11, 12). The recovery of dilute acetic acid via esterification in a reactive distillation column was examined by Saha et al. (13). They carried out the esterification with *n*-butanol and *iso*-amyl alcohol in an aqueous solution of 30% acetic acid and the catalyst Indion 130, a cation exchange resin. Acetic acid conversion of 58% was reported. The molar ratio of acetic acid to *n*-butanol was 1:2. However, investigation of the influence of formic acid on the separation efficiency of acetic acid has not been considered. Catalyst deactivation of the cation exchange resin by fouling and precipitation of nonspecific matrix constituents, like contaminations in the waste water at elevated temperature is a major process constraint.

The simultaneous esterification of formic acid and acetic acid with cyclohexene in a batch distillation column was investigated by Saha and Sharma (14). The feed contained equal molar amounts of acetic acid and formic acid without water. Experiments at a molar ratio of 1:1.1 of the acids to cyclohexene resulted in cyclohexene conversion of 85%. Selectivities of 64% cyclohexyl formate and 30% cyclohexyl acetate were recorded. For application of esterification in aqueous effluents, the influence of water on esterification reactions is an important boundary in process development since water shifts the reaction equilibrium composition to the reactant side. With these constraints in mind the target of this project has been the identification and selection of a technology sufficing the needs of

Received 12 November 2014; accepted 18 June 2015.

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successful isolation of formic acid and acetic acid from dilute aqueous effluents.

MATERIALS AND METHODS

Chemicals

Methanol ($\geq 99\%$, MeOH, CH₃OH) and formic acid with 98% grade were provided by Roth, Karlsruhe, Germany and acetic acid (99-100%) by Merck, Wien, Austria. Formic acid of 85% grade was purchased from Brenntag, Wien, Austria. Deionized water was used for the preparation of aqueous solutions. All chemicals were used as supplied.

Method

Reactive distillation is an appropriate tool for the separation of azeotropic mixtures as thermodynamic limitations are easily overcome by changing the substance properties via chemical reaction. The fatty acids acetic acid and formic acid for example may be esterified with methanol (Equation 1 and 2) and the low boiling products methyl formate (MeFo, HCOOCH₃, T_b = 31.7°C) and methyl acetate (MeAc, CH₃COOCH₃, T_b = 56.87°C) (15) are continuously removed in the distillate. Therefore, the reaction equilibrium is forced to complete conversion of reactants. Hydrolysis reactions of the esters in the distillate fraction do not need attention since carryover of water is not significant.



Formic acid esterification is faster than acetic acid esterification due to the inductive effect and the lower steric hindrance of formic acid (16). Additionally, formic acid ($\text{pK}_{\text{a,HF}_0} = 3.75$ (15)) is a stronger acid than acetic acid ($\text{pK}_{\text{a,HAc}} = 4.756$ (15)). Therefore, its intramolecular catalytic effect is more distinctive. In simultaneous esterification of both acids, formic acid acts as a catalyst for acetic acid esterification, giving access to esterification without catalysts.

Batch Reactive Distillation

Batch reactive distillation experiments were carried out in a 20 mm inner diameter glass column in laboratory scale. The reboiler was a 500 cm³ three-neck flask, equipped with a heating plate and a magnetic stirrer from Heidolph. A 30 cm vigreux column was connected to the reboiler. For insulation the column was wrapped with a polyethylene foam sleeve. For condensation of the vaporous distillate the top condenser was cooled to 5°C by a Lauda cryostat. The reflux was maintained by a magnetic reflux splitter with a Lab.-Kybernet (Brand) controller. The distillate was collected in a funnel, which was cooled to 5°C. The temperature in the reboiler and on top of the vigreux column just below the condenser was recorded.

Experiments were started through mixing aqueous fatty acid feed solutions with methanol in the reboiler and heating at total reflux until boiling. Reboiler samples were taken every 20 minutes. After constant temperature in the reboiler was obtained and kept constant for 20 minutes, the reflux ratio $r = R/D$ (R...reflux, D...distillate) was set to 10 and distillate samples were taken every hour. For replication sample taking time was varied for a more detailed concentration profile. Boiling conditions in the reboiler were maintained by manual control. Mean duration of experiments was 5.5 hours.

Four different feed mixtures of acetic acid, formic acid, and water (60/30/10, 30/65/5, 10/80/10, and 10/60/30), representing specific compositions of the four distillation areas of this ternary system, were investigated. Methanol was applied in stoichiometric amount with respect to formic acid and in a molar ratio of 2.4 with respect to formic acid.

Continuous Reactive Distillation

Continuous reactive distillation experiments were performed in a 2 m rectification column (DN 35) filled with 6 mm Raschig rings. The aqueous acetic acid–formic acid feed mixture and the methanol feed were metered separately to the reboiler with an Ismatec Reglo ICC pump. The reboiler acted as the reaction vessel of the distillation column. In Fig. 1 a schematic drawing of the experimental setup is shown. The fatty acid–water mixture contained 28 wt% formic acid, 62 wt% acetic acid, and 10 wt% water, according to a representative mixture of acids obtained from extractive isolation. The total feed flow rate was 0.12 dm³ h⁻¹. The reboiler was heated by electrical heating elements with 250 W power. The reflux ratio was set to 10. The condenser was cooled to 5°C by a RCS LAUDA cryostat to ensure total condensation of methyl formate. Additionally, the distillate was cooled to 1°C in the product cooler with a LAUDA ecoline Staredition RE 300 cryostat filled with isopropanol.

The temperature in the reboiler, in the middle of the column and at the top of the column and the pressure were recorded continuously. Every hour, samples of the bottom product and the distillate were taken, cooled, and analyzed immediately. Experiments were performed with different methanol to acid ratios. Methanol was used in double and triple molar amount with respect to formic acid and in double molar ratio with respect to both fatty acids.

Analytics

Samples were analyzed by gas chromatography. The gas chromatograph (Shimadzu 2010 Plus) was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Acetic acid, methanol, methyl acetate, and methyl formate were quantified with FID. For quantification of the components formic acid and water, the TCD was used. The TCD worked with 70 mA and Helium as carrier gas. The column was a Supel-QTM plot fused silica capillary column (30 m × 0.53 mm × 30 μm).

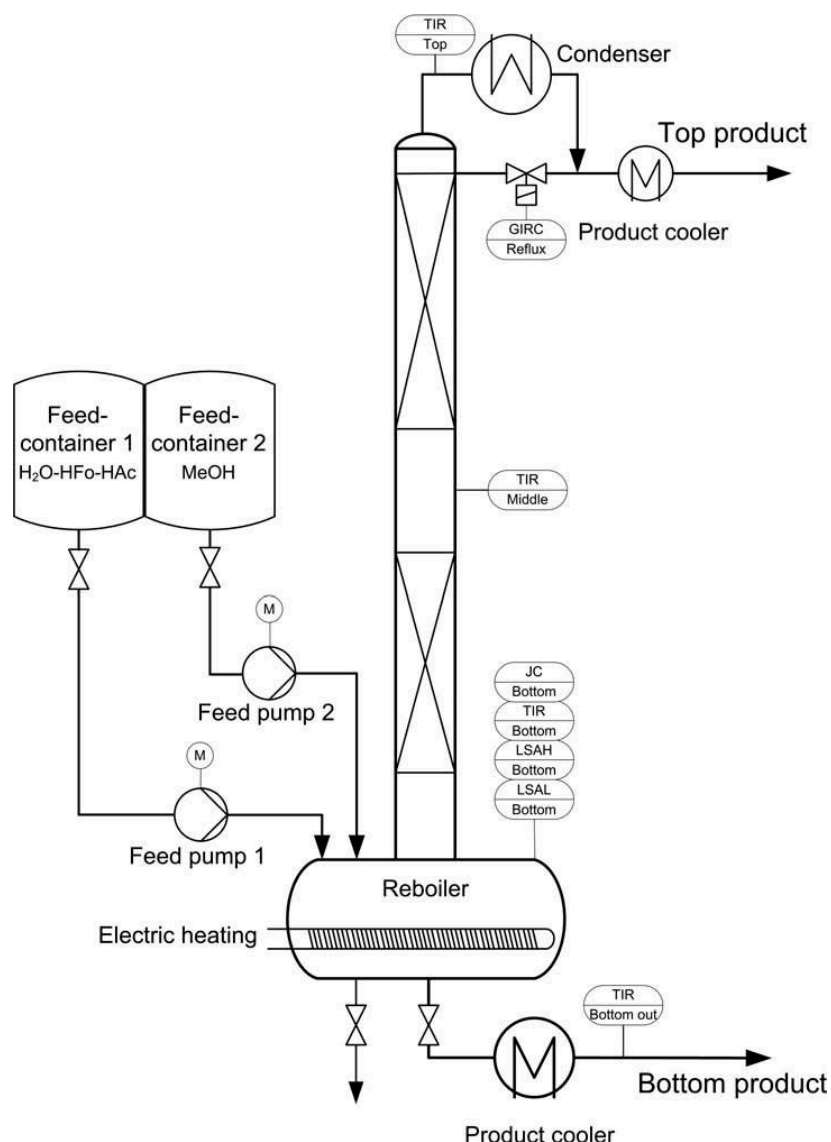


FIG. 1. Schematic drawing of the experimental setup for continuous reactive distillation experiments (4). © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced by permission of Wiley-VCH Verlag GmbH & Co. KGaA. Permission to reuse must be obtained from the rightsholder.

The auto injector AOC-20i was operated in split mode with a ratio of 30:1 at an injection temperature of 240°C. The tray of the auto sampler AOC-20s was cooled to 5°C by a Lauda Thermostat guaranteeing a constant sample temperature and suppressing further reaction in the sample vials. The total analyzing time was 17.7 min; starting at 40°C for 2 min, ramping up to 150°C with a heating rate of 15°C min⁻¹, a hold at 150°C for 5.7 min, and ramping up to 200°C, afterwards with a heating rate of 30°C min⁻¹ and a hold at 200°C for 1 min.

RESULTS AND DISCUSSION

Batch Reactive Distillation

In order to investigate the separation efficiency of reactive distillation via esterification of formic acid and acetic acid with methanol batch experiments were performed with various feed compositions. The molar ratio of methanol to formic acid was varied between 1 and 2.4. Fatty acid compositions (in wt%) in the aqueous feed mixture were 30–60–10, 65–30–5, 80–10–10, and 60–10–30 for formic acid–acetic acid–water, respectively.

Complete separation of formic acid with methanol in a molar ratio of 2.4 with respect to formic acid for all starting compositions was possible.

Figure 2 and Fig. 3 show the composition of the reboiler phase and the distillate phase for a feed mixture of 65 wt% formic acid, 30 wt% acetic acid, and 5 wt% water and stoichiometric admixture of methanol with respect to formic acid. The batch rectification column was operated at total reflux for one hour to provide sufficient reaction time for the esterification of formic acid and acetic acid. Then a reflux ratio of 10 was adjusted. During the reaction phase at total reflux increasing concentration of methyl formate and methyl acetate in the reboiler was recorded, followed by steady depletion due to

distillate removal at a reflux ratio of 10. The water fraction in the bottom mixture steadily increased due to loss of the lower boiling substances methyl formate, methyl acetate, and methanol plus water was formed during the reaction.

During the first 120 minutes of distillate collection a methyl formate grade of 95 mol% was achieved. Methanol molar fraction was complementary lower than 5%. With ongoing operation the concentration of methyl formate in the distillate decreased due to depleting formic acid concentration in the reaction section. Methanol and methyl acetate concentrations in the distillate increased with ongoing process. When methanol was almost consumed, methyl acetate concentrations in the distillate dropped drastically and water breakthrough was observed.

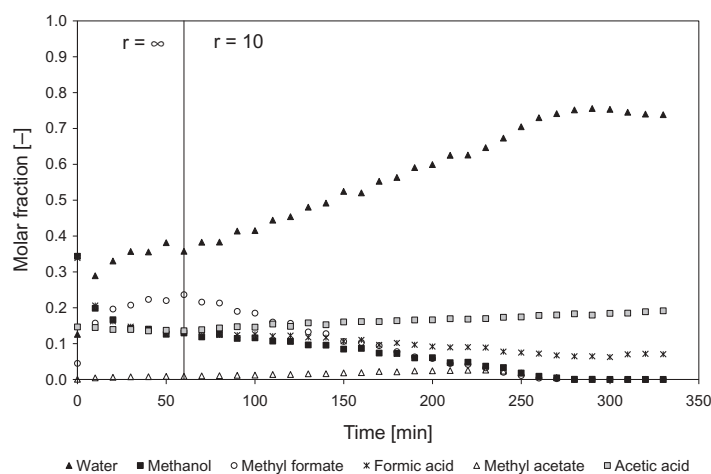


FIG. 2. Reboiler composition during batch reactive distillation of formic acid–acetic acid–water mixtures (65 wt% formic acid, 30 wt% acetic acid, 5 wt% water) with methanol; molar ratio of methanol to formic acid = 1, total reflux for 60 min, then reflux ratio $r = 10$, ambient pressure.

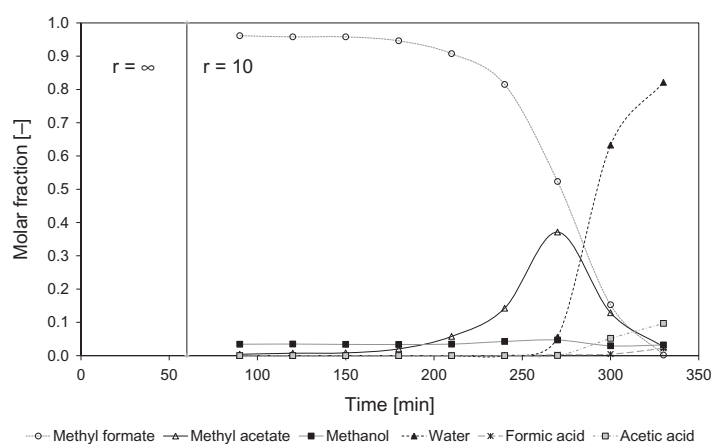


FIG. 3. Distillate composition during batch reactive distillation of formic acid–acetic acid–water mixtures (65 wt% formic acid, 30 wt% acetic acid, 5 wt% water) with methanol; molar ratio of methanol to formic acid = 1, total reflux for 60 min, then reflux ratio $r = 10$, ambient pressure.

4. Recovery of Formic Acid and Acetic Acid from Waste Water

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TABLE 1

Formic acid (HfO) and acetic acid (HAc) conversions and final compositions of the bottom phase for batch reactive distillation experiments with different feed compositions and methanol to formic acid ratios of 1 and 2.4, reflux ratio $r = 10$, ambient pressure

Feed		Bottom phase						Conversion	
Molar ratio	[wt%]	[wt%]						[%]	
MeOH:HfO	HfO/HAc/H ₂ O	H ₂ O	MeOH	MeFo	HfO	MeAc	HAc	HfO	HAc
1:1	30/60/10	26.0	–	–	8.6	0.1	65.3	76.8	16.4
	65/30/5	47.3	–	–	11.5	–	41.2	87.7	21.1
	80/10/10	75.3	–	–	11.2	–	13.5	91.7	29.1
	60/10/30	80.3	–	–	9.1	–	10.6	89.0	25.8
2.4:1	30/60/10	42.7	0.2	–	–	–	57.1	100.0	44.3
	65/30/5	59.9	0.1	–	–	–	40.0	100.0	40.7
	80/10/10	88.0	–	–	–	–	12.0	100.0	32.1
	60/10/30	89.9	–	–	–	–	10.1	100.0	48.9

It has to be outlined that the setup for batch reactive distillation was bench scale equipment with very limited mass transfer height. Against this experimental background the results of the batch experiment shown in Fig. 2 and Fig. 3 confirm low separation demand because of the high purity of methyl formate in the distillate at the beginning of the experiments.

In Table 1 the results for formic acid and acetic acid conversion and the final composition of the bottom phase for the different experimental conditions are summarized. In general, high conversion of formic acid was confirmed. These results are in good agreement with the study performed by Saha and Sharma (14).

Experiments carried out with stoichiometric amounts of methanol and formic acid confirmed significant reduction of formic acid. Methanol conversions of 93.7 to 97.6% and formic acid conversions of 76.8 to 91.7% were monitored. Because of the stronger acidity of formic acid and its lower inductive effect formic acid esterification is faster than acetic acid esterification. Therefore, conversion of acetic acid (16.4 to 29.1%) was suppressed. At the end of a reactive distillation run, the composition of constituents in the reboiler shifted to nearly unaffected acetic acid concentrations due to loss of product, negligible formic acid concentration, and the complete amount of water of the feed plus water formed during reaction. The distillate consisted of highly pure methyl formate (94.9 to 96.2 mol%) with retarded increase of methyl acetate and methanol content according to the progress of conversion.

In all bench scale experiments with a molar ratio of methanol to formic acid of 2.4 complete conversion of formic acid in the reboiler was confirmed. Figure 4 shows the basic distillation map of the ternary system with the four distillation fields separated by the binary azeotrope formic acid–water and the ternary saddle azeotrope. A feed composition was chosen in each distillation field and the bottom product at the end of each experiment was added. Because of total removal of the light boiling components methyl formate, methyl acetate, and methanol during the experiments, it is possible to show the

results in a ternary map. As shown in Fig. 4, the binary system acetic acid–water was obtained as bottom product due to complete conversion of formic acid. Depending on the operation conditions acetic acid can either be left in the reboiler or isolated in the distillate via esterification. In bench scale higher conversions of acetic acid of 32.1 to even 48.9% were achieved with sufficient methanol surplus in the reboiler. The methanol content in the distillate phase depends on the separation capability of the column and the reflux ratio. In the distillate phase water was only detected at the end of experiments after complete conversion of formic acid and lack of methanol.

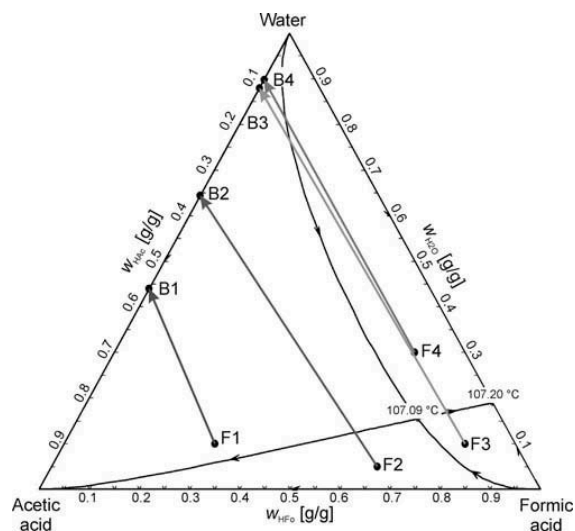


FIG. 4. Batch reactive distillation of different feed mixtures (F1 to F4) of acetic acid, formic acid and water through esterification with methanol with their final bottom product composition; molar ratio of methanol:formic acid = 2.4:1, reflux ratio $r = 10$; ambient pressure (F...Feed, B...Bottom product).

Continuous Reactive Distillation

Separability of constituents by reactive distillation was confirmed in batch experiments. For process validation purposes, reactive distillation experiments of the ternary system acetic acid–formic acid–water were also performed in continuous mode. A representative feed composition of 28 wt% formic acid, 62 wt% acetic acid and 10 wt% water was chosen. In order to examine the effect of different methanol admixture, the molar ratio of methanol with respect to formic acid was varied between 2 and 3. Experiments were also carried out with a molar feed ratio of methanol with respect to both formic acid and acetic acid of 2.

Temperature profiles along the rectification column were comparable for all experiments. Increasing methanol concentration in the feed resulted in decreasing temperatures in the reboiler and increasing temperatures in the middle section and at the top of the column. The temperature in the reboiler decreased from 81.4°C (MeOH:HFO = 2) to 76.2°C (MeOH:(HFO+HAc) = 2). The temperature in the middle section of the column increased with increasing amount of methanol in the feed from 50.2°C to 61.3°C, whereas the top temperatures increased from 43.6°C to 48.7°C. The temperature readings clearly indicate the effect of surplus methanol on product composition in the distillate. When the temperature increases in the distillate product with increasing amount of methanol in the feed, the purity of methyl formate ($T_b = 31.7^\circ\text{C}$ (15)) and methyl acetate ($T_b = 56.87^\circ\text{C}$ (15)) will decrease because the methanol ($T_b = 64.6^\circ\text{C}$ (15)) is also removed to the distillate.

Figure 5 shows the composition of the bottom product in comparison to the feed composition for different methanol ratios in the feed. Distillate compositions and conversions of acetic acid and formic acid are summarized in Table 2. Almost complete separation of formic acid (98%) was possible with methanol applied in double molar ratio with respect to formic acid in the feed. Acetic acid conversion of 60.8% was observed too. The molar

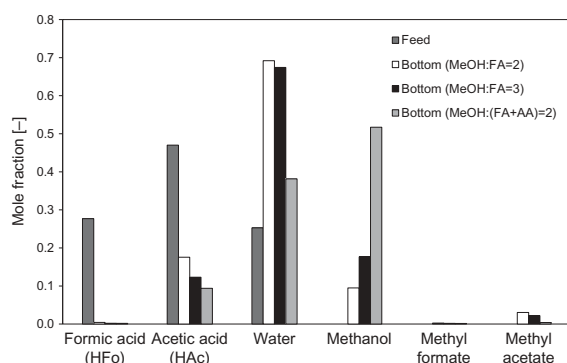


FIG. 5. Comparison of the bottom product composition for different molar ratios of methanol (MeOH) to the acids in the continuous reactive distillation of aqueous formic acid (HFO)–acetic acid (HAc) effluents (reflux ratio $r = 10$, ambient pressure) (4).

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TABLE 2

Distillate compositions, formic acid (HFO) and acetic acid (HAc) conversions obtained from continuous reactive distillation of aqueous acetic acid and formic acid effluents (28 wt% formic acid, 62 wt% acetic acid, 10 wt% water) for different molar ratios of methanol (MeOH) with respect to the feed concentrations of acids, reflux ratio $r = 10$, ambient pressure (4)

	MeOH:HFO = 2	MeOH:HFO = 3	MeOH:(HFO +HAc) = 2
Distillate composition (mol%)			
Methanol	20.4	24.4	46.0
Methyl formate	41.6	33.5	27.6
Methyl acetate	38.0	42.1	26.2
Conversion (%)			
Formic acid	98.0	99.3	98.7
Acetic acid	60.8	71.5	64.4

fractions of acetic acid in the bottom product were 12.3% and 9.4%, when methanol with a molar ratio of 3 with respect to formic acid and methanol with a molar ratio of 2 with respect to both acids was fed. Continuous withdrawal of the esters with the distillate resulted in ester contents in the bottom product of less than 3.3 mol%. As expected, the water content in the bottom product decreased with increasing feed methanol concentration due to dilution.

CONCLUSIONS

Reactive distillation of aqueous formic acid–acetic acid mixtures through esterification with methanol was investigated in batch mode and continuous mode for different feed compositions according to the distillation fields of the ternary system. The effect of methanol on conversion and product composition was quantified. The major finding of the project was that complete separation of formic acid from the ternary feed is possible. For separation and isolation of acetic acid either esterification or alternatively distillative separation may be applied. Process economics rather prefer esterification of acetic acid too. Isolation of methyl formate in the distillate with any appropriate quality is possible. In conclusion, reactive distillation has proven applicable in separating and isolating valuable constituents from complex broths and may therefore well contribute to biorefinery.

NOMENCLATURE

D	$[\text{m}^3 \text{h}^{-1}]$	distillate
P	[bar]	pressure
r	[-]	reflux ratio
R	$[\text{m}^3 \text{h}^{-1}]$	reflux
T	$[\text{°C}]$	temperature
T_b	$[\text{°C}]$	boiling point

ACKNOWLEDGEMENTS

The authors acknowledge support from Candela Campos Dominguez and Raphael Neubauer during their project work at TU Graz. The authors also appreciate the support of Herta Luttenberger and Peter Letonja.

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Solvent recovery via reactive
distillation to intensify bio-based
chemical production from waste
effluents

Solvent recovery via reactive distillation to intensify bio-based chemical production from waste effluents

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ABSTRACT

Biomass converting processes often struggle with downstream processing of dilute multicomponent mixtures. Liquid–liquid extraction is perfectly suited for removing carboxylic acids from aqueous streams, but solvent recovery is still energy intensive. Solvent recovery is simplified by reactive distillation, whereas the carboxylic acids are directly converted into their corresponding methyl esters. A process concept on the basis of formic acid and acetic acid isolation was evaluated and discussed for uncatalyzed and catalyzed batch reactive distillation with the acid laden solvent Cyanex® 923. 4-Dodecylbenzenesulfonic acid was used as catalyst. Catalytic conversion yielded 100% methyl formate and 88% methyl acetate formation.

ARTICLE HISTORY

Received 15 November 2016
Accepted 17 January 2017

KEYWORDS

Solvent regeneration;
reactive distillation;
carboxylic acids

Introduction

Sustainable production of chemicals and “waste to value” approaches is gaining increasing global interest. In the bio-based industry, complete utilization of the biomass feedstock is expected to sustainably contribute to the substitution of oil-based bulk products. Aqueous effluents from the biorefinery may contain several by-products. However, isolating pure constituents from dilute multicomponent mixtures is challenging, especially when the constituents tend to form azeotropes. Consequently, many side streams are rather disposed of than exploited. The pulping industry, for instance, focuses on the production of cellulose fibers, while the by-products lignins, hemicellulose, and volatile and non-volatile carboxylic acids are only considered as a source for thermal energy. However, carboxylic acids and their esters are base chemicals with a huge variety of application. Sjöström^[1] evaluated the annual production of carboxylic acids from a Kraft pulp plant to be 75,500 t a⁻¹ given a plant output of 200,000 t a⁻¹ birch pulp. The main volatile carboxylic acids are formic acid (HCOOH, HFO) and acetic acid (CH₃COOH, HAC) with an annual production of 9100 t a⁻¹ and 21,800 t a⁻¹, respectively. Type and amount of by-products are strongly dependent on the used wood and process.^[2] Before incineration of the spent pulping liquor, water must be removed by evaporation. During evaporation, the volatile constituents are also removed from the spent liquor and collected in the condensate, producing an aqueous effluent laden with formic

acid and acetic acid. This ternary mixture forms a binary high boiling azeotrope of formic acid and water ($T_{b,HFO-H_2O}=105.6^{\circ}\text{C}$ at 0.95 bar) and also a ternary saddle point azeotrope ($T_{b,HFO-HAC-H_2O}=105.2^{\circ}\text{C}$ at 0.95 bar).^[3] State-of-the-art wastewater treatment is liquid–liquid extraction combined with distillation for solvent recovery and entrainer distillation for azeotrope separation.^[4] For extraction of carboxylic acids from aqueous effluents, organophosphorus-based solvents (e.g., trialkylphosphine oxide, tributyl phosphate) or aliphatic tertiary amines (e.g., trioctylamine, tri-*n*-hexylamine) are preferably used.^[5,6] For recovery of the acetic acid laden tributyl phosphate, Cai *et al.*^[7] used distillation at 0.003 MPa and 120°C. Acetic acid recovery was more than 90 wt.%. Ren *et al.*^[8] recommended vacuum evaporation instead of hot water re-extraction for solvent recovery. Operation conditions were 100°C and 0.095 MPa for vacuum evaporation for tributyl phosphate regeneration. A stripping efficiency of 89.62% for acetic acid was achieved. Demesa *et al.*^[9] achieved 75 wt.% removal of formic acid from Cyanex® 923 at 3.1–4.9 kPa and 195°C in a spinning band distillation column. About 97.6 wt.% of formic acid was stripped from the solvent Alamine® 336 at 173°C and a vacuum pressure of 4.1–6.8 kPa. Due to co-extraction of water, the distillate from solvent recovery again contains the ternary mixture acetic acid (about 60 wt.%) / formic acid (about 30 wt.%) / water. For downstream processing of these azeotropic distillate mixtures, dewatering by distillation with an entrainer (e.g., di-*n*-propylether^[4] or

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ethyl-*n*-butylether^[4,10]) followed by catalytic decomposition of formic acid (with *e.g.*, alumina catalysts^[11]) or reactive distillation^[12–14] is suggested. However, distillation with an entrainer is generally energy intensive, and catalytic decomposition destroys a valuable component. Reactive distillation offers an elegant separation route by transforming the substance properties and separation properties via chemical reaction. Besides simplifying the separation task, the value of the side products and the process efficiency may be increased with a properly chosen chemical conversion.

Painer *et al.*^[14] demonstrated a feasible application of reactive distillation for the separation of acetic acid/formic acid/water mixtures by esterification with methanol (CH₃OH, MeOH) in batch and continuous operation mode. Without any additional catalyst, formic acid was completely converted and removed as methyl formate. Acetic acid was partly esterified owing to the slower reaction rate. Conversions between 32.4 and 48.9% were achieved with a methanol to formic acid ratio of 2.4 depending on the initial acid concentration in batch reactive distillation experiments. The difference in reaction rates was also used by Saha *et al.*^[15] to selectively esterify formic acid with cyclohexene from acetic acid in a distillation column. With a molar ratio of acids to cyclohexene of 1:1.1, a selectivity to cyclohexyl formate of 64% and to cyclohexyl acetate of 30% was realized. Reactive distillation for removal of acetic acid (up to 30 wt.%) from aqueous effluents was generally done using heterogeneous catalysts to increase reaction rates. Saha *et al.*^[16] used the ion-exchange resin Indion 130 for the catalytic esterification of an aqueous mixture of acetic acid (30 wt.%) with *n*-butanol or *iso*-amyl alcohol. An acetic acid conversion of 58% for *n*-butanol and 51% for *iso*-amyl alcohol was achieved at a molar ratio of 1:2. Xu *et al.*^[17]

investigated catalytic reactive distillation to recover aqueous acetic acid (2.6–9.9 wt.%) with methanol using the catalyst Amberlyst® 15. The conversion of acetic acid was between 20 and 60% depending on the location of the aqueous acetic acid feed, reflux ratio and the top product rate. Singh *et al.*^[18] examined reactive distillation experiments and simulation of the esterification of aqueous mixtures of acetic acid (11–30 wt.%) with methanol using Amberlyst-CSP2. The best result was 81.9% conversion of acetic acid at a molar ratio of methanol to acetic acid of 12.14. High water content hinders acetic acid esterification because water is also a reaction product. Therefore, high acetic acid conversion was difficult to achieve.

With the conventional wastewater treatment of the pulping process in mind—liquid–liquid extraction, solvent recovery, separation of the azeotropic mixture—solvent recovery via reactive distillation is a promising approach for process intensification (Figure 1). To the best of our knowledge, this combination was only mentioned in a patent of 2013,^[19] missing systematic investigation as well as examination of catalyzed esterification in reactive distillation. Fast reaction rates are essential for suitable application of reactive distillation in solvent recovery due to the direct impact on equipment size. However, the use of acidic catalysts in combination with reactive extractants with a distinct tendency to form adducts with strong acids (*e.g.*, organophosphorus compounds) leads to a deactivation of the catalyst and a decrease in extraction efficiency. This paper discusses the feasibility of solvent recovery via batch reactive distillation using the example of acetic acid and formic acid esterification with methanol in a solvent phase of Cyanex® 923/*n*-undecane. The focus is on the applicability of the homogeneous catalyst 4-dodecylbenzenesulfonic acid (4-DBSA) for reactive distillation and its influence on liquid–liquid extraction. 4-DBSA was chosen due to its

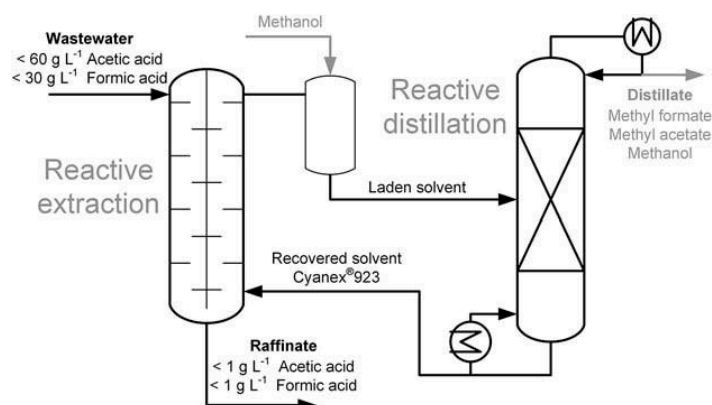


Figure 1. Reactive process concept for formic acid and acetic acid recovery from aqueous effluents through reactive extraction and an intensified solvent recovery step.

excellent performance in esterification of oleic acid with methanol^[20] as well as in transesterification of rape seed oil with ethanol.^[21] Additionally, 4-DBSA, with its long alkyl chain, is mainly present in the solvent phase where the reaction is also expected due to the higher carboxylic acid content in contrast to the aqueous phase. Besides acidity, 4-DBSA also has surface active properties. This may lead to undesired emulsion formation in liquid–liquid extraction. Despite its excellent catalytic performance in transesterification of rape seed oil, the surface active properties of 4-DBSA hindered separation of the biphasic product stream and industrial application were not recommended.^[21] Combining Cyanex[®] 923 and 4-DBSA in the solvent phase causes adduct formation between 4-DBSA and Cyanex[®] 923 due to the preference of Cyanex[®] 923, a Lewis base, to strong acids. Thereby a part of Cyanex[®] 923 is blocked with 4-DBSA in the extraction step, but emulsification is prevented. The 4-DBSA/Cyanex[®] 923 adduct can be broken at elevated temperatures, and free 4-DBSA may provide catalytic activity in reactive distillation. After having left the rectification column via the bottoms, the solvent phase is cooled down, and the adduct between Cyanex[®] 923 and 4-DBSA is formed again.

Due to the expected influence of 4-DBSA on the extraction efficiency, the liquid–liquid equilibrium of simultaneous extraction of acetic acid and formic acid with and without 4-DBSA was investigated and compared with single acid extraction.

Materials and methods

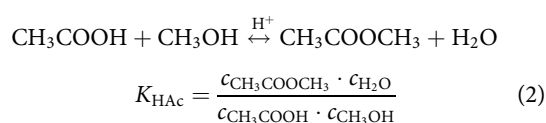
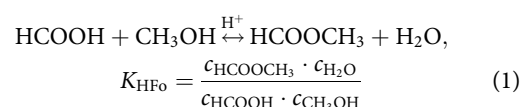
Chemicals

Formic acid (98–100%), acetic acid (99–100%), and methanol (99,8%) were provided by ChemLab, Belgium. 4-Dodecylbenzenesulfonic acid ($\geq 95\%$) and *n*-undecane (99%) were purchased from Sigma-Aldrich, Germany and Cyanex[®] 923 (93%) from Cytec, France. All chemicals were used as supplied.

Methods

The valuable constituents formic acid and acetic acid are removed from the wastewater via reactive extraction. Cyanex[®] 923 is a mixture of four trialkylphosphine oxides (*n*-hexyl and *n*-octyl groups) and is used as the reactive extractant. Due to Lewis acid/Lewis base interactions, Cyanex[®] 923 forms adducts with strong acids. One method to break these adducts is to raise the temperature of the solvent.^[22] By esterification of the carboxylic acids with methanol (Eqs. (1) and (2)), low boiling methyl esters are formed. Methyl formate (HCOOCH₃, MeFo), the

methyl ester of formic acid, is the low boiling component in the mixture with a boiling point of 31.7°C at 1.013 bar.^[23] Methyl acetate (CH₃COOCH₃, MeAc), the methyl ester of acetic acid, boils at 56.87°C at 1.013 bar.^[23] Esterifications are equilibrium reactions with an equilibrium constant for acetic acid esterification with methanol of 6.3 at 40°C after 49 days^[24] and for formic acid esterification of 4.3 at 25°C.^[25] The combination of chemical conversion with distillation offers three main advantages. Firstly, the continuous removal of the reaction products methyl formate and methyl acetate forces the chemical equilibrium to the product side of the reaction. Secondly, the azeotropes are easily overcome by changing the substance properties through chemical conversion. And thirdly, due to elevated boiling points of the solvent phase ($T_{b,\text{Cyanex}^{\circ}923}=310^{\circ}\text{C}$ at 6.67 kPa^[26]), the temperature in the reboiler is elevated, and therefore, the reaction rates are enhanced. Generally, formic acid reacts faster with methanol than acetic acid due to the smaller steric hindrance and inductive effect.^[27]



Experimental setup and procedure

Liquid-liquid extraction: The liquid–liquid equilibria of formic acid and/or acetic acid between Cyanex[®] 923/*n*-undecane and water were measured at 25°C with and without 5 wt.% 4-DBSA in the solvent phase. The solvent phase contained 70 wt.% Cyanex[®] 923 and 30 wt.% *n*-undecane. Acetic acid and formic acid were admixed to the aqueous phase in a concentration range from 0 to 0.2 g cm⁻³. About 30 cm³ of each phase was filled in a temperature controlled shaking flask and was shaken for 30 min for equilibrium adjustment. After phase separation, the mass of each phase was recorded. Acid concentrations were measured by gas chromatography, and water content in the solvent phase was analyzed by Karl-Fischer titration.

Reactive distillation: Batch reactive distillation experiments were carried out in a 500 cm³ flask equipped with a 30 cm Vigreux column, a condenser, and a reflux splitter. The reboiler was heated with a heating plate (Heidolph) and was stirred steadily. The temperature was measured and recorded in the reboiler

and on top of the Vigreux column. The Vigreux column was insulated with a polyethylene foam sleeve. For condensation and cooling of the distillate, the condenser and the product funnel were cooled to 5°C with a Lauda cryostate. The reflux ratio was adjusted with a Lab.-Kybernet controller from Brand. All experiments were carried out at ambient pressure.

After mixing the solvent phase (70 wt.% Cyanex® 923 diluted in *n*-undecane) with the carboxylic acids and methanol, the laden solvent was heated until boiling. For the following reaction period of 1.5 h, the setup was operated with total reflux. This period offered sufficient time for the esterification of formic acid and acetic acid to produce the methyl esters. Subsequently, the reflux ratio was set from infinite to 10:1, and the distillate product removal was started. Simultaneously, a sample of the bottom phase was withdrawn. After the adjustment of the reflux ratio to 10:1, samples were taken from the reboiler every second hour and from the distillate at intervals of 30 min. All samples were immediately cooled in ice water and analyzed via gas chromatography or acid–base and Karl-Fischer titration. During the experiment, the low boiling components were constantly removed via the distillate, and therefore, the heating plate temperature was increased due to the increase in the boiling point of the bottoms mixture. The experiment finished when either a biphasic distillate was collected or similar temperatures were observed in the reboiler and at the top of the column, which indicated that complete removal of the low boiling components had been achieved. Experiments were repeated with varied sampling times for a more detailed concentration profile and to prove reproducibility.

The yield of methyl esters Y_{RD} in the batch reactive distillation experiments was determined with the initial carboxylic acid moles $n_{Acid,0}$ and the collected moles of the corresponding esters in the distillate phase $n_{Ester,Distillate,t}$ after the time t according to Eq. (3):

$$Y_{RD}[\%] = \frac{n_{Ester,Distillate,t}}{n_{Acid,0}} \times 100 \quad (3)$$

Batch reactive distillation experiments were carried out with three different solvent loads, denoted with low, medium, and high (low: 1.9 wt.% formic acid, 5.6 wt.% acetic acid; medium: 6.7 wt.% formic acid, 11.9 wt.% acetic acid; high: 13.5 wt.% formic acid, 23.8 wt.% acetic acid). The low and high starting concentrations were gained from reactive extraction experiments from aqueous mixtures containing 3 to 30 wt.% formic acid and 6 to 60 wt.% acetic acid. The molar ratio of methanol to both carboxylic acids was chosen with 0.4, 1, 1.5,

and 2. The molar ratio of 0.4 equals a molar ratio of methanol to formic acid of 1.

Experiments with catalyst were performed in the same equipment by adding 5 wt.% 4-DBSA to the solvent phase (70 wt.% Cyanex® 923 diluted in *n*-undecane). The procedure was similar, only the reaction period was omitted because of elevated reaction rates.

Analytics

All aqueous samples were analyzed by gas chromatography (Shimadzu 2010 Plus) equipped with a thermal conductivity detector for water and formic acid and a flame ionization detector for acetic acid, methanol, methyl formate, and methyl acetate. The detectors were connected in parallel. For uncatalyzed reactive distillation experiments, the used column was a Supel-Q™ plot fused silica capillary column (length 30 m, inner diameter 0.53 mm, average thickness 30 μm). The auto injector AOC-20i worked in split mode with a split ratio of 30:1 at 240°C. The starting temperature of the column oven was set to 40°C, held for 2 min, ramped up to 150°C with a heating rate of 15°C min⁻¹, held for 5.7 min and followed by heating to 200°C with 30°C min⁻¹, and a hold for 1 min. Total analyzing time was 17.7 min. Both detectors worked at 250°C. The thermal conductivity detector operated at 70 mA. Helium was used as carrier gas.^[14]

The samples from the solvent phase were analyzed by automatic acid–base titration (TitraLab™ sample station SAM55 with ABU93 Triburette from Radiometer Copenhagen) with 0.1 and 1 mol L⁻¹ potassium hydroxide and Karl-Fischer titration (SI Analytics TitroLine® 7500 KF) for water quantification.

In catalytic batch reactive distillation experiments, all samples were analyzed with gas chromatography using a polar CP-WAX 57CB column from Agilent (length 50 m, inner diameter 0.32 mm, film thickness 20 μm). The temperature program in the oven was changed to a starting temperature of 50°C, holding for 3 min, ramping up to 200°C with a heating rate of 8°C min⁻¹ and holding for 4 min.

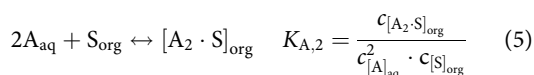
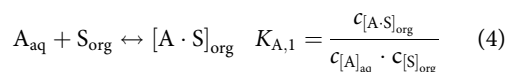
Results and discussion

To prove the applicability of the reactive process concept for solvent recovery, simultaneous extraction of formic acid and acetic acid in the presence and absence of 4-DBSA was performed followed by uncatalyzed and catalyzed batch reactive distillation experiments.

Influence of acid strength on the liquid–liquid equilibrium

Extraction of carboxylic acids is commonly performed with reactive extractants to improve extraction efficiency and selectivity. Cyanex® 923 prefers adduct formation with strong acids. Therefore, acid extraction efficiency is strongly influenced by acid strength. To evaluate the influence of multicomponent mixtures and 4-DBSA on the extraction efficiency, liquid–liquid equilibrium experiments were executed.

Modeling of liquid–liquid equilibrium behavior is needed for process design. Stoichiometry of the adducts formed between Cyanex® 923 and acids is effected by the acid concentration. With increasing acid concentration, the number of acid molecules attached to one molecule of trialkylphosphine oxide increases. Eqs. (4) and (5) show the liquid–liquid equilibrium constants $K_{A,1}$ and $K_{A,2}$ for different stoichiometries in adduct formation where A depicts the carboxylic acid and S the reactive extractant. Cai *et al.*^[7] proposed a model for calculating the equilibrium concentrations of carboxylic acids $c_{A,org}$ in the solvent phase where two types of adduct formation were considered, with stoichiometries of 1:1 and 2:1 between acid A and Cyanex® 923 (Eq. (6)). It is assumed that at low acid concentration in the aqueous phase, 1:1 adducts are formed and with increasing acid concentration the adduct changes to 2:1 stoichiometry. This equation was extended for a second acid B for predicting extraction behavior of multicomponent liquid–liquid equilibrium using equilibrium constants from single acid extraction (Eq. (7)). Therefore, multicomponent extraction can be modeled with single acid equilibrium data.



$$c_{A,org} = \left(\frac{K_{A,1} \cdot c_{A,aq} + 2 \cdot K_{A,2} \cdot c_{A,aq}^2}{1 + K_{A,1} \cdot c_{A,aq} + K_{A,2} \cdot c_{A,aq}^2} \right) \cdot c_{S,org} \quad (6)$$

$c_{A,org}$

$$= \frac{(K_{A,1} \cdot c_{A,aq} + 2 \cdot K_{A,2} \cdot c_{A,aq}^2) \cdot c_{S,org}}{1 + K_{A,1} \cdot c_{A,aq} + K_{A,2} \cdot c_{A,aq}^2 + K_{B,1} \cdot c_{B,aq} + K_{B,2} \cdot c_{B,aq}^2} \quad (7)$$

Figure 2a shows the single and multicomponent liquid–liquid equilibria of formic acid and acetic acid between Cyanex® 923/*n*-undecane and water. Results from single acid extraction were similar for both carboxylic acids; no significant influence of the acid

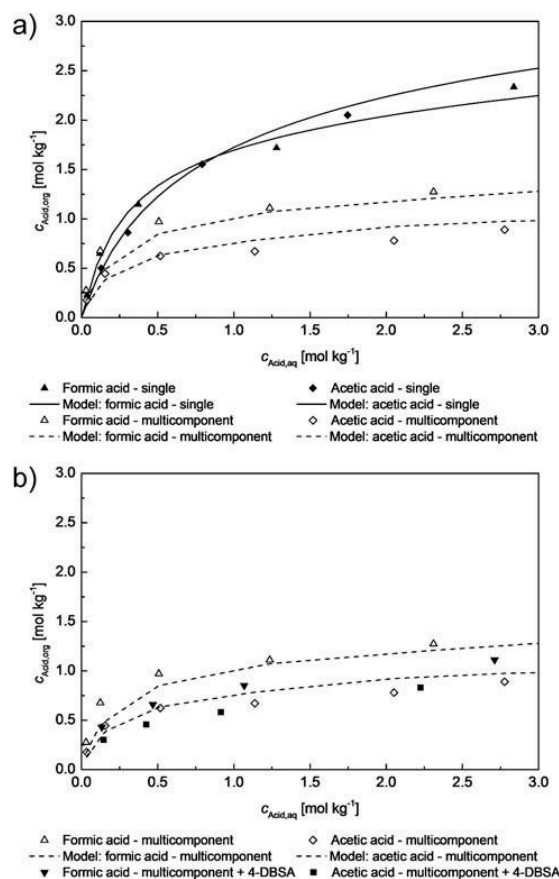


Figure 2. (a) Single and multicomponent liquid–liquid equilibria of formic acid and acetic acid between Cyanex®923 (70 wt.%)/*n*-undecane and water at 25 °C (markers represent the experimental data, lines show the model); (b) Influence of 5 wt.% of 4-DBSA on the multicomponent liquid–liquid equilibrium (experimental data).

strength on constituent distribution was observed. In particular, at low acid concentration in the aqueous phase, high equilibrium concentration in the solvent phase was obtained. This fact makes reactive extraction perfectly suited for recovery of carboxylic acids from low-grade wastewater. The equilibrium constants were calculated with these experimental data sets and summarized in Table 1. Average deviation between

Table 1. Equilibrium constants $K_{A,1}$ and $K_{A,2}$ for formic acid and acetic acid extraction between Cyanex® 923 (70 wt.%)/*n*-undecane and water at 25°C.

	$K_{A,1}$	$K_{A,2}$	average deviation _{single acid} (%)
Formic acid	3.8	0.46	4.4
Acetic acid	2.5	0.64	2.8

experimental data and model was calculated with Eq. (8). Model and experimental data accord well, average deviation was 4.4% and 2.8% for formic acid and acetic acid extraction, respectively. For simultaneous extraction, both acids were present in the aqueous feed at the same concentration. Generally, a lower equilibrium concentration was observed for both acids compared to single acid extraction due to competitive extraction. Equilibrium concentration of formic acid in the solvent phase was constantly higher compared to acetic acid, due to its higher acidity and the affinity of Cyanex® 923 to stronger acids. At low acid concentration in the aqueous phase, good extraction performance for both acids was still observed. The model for simultaneous extraction is able to predict very accurately the liquid–liquid equilibrium behavior of formic acid at high concentration. Acetic acid equilibrium is slightly overestimated. At a lower acid concentration in the aqueous phase, the model underestimates the equilibrium concentration for both acids. This may be due to earlier adduct formation with stoichiometry of 2:1 because the total acid amount is higher, which was not considered in the model. The simultaneous extraction of both carboxylic acids already shows the strong influence of acid strength on equilibrium concentration.

To evaluate the influence of 4-DBSA on simultaneous extraction of acetic acid and formic acid from water, 5 wt. % 4-DBSA was added to the solvent phase (Figure 2b). For acetic acid extraction, no significant difference was observed between the solvent with and without 4-DBSA. Formic acid extraction clearly decreased when 4-DBSA was added to the solvent phase. In simultaneous extraction of both acids in absence of 4-DBSA, formic acid was preferred by Cyanex® 923. With 4-DBSA in the solvent phase, the preference of Cyanex® 923 shifted to 4-DBSA. This leads to decreased formic acid extraction. To counteract the loss in extraction efficiency, the Cyanex®923 concentration in the solvent phase could be increased. Furthermore, the catalyst load needs to be optimized in terms of reaction rates and loss in extraction efficiency.

Average Deviation

$$= \frac{1}{n_{\text{exp}}} \sum_{i=1}^{n_{\text{exp}}} \frac{|c_{\text{org,exp}} - c_{\text{org,model}}|}{c_{\text{org,exp}}} \cdot 100\% \quad (8)$$

Batch reactive distillation without catalysis

Uncatalyzed batch reactive distillation experiments of the solvent phase show generally higher conversion of formic acid and limited acetic acid conversion due to higher reaction rates of formic acid esterification.^[22]

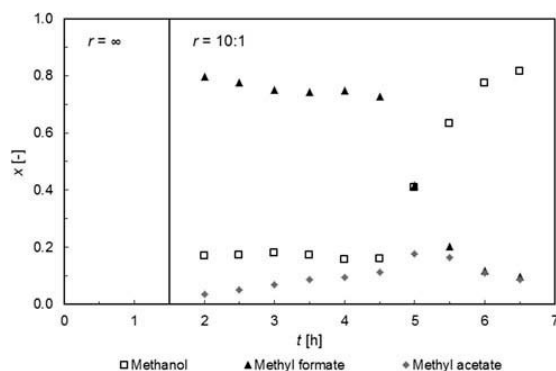


Figure 3. Distillate composition in batch reactive distillation of the laden solvent phase containing formic acid and acetic acid; esterification with equimolar ratio of methanol to both acids; solvent phase: 70 wt.% Cyanex®923 diluted in *n*-undecane; medium solvent load: 6.7 wt.% formic acid, 11.9 wt.% acetic acid; total reflux for 1.5 h and reflux ratio $r = 10:1$ afterwards; ambient pressure.

Figure 3 shows the distillate composition for recovery of a laden solvent with 6.7 wt.% formic acid and 11.9 wt.% acetic acid with a molar ratio of methanol to both acids of 1. After a reaction period of 1.5 h, the reflux ratio was changed from infinite to 10:1. In this time, the boiling point of the bottom phase reduced from 84.1°C to 76.2°C which indicated the generation of the low boiling reaction products methyl formate and methyl acetate. In the first 3 hours of distillate removal, the concentration of methyl formate in the distillate phase decreased slightly from 80 mol% to 73 mol%. As long as sufficient formic acid was present in the bottom phase, the concentration of methyl formate in the distillate remained almost constant. Due to the higher reaction rate of formic acid esterification compared to acetic acid esterification and the lower boiling point of methyl formate, formic acid was consumed and removed first. Furthermore, when formic acid was almost depleted in the bottom phase, the concentration of methyl formate in the distillate decreased and the top temperature increased. The concentration of methyl acetate in the distillate phase increased slightly and reached 18 mol% after 5 hours due to the limited conversion of acetic acid. With the increase in the top temperature, the methanol concentration increased in the distillate product. No water and acids were detected in the distillate, although methyl acetate and water form a low boiling azeotrope ($T_{b,\text{MeAc-H}_2\text{O}}=55.9^\circ\text{C}$ at 1.013 bar^[28]). This may be due to the modifier performance of methyl formate, which also has the ability to suppress azeotrope formation.^[29] Continuous loss of methanol to the distillate can easily be circumvented

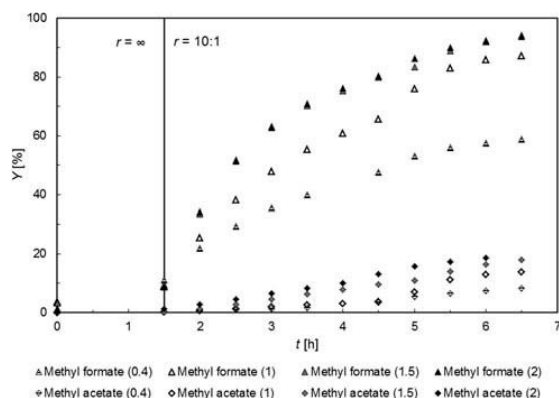


Figure 4. Yield of methyl formate and methyl acetate in batch reactive distillation of laden solvent phase containing formic acid and acetic acid with a varying molar ratio of methanol to both acids of 0.4, 1, 1.5 and 2 (number in brackets); solvent phase: 70 wt.% Cyanex®923 diluted in *n*-undecane; medium solvent load: 6.7 wt.% formic acid, 11.9 wt.% acetic acid; total reflux for 1.5 h and reflux ratio = 10:1 afterwards; ambient pressure.

by increasing the reflux ratio or by a higher separation efficiency of the rectification column.

The total acid concentration in the solvent phase decreased from 3.20 mol kg^{-1} to 2.06 mol kg^{-1} .

A comparison of the yield of methyl formate and methyl acetate in batch reactive distillation with different molar ratios of methanol to both acids for medium solvent load is shown in Figure 4. The difference in reaction rates between formic acid and acetic acid and the removal of methyl formate in a first step can be seen. The yield of methyl formate increased immediately at the beginning of distillate removal. Methyl acetate yield rose slowly because of the low reaction rate of acetic acid. The lowest yield of methyl acetate was obtained for the substoichiometric ratio of methanol to both acids of 0.4, which equals an equimolar admixture of methanol with respect to formic acid. In this experiment, a yield of 62% of methyl formate and a yield of 10% of methyl acetate were reached. For selective removal of formic acid, the difference in reaction rates of formic acid and acetic acid is not sufficient. Therefore, methanol partially reacted with acetic acid. In experiments with an equimolar ratio of methanol to both acids, the yield for both methyl esters increased. The yield was 89% for methyl formate and 15% for methyl acetate. The difference in the yield between a molar ratio of 1.5 and 2 for both esters was insignificant. The yields of methyl formate and methyl acetate were 95% and 19%, respectively. Sufficient methanol was present for esterification of both acids, and the excess

Table 2. Summary of methyl formate and methyl acetate yield of batch reactive distillation with low solvent load (1.9 wt.% formic acid, 5.6 wt.% acetic acid), medium solvent load (6.7 wt.% formic acid, 11.9 wt.% acetic acid), and high solvent load (13.5 wt.% formic acid, 23.8 wt.% acetic acid); molar ratio of methanol to both acids was 0.4, 1, 1.5 and 2; total reflux for 1.5 h, then reflux ratio $r = 10:1$; ambient pressure.

Molar ratio of MeOH:Acids	low solvent load		medium solvent load		high solvent load	
	Y_{MeFo} [%]	Y_{MeAc} [%]	Y_{MeFo} [%]	Y_{MeAc} [%]	Y_{MeFo} [%]	Y_{MeAc} [%]
0.4			62.1	9.6	70.7	13.4
1	40.5	5.2	88.8	14.6	97.8 [22]	28.2 [22]
1.5	57.7	7.2	95.5	18.6	95.9	27.0
2	56.2	6.9	94.7	18.9	97.2	28.0

Table 3. Summary of initial boiling point ($T_{b,0}$) and boiling temperature after reaction period ($T_{b,R}$) in the bottom phase of batch reactive distillation with low solvent load (1.9 wt.% formic acid, 5.6 wt.% acetic acid), medium solvent load (6.7 wt.% formic acid, 11.9 wt.% acetic acid), and high solvent load (13.5 wt.% formic acid, 23.8 wt.% acetic acid); molar ratio of methanol to both acids was 0.4, 1, 1.5 and 2; total reflux for 1.5 h, then reflux ratio $r = 10:1$; ambient pressure.

Molar ratio of MeOH:Acids	low solvent load		medium solvent load		high solvent load	
	$T_{b,0}$ [°C]	$T_{b,R}$ [°C]	$T_{b,0}$ [°C]	$T_{b,R}$ [°C]	$T_{b,0}$ [°C]	$T_{b,R}$ [°C]
0.4			96.8	88.0	88.8	72.7
1	105.1	98.9	84.1	76.2	79.7	65.8
1.5	95.2	91.2	79.7	72.9	75.7	64.3
2	88.7	86.7	76.9	71.0	73.5	63.4

methanol was separated in the distillate. Therefore, a high surplus is not beneficial.

Table 2 summarizes the yield of methyl formate and methyl acetate for all investigated solvent loads and molar ratios of methanol to both acids. Generally, the yield increased with increasing solvent load. The slight decrease in the yield at higher molar ratios may be explained by the decrease in the boiling temperature of the bottom phase with increasing methanol supply. In Table 3, an overview is given of the initial boiling point after mixing all components $T_{b,0}$ and of the boiling temperature after the reaction period $T_{b,R}$. With an increasing supply of methanol, the boiling temperature of the bottom phase decreased due to the low boiling point of methanol. Reduction in boiling temperature was also observable with increased solvent load.

Batch reactive distillation with homogeneous catalysis

Formic acid esterification showed high conversion in uncatalyzed reactive distillation experiments. In

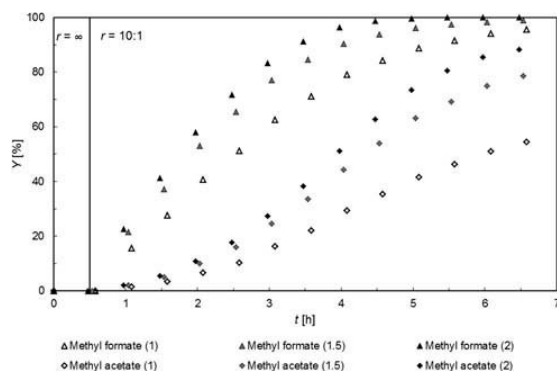


Figure 5. Yield of methyl formate and methyl acetate in homogeneous catalytic batch reactive distillation of laden solvent phase containing formic acid and acetic acid with a varying molar ratio of methanol to both acids between 1 and 2 (number in brackets) catalyzed with 5 wt.% 4-DBSA; solvent phase: 70 wt.% Cyanex®923 diluted in *n*-undecane; medium solvent load: 6.7 wt.% formic acid, 11.9 wt.% acetic acid, reflux ratio $r = 10:1$; ambient pressure.

comparison, acetic acid esterification is much slower, yielding low conversion during the reaction period. To enhance acetic acid esterification 5 wt.% 4-DBSA for catalysis was added to the solvent phase.

Figure 5 compares methyl formate and methyl acetate yield for different molar ratios of methanol to both acids in batch reactive distillation experiments with 5 wt% 4-DBSA in the solvent phase at medium solvent load. Yield of methyl formate shows similar behavior in non-catalytic and catalytic batch reactive distillation experiments. This can be explained by the high reaction rate of formic acid esterification, also in uncatalyzed experiments. A greatly improved yield of methyl acetate was observed. For an equimolar ratio of methanol to both acids, the yield of methyl acetate increased from 14.6% in uncatalyzed experiments to 54.4% with 4-DBSA. With an excess of methanol, conversion of acetic acid increased continuously. A molar ratio of methanol to both acids of 1.5 enabled a methyl acetate yield of 78.6%. With a double molar ratio of methanol to both acids, complete conversion of formic acid and a methyl acetate yield of 88.2% was achieved. This significant increase in acetic acid conversion confirms that the adduct between 4-DBSA and Cyanex® 923 was cleaved at elevated temperature to let 4-DBSA act as catalyst.

Summary

Batch reactive distillation was proven to be applicable for solvent regeneration in liquid–liquid extraction of

carboxylic acids with Cyanex® 923. Uncatalyzed esterification of acetic acid and formic acid with methanol combined with distillation showed a high yield of 97% for methyl formate, while the yield for acetic acid methyl ester was only 28%. By adding 4-DBSA, a homogeneous catalyst for esterification reactions, the yield was improved to 100% and 88% for methyl formate and methyl acetate, respectively. 4-DBSA in the solvent phase diminished slightly the extraction efficiency of Cyanex® 923.

Therefore, solvent recovery via reactive distillation offers a promising opportunity for process intensification in wastewater treatment. By changing the properties of the target constituents via an appropriate chemical reaction, the separation step can be simplified, and the market value of the components will increase.

Nomenclature

0	[-] initial condition
c	[mol kg ⁻¹] concentration
K	[-] equilibrium constant
n	[mol] number of moles
n_{exp}	[-] number of experimental data points
r	[-] reflux ratio (reflux/distillate)
R	[h] reaction period
t	[h] time
T	[°C] temperature
T_b	[°C] boiling point
x	[-] mole fraction
Y	[-] yield

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Summary and Future Directions

In biorefineries downstream processing is a challenge. In these processes dilute multicomponent mixtures are produced with valuable components at low concentration and a high tendency of azeotrope formation. A representative example is an aqueous mixtures of formic acid and acetic acid, as produced during pulping, by fermentation or in fast pyrolysis of biomass. The recovery of carboxylic acids from water is commonly performed via reactive liquid-liquid extraction combined with distillation for solvent regeneration. Solvent regeneration and product isolation are still energy intensive state of the art processes.

The task of this PhD-Thesis was the development of processes and process combinations for the isolation of carboxylic acids (formic acid and acetic acid) from dilute aqueous feed broths targeting industrial implementation under economically feasible conditions. The approach of changing the substance properties combined with changing the physical state based on TIPS suggestions for separating azeotropic mixtures was investigated. The carboxylic acids were converted with methanol to the low-boiling methyl esters, which can be easily removed in reactive distillation.

The basis for reactive distillation design is the knowledge of the reaction rates. Therefore, the reaction kinetics were investigated for formic acid, acetic acid and propionic acid esterification in single acid and multi-acid experiments without additional catalysts. Interactions in multi-acid esterification due to differences in acid strengths have significant influence on the individual rates. A model was developed based on single acid esterification data including intramolecular catalysis by the H^+ -ion concentration from acid dissociation. This model is capable of predicting multi-acid esterification with the catalytic effect of the stronger acid on the weaker acid esterification with standard deviations less than 1.7 %. Transesterification of methyl formate with acetic acid and propionic acid to methyl acetate and methyl propionate is also represented by the model.

To validate reactive separations for the ternary mixture acetic acid, formic acid and water, reactive distillation was performed in batch and continuous operation mode with methanol as esterifying agent in absence of additional catalysts. As kinetics suggest, formic acid esterification showed high conversion in reactive distillation (99 %) according to the fast reaction rate, while uncatalyzed esterification of acetic acid is slow. The highest acetic acid conversion was found to be 71 % at a molar ratio of methanol to formic acid of 3 in continuous operation mode. In the distillate the ternary mixture methyl formate, methyl acetate and the excess of methanol was obtained. For further isolation pervaporation could be used to break the methyl acetate/methanol azeotrope. High methanol surplus is not helpful because of dilution of H^+ -ion concentration for catalysis, low

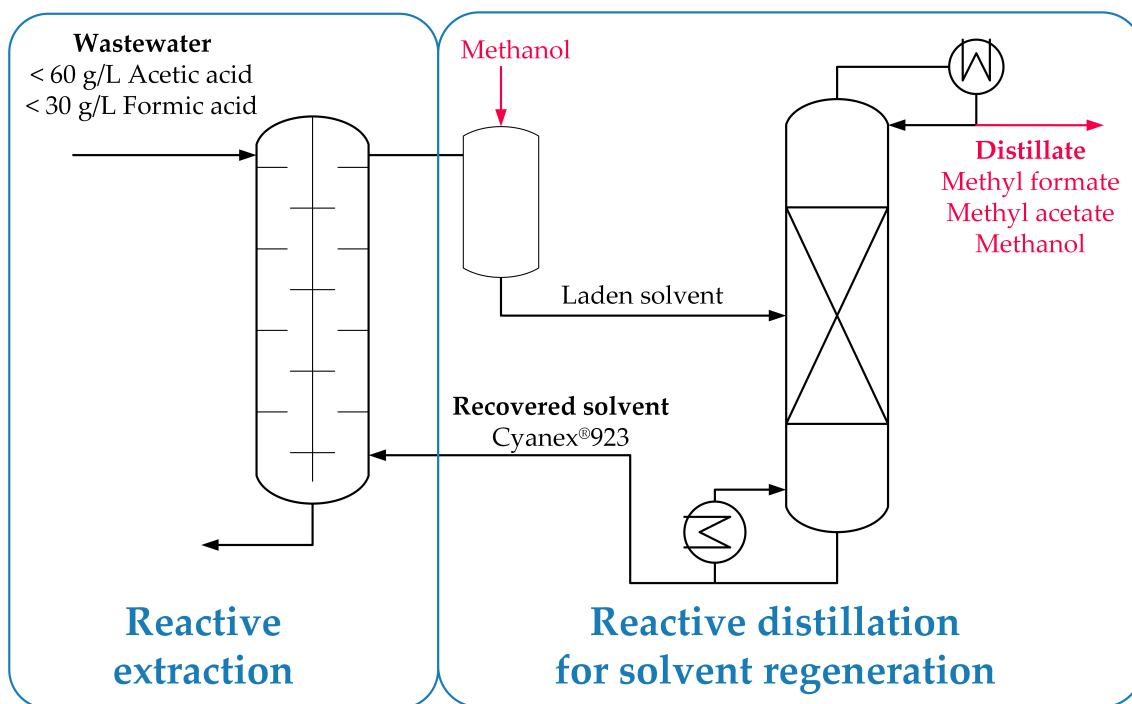


Figure 6.1: Recovery of low molecular weight carboxylic acids via reactive extraction and intensified solvent regeneration by reactive distillation

boiling temperature of the mixture as well as increased heat duty is required by excess methanol removal. A future task is to find the optimum between methanol surplus, heat duty, reflux ratio etc. via process simulation. With the kinetic model of multi-acid mixtures the base is established for reactive distillation simulation.

For further improvement of solvent regeneration and product isolation, solvent regeneration by reactive distillation as displayed in Figure 6.1 was investigated. Solvent regeneration with reactive distillation reduces energy and apparatus demand. Uncatalyzed batch reactive distillation has confirmed high formic acid conversion of 97 % like in aqueous reactive distillation but acetic acid conversions reached only 28 %. High regeneration efficiency is essential for an economic extraction process. Admixture of 5 wt.% 4-dodecylbenzenesulfonic acid for catalysis leads to complete formic acid conversion and 88 % yield of methyl acetate. Catalyst recovery from the solvent phase is not mandatory with the homogenous catalyst 4-dodecylbenzenesulfonic acid due to the extractive interaction between Cyanex®923 and the catalyst at extraction temperature. Therefore the catalyst is kept in the solvent phase during extraction by adduct formation with the extractant. In reactive distillation it is cleaved due to adduct breakage at elevated temperature. Optimization between catalyst concentration needed for appropriate reaction rates and decrease in extraction efficiency due to blockage of extractant by adduct formation with the catalyst is a future task.

Future investigation could make use of methyl formate as entrainer for sepa-

ration of the methyl acetate/methanol azeotrope. The entrainer properties were already observed in reactive distillation due to the absence of water in the distillate, although methyl acetate forms a low-boiling azeotrope with water. For simplifying the separation of the distillate product, methyl formate can be recycled. The methyl esters show an excellent vapor-liquid equilibrium behavior for product isolation by simple distillation.

For industrial application of process intensification, process simulation needs to be performed for the final design of the intensified process with reactive distillation.

Appendix

Reaktive Trennung von Essigsäure/Ameisensäure/Wasser-Gemischen aus der Bioraffinerie

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DOI: 10.1002/cite.201400130

Die Verarbeitung von Biomasse als Rohstoff in industriellen Prozessen kann zur Bildung von Multikomponentengemischen führen, die bei der destillativen Trennung zur Azeotropbildung neigen. Das ternäre Gemisch Essigsäure/Ameisensäure/Wasser ist dafür ein repräsentatives Beispiel. Eine vielversprechende Lösungsstrategie für die Auftrennung azeotroper Gemische bieten reaktive Trennverfahren, wie beispielsweise die Reaktivdestillation. Durch die Veresterung beider Fettsäuren und die gleichzeitige Abtrennung der leichter siedenden Ester mittels Destillation können die Azeotrope umgangen und eine Isolierung der Reinstoffe ermöglicht werden.

Schlagwörter: Fettsäuren, Reaktivdestillation, Veresterung

Eingegangen: 26. September 2014; *revidiert:* 26. Februar 2015; *akzeptiert:* 03. März 2015

Reactive Separation of Acetic Acid/Formic Acid/Water Mixtures from Biorefinery

Processing of biomass may lead to the formation of multicomponent mixtures, which tend to forming azeotropes in distillative separation. The ternary mixture acetic acid/formic acid/water is a representative example for an azeotropic mixture from the pulp and paper industry. Reactive separations provide an alternative solution strategy, especially reactive distillation. Esterification of both fatty acids may change the separation properties to avoid formation of azeotropes and to reduce the energy demand for isolation of the pure components.

Keywords: Esterification, Fatty acids, Reactive distillation

1 Einleitung

Durch den zunehmenden Einsatz von Biomasse als Ausgangsstoff für verschiedene Prozesse verändern sich die Anforderungen an die Isolierung von Nebenprodukten und die Aufbereitung von Abwasserströmen. Der Aufreinigungsschritt von wässrigen Prozessströmen wird oft durch die Bildung von Multikomponentengemischen, durch die geringen Konzentrationen der wertvollen Nebenprodukte und/oder durch das Auftreten von Azeotropen erschwert. Das Brüdenkondensat aus dem Papier- und Zellstoffprozess beispielsweise enthält Essigsäure (CH_3COOH , HAc) und Ameisensäure (CHOOH , HFO) in geringen Konzentrationen. Die Aufkonzentrierung von wässrigen Lösungen niedermolekularer Fettsäuren wie Essigsäure und Ameisensäure mittels Extraktion mit phosphanoxidbasierten Extraktionsmitteln und anschließender Lösungsmittelregeneration

durch Strippen ist Stand der Technik [1]. Diese Verfahren haben jedoch lediglich eine Aufkonzentrierung der verdünnten, wässrigen Lösungen zur Folge und resultieren wieder im Dreistoffgemisch Essigsäure/Ameisensäure/Wasser.

Das ternäre System Essigsäure/Ameisensäure/Wasser weist ein binäres Hochsiedezeotrop zwischen Ameisensäure und Wasser und ein ternäres Sattelpunkazeotrop auf (Abb. 1). Diese Azeotrope sind zwar in der Literatur dokumentiert, allerdings weichen die Angaben zur Lage voneinander ab. Aristovich et al. [2] fanden das Sattelpunkazeotrop bei einem Druck von 1,013 bar (760 mmHg) bei einer Zusammensetzung von 49,1 Mol-% Ameisensäure, 35,5 Mol-% Wasser und 15,4 Mol-% Essigsäure mit einem Siedepunkt von 107,05 °C. Zwei Jahre später veröffentlichten Aristovich et al. [3] wieder Studien zur Lage des Sattelpunkazeotrops und berichteten von einer Zusammensetzung von 48,2 Mol-% Ameisensäure, 39,3 Mol-% Wasser und 12,5 Mol-% Essigsäure. Wisniak und Tamir [4] überprüften diese Werte und kamen zum Ergebnis, dass das Azeotrop bei 46,9 Mol-% Ameisensäure, 36,3 Mol-% Wasser und 16,8 Mol-% Essigsäure bei 1,013 bar (760 mmHg) liegt. Aufgrund dieser teils widersprüchlichen Ergebnisse in der

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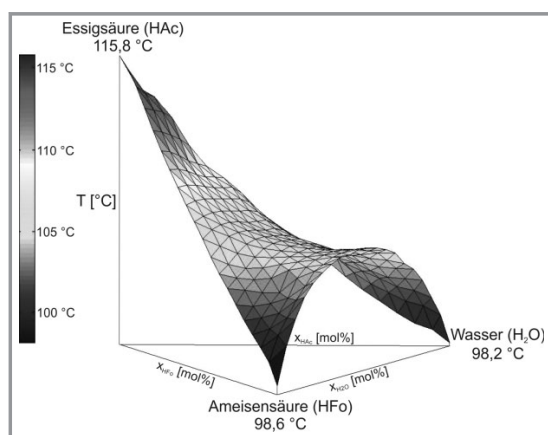


Abbildung 1. Siedefläche des ternären Systems Essigsäure/Ameisensäure/Wasser bei 950 mbar. Binäres Hochsiedeazeotrop: 105,6 °C, ternäres Sattelpunkazeotrop: 105,2 °C.

Literatur wurde die Lage des Sattelpunkazeotrops im Zuge dieses Projektes erneut untersucht. Bei einem Druck von 950 mbar wurde das Sattelpunkazeotrop bei einer Zusammensetzung von 49,8 Mol-% Ameisensäure, 39,0 Mol-% Wasser und 11,2 Mol-% Essigsäure und einer Siedetemperatur von 105,2 °C ermittelt. Die Messgenauigkeit betrug $\pm 2\%$. In Abb. 1 ist die Siedefläche dieses ternären Systems bei 950 mbar gezeigt.

Auch die Binärsysteme stellen für die destillative Auftrennung eine Herausforderung dar. Das binäre System Essigsäure/Ameisensäure weist eine geringe relative Flüchtigkeit über den gesamten Konzentrationsbereich auf und das System Essigsäure/Wasser zeigt bei hohen Wasserkonzentrationen ein azeotropähnliches Verhalten. Die Isolierung der Reinstoffe ist daher mit einfacher Destillation nicht möglich.

In der Literatur werden zur Auftrennung des ternären Gemisches unter anderem die Azeotropdestillation [5,6], Extraktion mit anschließender Destillation [7,8] oder die katalytische Zersetzung der Ameisensäure [9] vorgeschlagen. Bei diesen Verfahren ist entweder der Energieaufwand enorm oder eine wertvolle Komponente wird zerstört.

Die Reaktivdestillation bietet sich als Alternative für diese Trennaufgabe an. Durch die Veresterung der Fettsäuren mit einem kurzkettigen Alkohol wie Methanol (MeOH, CH₃OH) werden die Stoffeigenschaften gezielt verändert und Azeotrope können umgangen werden. Die Fettsäuremethylester haben einen niedrigeren Siedepunkt als die Fettsäuren und können daher kontinuierlich über das Destillat aus dem System entfernt werden. Dadurch wird das Reaktionsgleichgewicht der Veresterung auf die Seite der Produkte verschoben und ein vollständiger Umsatz der Säuren wird möglich.

In den frühen 1970er Jahren wurden zwei Patente zur Trennung von verunreinigter Essigsäure mit Ameisensäure und Wasser mittels Reaktivdestillation, mit dem Ziel reine

Essigsäure zu erzeugen, angemeldet [10,11]. Allerdings waren viele Trennstufen und hohe Rücklaufverhältnisse notwendig, um eine Auftrennung zu erzielen. In diesen Patenten wurde zwar das große Potenzial der Reaktivdestillation für dieses Einsatzgebiet gezeigt, allerdings fehlen eine systematische Untersuchung sowie eine optimierte Prozesskonfiguration.

Die Rückgewinnung von Essigsäure aus wässriger Lösung durch Reaktivdestillation mit *n*-Butanol und Isoamylalkohol unter Einsatz des Katalysators Indion 130 wurde von Saha et al. [12] geprüft. Der Feed bestand aus einer wässrigen Lösung mit 30 % Essigsäure und wurde mit dem Alkohol im molaren Verhältnis von 1:2 gemischt. Essigsäureumsätze von 58 % mit *n*-Butanol und 51 % mit Isoamylalkohol konnten erreicht werden.

Die selektive Veresterung von Ameisensäure aus einem wasserfreien Gemisch von Ameisensäure (Reinheit 98 %) und Eisessig mit Cyclohexen in einer Batch-Reaktivdestillation wurde von Saha und Sharma [13] untersucht. Dem Säuregemisch wurde Cyclohexen im molaren Verhältnis 1:1,1 zugesetzt, was zu einem Umsatz von 85 % von Cyclohexen führte, wobei die Selektivität zu Cyclohexylformiat 64 % betrug.

Für die Abwasserbehandlung ist der Einfluss von Wasser im Ausgangsgemisch auf die Reaktivdestillation zur Isolierung niederer Fettsäuren von wesentlichem Interesse. Da das Wasser auch ein Nebenprodukt der Veresterung darstellt, verschiebt es das Reaktionsgleichgewicht in Richtung der Edukte, wodurch die Entfernung der Fettsäuren behindert wird. In dieser Arbeit wird der Einsatz der Reaktivdestillation für die Trennung wässriger Essigsäure/Ameisensäure-Gemische ohne Verwendung von Katalysatoren untersucht und ein energieeffizientes Trennungskonzept für Abwasserströme vorgeschlagen.

2 Experimentelles

2.1 Verwendete Chemikalien

Methanol ($\geq 99\%$) wurde von Roth, Essigsäure (99 – 100 %) von Merck und Ameisensäure (85 %) von Brenntag bzw. Ameisensäure (98 %) von Roth bezogen. Die Chemikalien wurden ohne weitere Aufreinigung verwendet.

2.2 Analytik

Alle Proben wurden mit einem Gaschromatographen (Shimadzu 2010 Plus) vermessen, der mit einem Flammenionisationsdetektor (FID) und einem Wärmeleitfähigkeitsdetektor (WLD) ausgestattet war. Für die Datenauswertung wurde für Ameisensäure und Wasser der WLD verwendet, für alle anderen Komponenten aufgrund der höheren Empfindlichkeit der FID. Es wurde eine gepackte Quarzglas-kapillarsäule (SUPEL-Q™ Plot) mit einer Länge von 30 m

und einem Innendurchmesser von 0,53 mm eingesetzt. Der Autoinjektor AOC-20i arbeitete im Split-Modus im Verhältnis von 30:1 bei einer Injektionstemperatur von 240 °C. Das Temperaturprogramm im Ofen startete bei 40 °C für 2 min, heizte anschließend mit einer Aufheizrate von 15 °C min⁻¹ auf 150 °C für 5,7 min auf und danach mit 30 °C min⁻¹ auf 200 °C für 1 min.

2.3 Reaktivdestillation

In der Reaktivdestillation werden die Fettsäuren mit Methanol verestert und gleichzeitig die leichtsiedenden Methylster im Destillat der Kolonne abgeführt. Wenn Methanol im Überschuss zugegeben wird, wird das bei der Reaktion nicht verbrauchte Methanol ebenfalls über das Destillat abgeführt.

Ziel der chemischen Reaktion ist die Veränderung der Stoffeigenschaften, um die Azeotrope im Gemisch Essigsäure/Ameisensäure/Wasser zu umgehen. Weiterhin kann der spezifische Energiebedarf gesenkt werden, da die Siedetemperaturen der Produkte geringer sind und das Wasser nicht verdampft werden muss. In Tab. 1 sind die Stoffdaten der Edukte und Produkte gegenübergestellt. Aus diesen Stoffdaten ist zu erkennen, dass Methanol nicht in hohem Überschuss verwendet werden soll, da die Verdampfungsenthalpie von Methanol relativ hoch ist und das überschüssige Methanol über das Destillat entfernt wird.

Tabelle 1. Stoffeigenschaften der betrachteten Komponenten [15].

	ΔH_v [kJ mol ⁻¹]	C_p [J mol ⁻¹ K ⁻¹]	Siedepunkt [°C]
	T^s , 1,013 bar	$T = 20$ °C	1,013 bar
Wasser	40,65	70	100
Ameisensäure	22,69	99	101
Essigsäure	23,70	123,3	117,9
Methanol	35,21	81,1	64,6
Methylformiat	27,92	119,1	31,7
Methylacetat	30,32	141,9	56,87

Die Veresterung ist eine reversible Reaktion, die sauer katalysiert abläuft. In Gl. (1) und (2) sind die Veresterungsreaktionen von Ameisensäure und Essigsäure mit Methanol dargestellt.



Die Ameisensäureveresterung verläuft im Vergleich zur Essigsäureveresterung aufgrund der geringeren sterischen

Hinderung und dem geringeren induktiven Effekt [14] schneller. Außerdem ist die intramolekulare Katalyse bei der Ameisensäureveresterung stärker ausgeprägt, da Ameisensäure die stärkere Säure ist ($\text{p}K_{\text{S}_{\text{HFO}}} = 3,75$; $\text{p}K_{\text{S}_{\text{HAC}}} = 4,756$ [15]). Rönnebeck et al. [16] untersuchten die Essigsäureveresterung bei 40 °C mit äquimolaren Mengen an Edukten und keinen Produkten im Ausgangsgemisch. Sie erhielten nach 49 Tagen eine Gleichgewichtskonstante K_C von 6,3 was einem Umsatz der Essigsäure von 71,5 % entspricht. Im Vergleich dazu wurde bei der experimentellen Untersuchung der Ameisensäureveresterung bei 40 °C und äquimolarem Edukteinsatz ein Gleichgewichtsumsatz von 57 % nach ca. 250 Minuten erreicht.

Die Reaktivdestillationsversuche wurden in einer 2 m hohen Füllkörperkolonne (DN 35) mit einem silberspiegelten Vakuummantel ausgeführt, die mit Raschig-Ringen ($d = 6$ mm) bestückt war. Der gesamte Feedstrom war für alle Versuchsläufe 120 cm³h⁻¹ und wurde der Kolonne im Sumpf zugeführt, wobei das wässrige Essigsäure/Ameisensäure-Gemisch getrennt von Methanol zugeführt wurde (Pumpe Ismatec Reglo ICC). Dadurch wurde der Sumpf mit einem Fassungsvermögen von 1,2 dm³ zur Reaktionszone der Destillationskolonne.

In Abb. 2 ist der Versuchsaufbau schematisch dargestellt. Die elektrischen Heizelemente des Sumpfvordampfers wur-

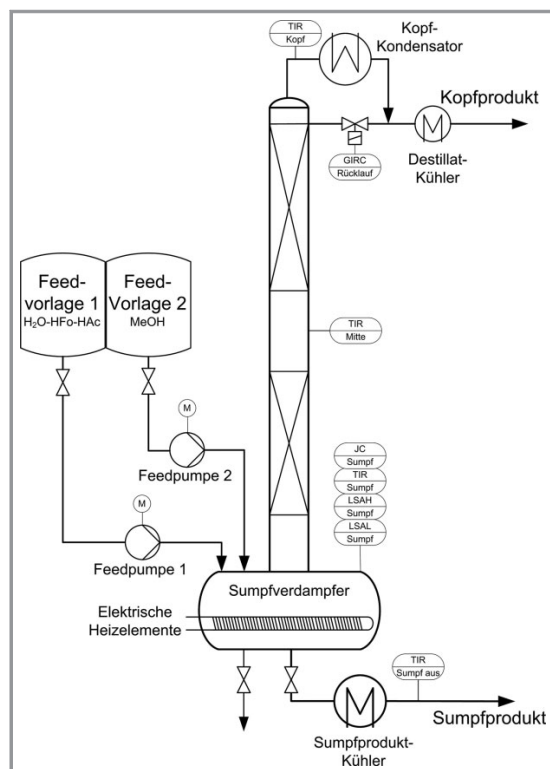


Abbildung 2. Schematische Darstellung des Versuchsaufbaus der kontinuierlichen Reaktivdestillation.

den mit 250 W betrieben. Das Rücklaufverhältnis wurde auf 10 eingestellt. Über das Prozessleitsystem wurden die Temperaturverläufe im Sumpf, in der Mitte und im Kopf der Kolonne kontinuierlich aufgezeichnet. Um das leichtflüchtige Methylformiat vollständig zu kondensieren, wurde der Kopfkondensator auf 5 °C mit einem RCS LAUDA Kryostaten gekühlt. Des Weiteren wurde das Destillat im Produktkühler auf 1 °C mit einem LAUDA ecoline Staredition RE 300 Kryostaten mittels Isopropanol gekühlt. Die Sumpf- und Destillatproben wurden stündlich gezogen und sofort mit Eiswasser gekühlt und analysiert.

Zur Untersuchung des Einflusses der Methanolmenge auf die selektive Abtrennung von Ameisensäure aus dem ternären Gemisch wurden drei verschiedene molare Verhältnisse von Methanol zu den Fettsäuren verwendet; Methanol:Ameisensäure = 2 bzw. 3 und Methanol:(beide Fettsäuren) = 2. Der wässrige Säure-Feed bestand aus 62 Gew.-% Essigsäure, 28 Gew.-% Ameisensäure und 10 Gew.-% Wasser.

3 Ergebnisse und Diskussion

In der kontinuierlichen Reaktivdestillation wurden das molare Verhältnis von Methanol zu Ameisensäure von 2 bzw. 3 sowie das molare Verhältnis von Methanol zu beiden Fettsäuren von 2 untersucht, um einen optimalen Betriebsbereich zu bestimmen. Die Temperaturprofile in der Kolonne waren bei den Versuchen ähnlich, die Sumpftemperatur sank mit zunehmender Methanolkonzentration von 81,4 °C auf 76,2 °C und die Kopftemperatur stieg von 43,6 °C auf 48,7 °C. In Tab. 2 sind die Temperaturen der Kolonne bei den unterschiedlichen Methanoleinsatzmengen zusammengefasst. Die Temperaturänderung zeigt bereits, dass mit zunehmender Methanolmenge im Feed auch die Methanolmenge im Destillat aufgrund der steigenden Kopftemperatur zunimmt und die Siedetemperatur des Gemisches im Sumpf abnimmt. In Abb. 3 sind die Feed- und die Sumpfproduktzusammensetzungen in Abhängigkeit vom molaren Verhältnis von Methanol zu den Fettsäuren gezeigt. Es ist ersichtlich, dass bereits mit einem doppelten stöchiometrischen Verhältnis von Methanol zu Ameisensäure 98 % der Ameisensäure aus dem System entfernt werden konnten

Tabelle 2. Temperaturprofil der Reaktivdestillation für verschiedene molare Verhältnisse von Methanol (MeOH) zu Ameisensäure (HFO) und Essigsäure (HAC).

	MeOH:HFO = 2	MeOH:HFO = 3	MeOH:(HFO+HAC) = 2
Sumpftemperatur [°C]	81,4	80,8	76,2
Temperatur in der Mitte [°C]	50,2	51,5	61,3
Kopftemperatur [°C]	43,6	45,8	48,7

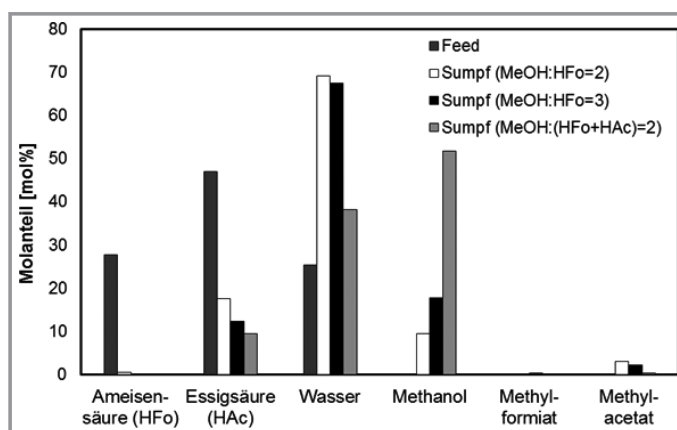


Abbildung 3. Vergleich der Sumpfzusammensetzungen bei der Reaktivdestillation von wässrigen Essigsäure/Ameisensäure-Mischungen mit Methanol für verschiedene molare Verhältnisse von Methanol (MeOH) zu Ameisensäure (HFO) und Essigsäure (HAC).

und 39 % der Essigsäure im Sumpfprodukt wiedergefunden wurden. Weiterhin ist in Abb. 3 zu erkennen, dass die gesamte Konzentration der Methylester im Sumpfprodukt max. 3,3 Mol-% betrug, da sie kontinuierlich über das Destillat abgezogen wurden. Bei den Versuchen mit der geringsten Methanolmenge wurden 60,6 g h⁻¹ Destillat mit einer Zusammensetzung von 20,4 Mol-% Methanol, 41,6 Mol-% Methylformiat und 38 Mol-% Methylacetat produziert.

Die Versuche mit einem molaren Verhältnis von Methanol zu beiden Säuren von 2 führten zu Umsätzen von 99 % der Ameisensäure und 64 % der Essigsäure und erreichten die geringste Destillatmenge von 45,8 g h⁻¹. Dieses Destillat enthielt 46 Mol-% Methanol. Das lässt auf eine langsamere Reaktion beider Säuren schließen. Die Sumpftemperatur war mit 76,2 °C bei diesen Versuchen geringer als bei den Versuchen mit doppeltem und dreifachem molarem Verhältnis von Methanol zu Ameisensäure. Zusätzlich war die H⁺-Ionenkonzentration in der Reaktionszone geringer, da es zu einer stärkeren Verdünnung durch die große Methanolmenge kam, wodurch die Reaktion verlangsamt wurde.

Bei den Versuchen mit einem Verhältnis von Methanol zu Ameisensäure von 3 wurden 64,3 g h⁻¹ Destillat abgezogen. Dieses Destillat wies eine Zusammensetzung von 24,4 Mol-% Methanol, 33,5 Mol-% Methylformiat und 42,1 Mol-% Methylacetat auf. Dabei wurden 99,3 % Ameisensäure und 71,5 % Essigsäure aus dem ternären Gemisch entfernt.

Verglichen mit den Gleichgewichtsumsätzen der Veresterungsreaktionen konnte in der Reaktivdestillation die Ameisensäure vollständig verestert werden und bei der Essigsäureveresterung wurde ein vergleichbarer Umsatz bei wesentlich geringerer Verweilzeit erzielt.

Das Destillat bestand bei allen Versuchen aus dem ternären Gemisch Methylformiat, Methylacetat und Methanol. Die Herausforderung bei der Auftrennung dieses Gemisches liegt im Vorhandensein eines binären Tiefsiedeazeotrops zwischen Methanol und Methylacetat. Winkler [17] untersuchte die Auftrennung von Methylacetat/Methanol mittels Pervaporation. Mit hydrophilen Membranen wurde im Bereich des Azeotrops die größte Auftrennung erzielt.

4 Zusammenfassung und Ausblick

Die Rückgewinnung verdünnter niederer Fettsäuren aus Abwasserströmen wird oft durch Azeotropbildung erschwert. In diesem Projekt wird der Einsatz reaktiver Trennverfahren für die Isolierung von Essigsäure und Ameisensäure aus einem wässrigen Gemisch untersucht. In der Reaktivdestillation werden die Fettsäuren mit Methanol ohne zusätzlichen Katalysator verestert, wobei die Ameisensäureveresterung wesentlich schneller abläuft. Bei einem molaren Verhältnis von Methanol zu Ameisensäure von 3 können dadurch 99,3 % der Ameisensäure und 71,5 % der Essigsäure aus der ternären Mischung abgetrennt werden. Das Destillat bestehend aus Methanol, Methylformiat und Methylacetat kann in einem weiteren Schritt, beispielsweise mittels Pervaporation, aufgetrennt werden.

Die Autoren bedanken sich bei Raphael Neubauer für das Engagement bei der Durchführung seiner studentischen Arbeit im Rahmen dieses Projektes sowie bei NAWI Graz für die finanzielle Unterstützung.

Formelzeichen

C_p	[J mol ⁻¹ K ⁻¹]	spezifische Wärmekapazität
K_C	[-]	konzentrationsbasierte Gleichgewichtskonstante
T	[°C]	Temperatur
T^S	[°C]	Siedetemperatur
ΔH_v	[kJ mol ⁻¹]	Verdampfungsenthalpie

Abkürzungen

FID	Flammenionisationsdetektor
MeOH	Methanol
HAc	Essigsäure
HFo	Ameisensäure
WLD	Wärmeleitfähigkeitsdetektor

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