Upgrading carboxylates from wastewater

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Upgrading carboxylates from wastewater

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by

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♫ Me despertaba con la paz del que aprendió,
que lo importante en esta vida es el tratar,
que lo que cuesta es lo que no voy a olvidar. ♫
(Como nosotros, Rubén Blades  *& Editus*  *)*

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Chapter 1

General Introduction

1.1. Chemicals from wastewater

The world population has multiplied rapidly over the last 50 years, and it is expected to reach 9 billion by 2050.[1] This increase in human population led to an increase in resource utilization and waste generation. Our society consumes a lot of resources (mainly from petroleum) for the production of the fuels and chemicals. Most of the petroleum in a conventional refinery is used for transportation, fuels and energy, and the rest (~ 5%) is used for the production of chemical products.[2] Therefore, several alternatives for energy and chemicals production have been considered. An alternative to solve this problem can be to recover resources from waste streams and upgrade them to valuable products. Traditional waste treatment approach is treatment-oriented, which focus on complying with environmental regulations.[3] However, innovations in resource recovery technologies are required to convert waste into commercially attractive chemicals.

Several compounds can be recovered from waste streams, and some examples are nitrogen, phosphorus, trace metals and organic carbon. For the recovery of organic carbon, an established technology is anaerobic digestion, which produces methane-containing biogas. This is a worldwide accepted technology and has been used for a variety of industries to treat diverse wastes.[4, 5] The utilization of anaerobic digestion worldwide focuses on the production of biogas. However, there is a growing interest to produce and recover higher-value chemicals such as carboxylic acids. The carboxylic acids produced by anaerobic open culture fermentation are linear short-chain aliphatic monofunctional compounds produced at pH above the pK_a of the acids. Therefore, the acids are produced in their salt form and are known as carboxylates. Carboxylates are a key group because their functional groups can be used as building blocks for the chemical industry to manufacture a wide range of chemicals, pharmaceuticals, and materials.[6] The term carboxylate platform has been used to describe this process that generates a mixture of carboxylates as intermediate platform chemicals.[7] The main short-chain carboxylates produced are acetate, propionate, lactate and *n*-butyrate, furthermore other carboxylates such as valerate, caproate and caprylate can be produced by a consecutive fermentation.[8, 9] Some examples of their applications are: acetic acid and derivatives are used as etching agent, as components in detergents, in the production of lignin-containing polyurethane and as preservation ingredient in the food industry; propionic acid is used as a preservative in the food industry, as compound in herbicides, in cellulose acetate propionate plastics, while the propionate salts, such as sodium and calcium propionate, are used in agriculture for animal feed and grain preservation; butyric acid is used in the perfume and fragrance industry, the polymer industry and the pharmaceutical industry.[10-12]

However, biogas production is the only product within the carboxylate platform that is currently utilized for complex waste treatment on a large scale because production of liquid chemicals presents important scientific and technical challenges. The main challenges that must be overcome are the inefficient recovery of the carboxylates and the requirement to inhibit the methanogen producers for directing the microbial process to the target carboxylate.[8]

1.2. Carboxylates production from wastewater

Anaerobic open culture fermentation is an interesting route to produce carboxylate because it reduces capital and operational cost compared to aerobic processes, by circumventing oxygen addition and sterilization requirements.[13]

Additionally, a variety of solid and liquid organic wastes can be used for the production of different carboxylates.[3] Some of the solid wastes that have been analyzed for the production of carboxylates are sludge, food waste and organic fraction of municipal solid waste, and wastewater generated from the agricultural, dairy, pulp and paper industries. Some specific examples are palm oil mill effluent,[14] cheese whey permeate and paper mill wastewater.[9, 15] The type of wastewater influences the carboxylate type and total carboxylate concentration. In general, acetate and propionate are the main carboxylates produced from waste streams. However, protein-rich, gelatin-enriched waste streams and activated sludge enhance the production of odd numbers and longer carboxylates such as valerate and caproate.[16] Additionally, wastewaters with high lactate concentrations promote butyrate production.[8]

The pH is a crucial factor during the anaerobic mixed-culture fermentation for the production of the carboxylates. Firstly, most of the acidogens cannot survive in extremely acidic or alkaline environments, while a pH close to neutral would favor methanogenic growth (pH between 6 and 8).[16-18] Secondly, pH can affect the type of carboxylate produced, particularly acetic, propionic and butyric acid, and it is dependent on the type of waste used.[3] Finally, the pH has a crucial effect during the subsequent recovery of the carboxylates, since their traditional recovery at pH above the pK_a involves high energy consumption and waste coproduction.[19]

Therefore, the development of efficient recovery and purification processes is critical to improve competitiveness with respect to petrochemicals.[20] A number of processes for carboxylates recovery from broth has been studied. They mainly include precipitation, chromatography, membrane separation, extraction and distillation.[19, 21]

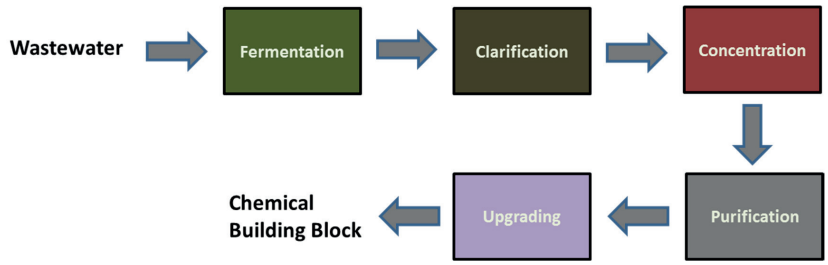

Figure 1.1. General recovery sequence for recovery, purification and upgrading of carboxylates produced by fermentation.

The recovery of carboxylates aims to remove water and major impurities such as solids and biomass, followed by a further purification and transformation into secondary products. A

traditional separation train requires clarification (removal of large particles, cells and their debris), concentration (removal of excess water), purification (removal of remaining impurities) and upgrading to chemical derivatives (Figure 1.1). Clarification is usually done by filtration or centrifugation. The major barrier in the use of carboxylates is the technical difficulty associated with their concentration and purification from the dilute aqueous solutions.[22] Therefore, several options for the concentration and further purification/upgrading of the carboxylates are discussed in section 1.3.

1.3. Technologies for the recovery of carboxylates from wastewater

Most of the technologies for the recovery of carboxylates are not integrated with the rest of the process and do not take into account the further upgrading of the chemicals. Lopez Garzon et al. (2014) present a detailed analysis of the different techniques for the recovery of carboxylic acids produced by fermentation.[19] Additionally, several reviews deal with specific carboxylic acids such as lactic acid [23-25] and citric acid.[26] However, not all methods can be used for carboxylates produced by open culture anaerobic fermentation.

Table 1.1. Properties of carboxylic acids produced by anaerobic mixed-culture fermentation (PubChem).

Carboxylic acid (PubChem CID)	pK_a	Solubility in water (at 25 °C) (g/L)	Log P	Boiling Point (° C)[a]	Melting Point (° C)
Acetic acid (176)	4.76	1000	-0.17	117.9	16.6
Propionic acid (1032)	4.88	1000	0.33	141.1	-20.7
Butyric acid (264)	4.82	60	0.79	163.7	-5.7
Valeric acid (7991)	4.84	24	1.39	186.1	-34
Caproic acid (8892)	4.88	10.3	1.92	205.8	-3.4
Caprylic acid (379)	4.89	0.789	3.05	239	16.3
Lactic acid (612)	3.86	1000	-0.72	122[b]	16.8

[a.] Boiling point at 1 bar [b.] Boiling point at 0.02 bar.

As discussed before, open culture anaerobic fermentation takes place at a pH above the pK_a of the acids, and results in the dissociated form of the carboxylic acid (carboxylate). The complications for carboxylic acids recovery are their low concentration (2-20 g/L), high solubility in aqueous solution, pK_a below operational pH, low partition coefficient (especially for small molecules) and boiling point above the water boiling point (Table 1.1). The melting point for some of the carboxylic acids, such as acetic acid, caprylic acid and lactic acid, is useful for freeze crystallization; however, the low concentration of the carboxylic acids impedes its utilization as a concentration step. Nevertheless, some technologies have been developed for the recovery of carboxylates from anaerobic open culture fermentation such as chain elongation (to improve the Log P);[13] electrodialysis for in-situ removal, concentration, demineralization and conversion of salt to the acid form;[27] electrodialysis coupled with ester formation (to remove the salt and regenerate the solvent);[28] bipolar membrane electrodialysis; [29, 30] adsorption and desorption with methanol plus hydroxide;[31] and multi-stage evaporation integrated with ketonization or esterification.[32]

However, these technologies have several limitations that interfere with their utilization at industrial scale. At industrial scale, the key requirements of a recovery process are high purity specification (>99.5%), high extent of recovery (90-100% yield in the recovery section), low chemicals and energy consumption and low waste production. For this reason, it is necessary to explore alternatives to integrate the recovery and upgrading steps of carboxylates.

1.4. Scope and thesis outline

In view of the limitations for recovery of carboxylic acids from waste streams, the aim of this thesis is to develop a method to recover carboxylic acids from wastewater at neutral pH that avoids waste salt co-production. This thesis starts evaluating a previously reported method that uses dimethyl carbonate, then a new desorption method with CO_2-expanded alcohols is developed and validated, and finally the limits for implementation of this method are determined.

In **Chapter 2** separation with catalytic conversion of carboxylates is studied for a previously developed technique using dimethyl carbonate. In this chapter, the carboxylate (acetate) is bound to different quaternary ammonium groups and the reaction equilibria and pathways are studied in detail. The aim is to understand and reduce the byproduct formation (methanol) during the alkylation reaction of acetate with dimethyl carbonate to produce methyl acetate. This chapter shows that the alkylation with dimethyl carbonate can achieve high yields; however, the highly dilute system and consumption of dimethyl carbonate compromised the feasibility for low value chemicals such as methyl acetate.

Since dimethyl carbonate can be produced from methanol and carbon dioxide, **Chapter 3** presents the proof of principle for performing the desorption with a mixture of methanol and carbon dioxide below the critical point, known as CO_2-expanded alcohols. This method produces a non-aqueous methyl carbonic acid that is used to protonate the carboxylate bound to the resin. It is proven to work for the recovery and desorption of acetate, lactate and succinate, with methanol and ethanol as alcohols. Different integration opportunities and applications are discussed in this chapter.

Chapter 4 presents the validation of the new CO_2-expanded alcohol method for the recovery of carboxylates (acetate, propionate, butyrate, valerate and lactate) from a paper mill wastewater. The effects of different carboxylates and counter-ions are presented with possible ways to operate this technology. The dilute nature of the resulting carboxylic acid and alcohol solution is identified as the main bottleneck of the system.

For this reason, the limits of the system are studied in **Chapter 5**, in which the ion exchange adsorption and desorption equilibria are studied for acetate, chloride and CO_2-expanded methanol. The adsorption isotherms are determined for acetate and chloride using a strong anion exchange resin and the desorption isotherms are determined at different CO_2 pressures (2-20 bar). The column dynamics are studied and modeled using an equilibrium dispersive model.

Finally, **Chapter 6** uses the knowledge generated in this research to evaluate the potential bottlenecks and applications of the technology. The price of the produced chemicals, the concentration (total amount) and the operational costs are the main factors taken into account. In this respect, technical recommendations are provided for further implementation of this or similar technologies.

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Chapter 2

Separation and Catalysis of Carboxylates: Byproduct Reduction during the Alkylation with Dimethyl carbonate

Abstract

Quaternary ammonium carboxylates (both ionic liquids and resins) can be used for formation of methyl carboxylate esters in an alkylation reaction with dimethyl carbonate (DMC). This reaction is pursued in the context of a low-waste process for recovery and upgrading of fermentative carboxylates. Byproducts, such as methanol, are produced during the alkylation reaction with DMC. A molar yield of methyl acetate on acetate of 0.84 and modest selectivity (0.54─ 0.95 mol methyl acetate/mol methanol) are obtained with an anion exchanger fully in the acetate form. Water and DMC concentrations have a strong effect on the yield and selectivity of the reaction. Model calculations indicate that an excess of 50 mol DMC_{in}/ mol $acetate_{in}$ in DMC is needed to achieve yields above 0.98 mol methyl acetate/mol $acetate_{in}$, and water concentrations in the resin below 0.04 g water/g resin to achieve a selectivity above 1.1 mol methyl acetate/mol methanol. The explanation for the modest selectivity is the hydrolysis and absence of methylating activity of the methyl carbonate anion. This indicates that 1 mol of DMC is consumed for the alkylation of 1 mol of a monocarboxylate salt. The utilization of a low amount of DMC is critical, especially for low value products such as methyl acetate.

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2.1 Introduction

Esters are important compounds that are used extensively in the industry and laboratory. They constitute a major backbone of numerous compounds because of the reactivity of their functional group. Some esters can be directly produced by fermentation,[1, 2] but traditionally they have been produced from an acid-catalyzed esterification of alcohols with carboxylic acids. Many carboxylic acids are obtained by fermentation.[3] The traditional recovery process of such carboxylic acids involves protonation (since the most efficient fermentations require neutral pH) and further isolation by different methods.[4] Figure 2.1 shows an example that involves a recovery by extraction and an acid catalyzed esterification with an alcohol (Figure 2.1, option A). The drawbacks with these separation-esterification methods are the high production of waste and the high energy requirements.

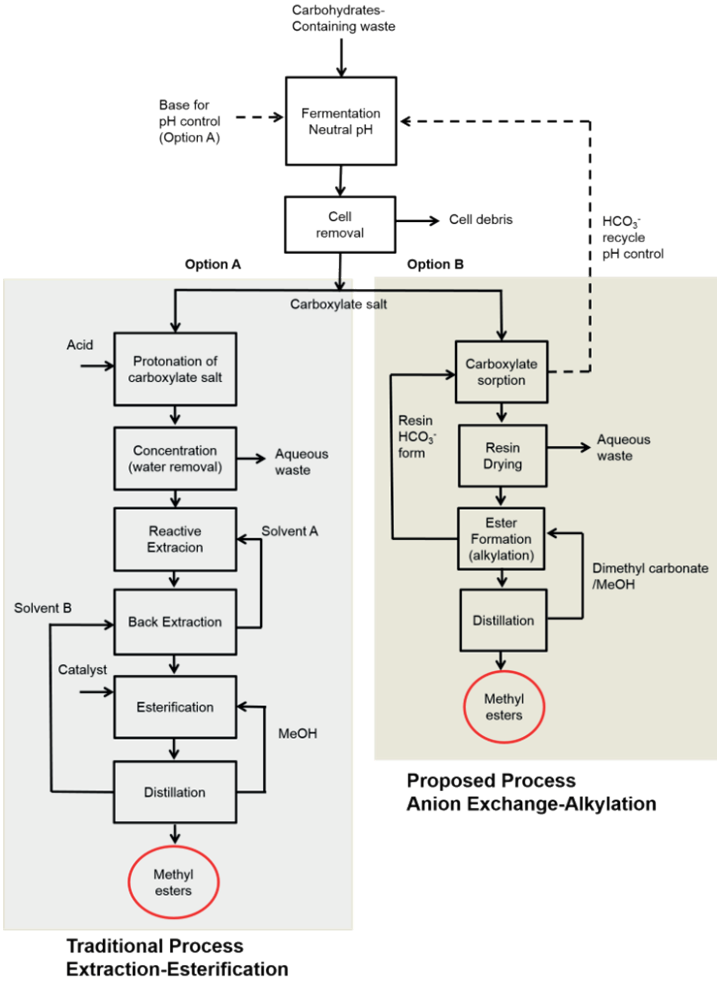

Figure 2.1. Block diagram for the production of esters from carboxylates produced via fermentation. Option A: traditional process: extraction and esterification. Option B: proposed process: anion exchange and alkylation.

An alternative is the direct downstream transformation of the carboxylate salt into esters (Figure 2.1, option B). The direct transformation of the carboxylates may reduce the amount of energy used and waste produced by traditional methods. In Figure 2.1, option B, the carboxylate salt is recovered using a strong anion exchange resin (containing quaternary ammonium group) followed by an alkylation reaction to produce methyl esters. The resin functions both as anion capturing agent in the separation and as catalyst in the alkylation. Different alkylating agents have been reported,[5, 6] but dimethyl carbonate is recognized as a promising option. Dimethyl carbonate (DMC) is a green solvent commercially produced from carbon monoxide and methanol, in the future potentially from carbon dioxide and methanol.[7, 8] It can react with a number of nucleophilic substrates, and it is an attractive option because of its lower toxicity compared with other methylating agents.[7, 9, 10] DMC may decompose into methanol and carbon dioxide in the presence of water. It has been used successfully for the alkylation of carboxylic acids in the presence of a strong base,[11-14] and with strong anion exchange resins.[5, 14]

Strong anion exchange resins have been used for the recovery of succinate and alkylation with dimethyl carbonate to produce dimethyl succinate. Recovery and alkylation yields above 98% have been obtained in a reaction with DMC, which was the alkylating agent as well as the solvent.[14] A drawback of the used procedure is the production of 5 mol of methanol per mole of dimethyl succinate, which indicates that only a minor portion of DMC was used for ester formation. It was suggested that a medium without water is necessary to avoid the undesired methanol formation.[4] However, this is only an alternative if the formation of methanol is based on a side reaction, and not due to the formation of the methyl ester. For this reason it is important to understand the role of each of the components, such as dimethyl carbonate, the quaternary ammonium group, the backbone of the resin, methanol, and water.

As in the succinate example, an excess of DMC is used during methylation in most of the reported data.[9, 15, 16] This excess of DMC might be necessary to obtain high yields, by directing the equilibrium to the products. There are only a few publications that focus on the utilization of DMC during alkylation reactions. In reported cases, the methylation of phenol or aniline produces stoichiometric methanol as coproduct. In these examples, protonated substrates are used, whereas carboxylates are unprotonated.[15, 17] The amount of DMC that is consumed for the production of different chemicals is important, depending on the prices and availability of each of the chemicals. Table 2.1 shows the price of different methyl esters that can be produced via alkylation of carboxylates (produced by fermentation). For instance, methyl acetate is a product that has a slightly lower price than DMC. In this particular case, the amount of DMC consumed in the reaction and the byproduct reduction is critical. To be commercially applied, the amount of DMC consumed during the reaction has to be minimized, implying that the background of byproduct formation (methanol) has to be understood.

A possible source of methanol is the direct hydrolysis of DMC to methanol and carbon dioxide (Figure 2.2, R.6).[14] Other pathways for methanol formation from DMC can occur. According to Tundo,[9] DMC behaves as a methoxycarbonylating agent at 90 °C and as methylating agent at temperatures higher than 120 ºC. Therefore, at temperatures lower than 120 °C, reaction R.1 forms an anhydride. Figure 2.2 shows the situation for acetate as carboxylate. Afterward, the methoxide intermediate attacks a carbonyl group of the anhydride, forming methyl acetate and the methyl carbonate ion (Figure 2.2, R.3).[18, 19] Methyl carbonate cannot serve as methyl donor for methyl acetate formation according to the mechanism of R.1 and R.3 (Figure 2.2). If this reaction mechanism takes place, the theoretical amount of methyl ester produced from DMC is in a ratio of 1:1 for a monocarboxylate anion. This also implies that

the resin is in the methyl carbonate form after reaction. The methyl carbonate ion can hydrolyze in the presence of water into the bicarbonate ion and methanol (R.5).

Table 2.1. Methyl esters that can be produced by the alkylation of carboxylates*

Compound	Molecular weight (g/mol)	Low Price (US $/kg)	High Price (US $/kg)	Low price (US $/mol)	High price (US $/mol)
Dimethyl carbonate	90.08	0.9	1.3	81	117
Methanol	32.04	0.2	0.4	6	13
Methyl acetate	74.08	0.6	1.3	44	96
Methyl propionate	87	2.8	3.2	244	278
Methyl butyrate	101.13	1	2	101	202
Methyl hexanoate	130.18	2	6	260	781
Methyl lactate	104.1	1	3	104	312
Dimethyl succinate	146.14	2	4	292	585

*Source: ICIS, and average of market prices from different suppliers (Zibo Nature International Trading Co., Zhengzhou Yi Bang Industry Co., Dongying City Longxing Chemical Co., Anhui Eapearl Chemical Co., Xiamen Aeco Chemical Industrial Co., Orchid Chemical Supplies Ltd.) on March 26 2015.

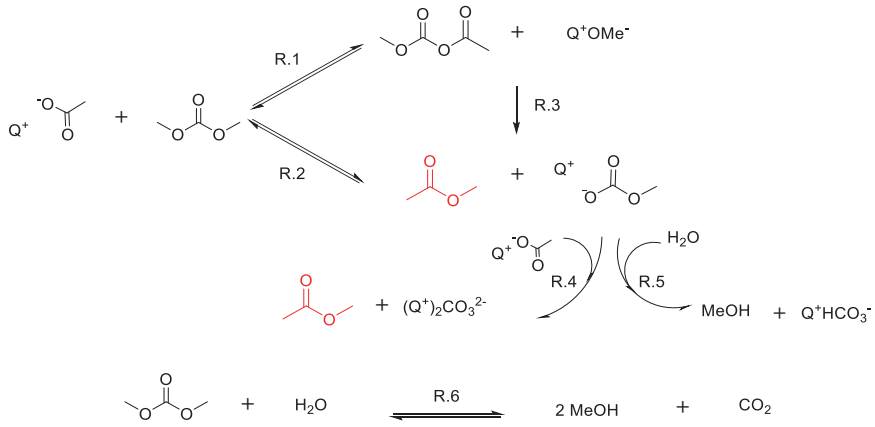

Figure 2.2. Reactions considered in the formation of methyl acetate by alkylation using DMC.

The second possible pathway, at high temperature (>120 °C), is methylation without the anhydride intermediate, in which case the acetate anion attacks a methyl group of DMC (Figure 2.2, R.2). If acetate can also attack the methyl group of methyl carbonate (R.4), there is the possibility of producing 2 mol of methyl ester per mol of DMC consumed. To accomplish this, we have to avoid reaction R.5, the hydrolysis of the methyl carbonate anion to bicarbonate and methanol. As a consequence, there would be no methanol formation, and the resin would turn into the carbonate form.

The stability of the methyl carbonate anion determines if hydrolysis (Figure 2.2, R.5) or a second methylation reaction (R.4) will occur. Alkylammonium methyl carbonate salts are stable at temperatures below 170-180 °C, but they hydrolyze promptly in the presence of water

(R.5).[20-22] An option for avoiding this hydrolysis step is to have an excess of methanol to push the equilibrium in the direction of the methyl carbonate anion.[20, 23]

Also, methanol can be formed by decomposition (Hoffman elimination) of certain quaternary ammonium groups. Quaternary ammonium groups are unstable at temperatures above 120 °C. It has been reported that at 200 °C tetramethylammonium acetate suffers a pyrolysis, and produces methyl acetate with yields of 60%.[24] Our experiments are performed at temperatures below 120 °C to avoid this decomposition. According to the reactivity of DMC at these temperatures[9] the reaction probably proceeds via the carboxylation (Figure 2.2, R.1 and R.3) which will limit the methylation of acetate with the methyl carbonate anion.

This chapter reports the reactivity and selectivity of several quaternary ammonium salts with dimethyl carbonate to produce methyl carboxylate esters. We studied the sources of the byproduct formation and the requirements for their reduction.

2.2. Materials and Methods

2.2.1. Materials

The chemicals were of analytical grade (received from Sigma-Aldrich) and were used directly: potassium acetate (≥99.9%), Dowex Marathon MSA resin (type I; macroporous, chloride form, total exchange capacity 1.1 equiv/L), methyl acetate (≥99.9%), dimethyl carbonate (≥99.9%), acetonitrile (≥99.9%), tetramethylammonium acetate (≥90%), tetrabutylammonium acetate (≥97%), tetrabutylammonium chloride (≥97%), and triethylmethylammonium methyl carbonate (50% in 2:3 m/m methanol:water). The aqueous solutions were prepared by diluting the potassium acetate salt to the required concentrations with deionized water from a Milli-Q water purification system (Millipore).

2.2.2. Loading of the dowex marathon MSA chloride with acetate

The resin Dowex Marathon MSA (Sigma-Aldrich) was converted from the chloride form to the hydroxide form by the column elution technique. The resin was washed with 10 bed volumes of a 1 mol/L solution of NaOH for 2 h. Then the resin was washed five times in a batch with 50 mL of deionized water (Mili-Q water purification system), and the excess water was removed using a vacuum filter. For the first experiments, the loading of the acetate to the resin was performed in a batch operation. In this batch, 3 g of resin was added to 50 g of a 15 g/L solution of sodium acetate. The batches were kept for 16 h, in which equilibrium was achieved. Samples of the liquid were taken before and after equilibrium was reached. Previous experiments showed that this was sufficient time to attain equilibrium.[14] The samples were analyzed by HPLC as discussed in section 2.5, and the amount of acetate adsorbed by the resin was calculated. For further experiments, the resin was completely loaded with acetate. In this case, the resin was converted from the chloride form to the acetate form by the column elution technique. Samples of the outlet from the column were checked for chloride concentration with a colorimetric method (QuantiChrom™), until the concentration was lower than 9 mg/L.

2.2.3. Resin preparation for alkylation reactions

The resin was loaded with the acetate anion as described in section 2.2.2. Then it was washed five times in a batch with 50 mL of deionized water as described in section 2.2.1. After this, the resin was collected and washed three times with 30 mL of methanol (anhydrous) using a

Millipore Steriflip 60 μm nylon net filtration unit. The resin was dried in an oven at 60 °C for 24 h.

2.2.4. Alkylation reactions

The alkylation reactions were carried out in closed glass tubes in a Greenhouse Plus Parallel Synthesizer (Radleys®). All the experiments were performed in triplicate. The acetate sources (quaternary ammonium acetate in salt or resin form) were added to have an amount of 0.2 mmol (0.04 mmol/g total) of acetate anion in the reaction tubes (0.4 mmol of acetate (0.08 mmol/ g total) in the case of tetramethylammonium acetate). The experiments with the chloride form of the resin or quaternary ammonium chloride had a molar amount of quaternary ammonium groups equal to their acetate counterpart. The amount of dry resin added is 0.15 g (capacity 0.12 g of acetate/g of resin). In the first set reaction tubes 5 g (55.5 mmol) of DMC was added as solvent. The tubes were flushed with N_2 gas to remove the air headspace. The tubes were heated in the Greenhouse Plus Parallel Synthesiser at 60 °C or 100 °C for 20 or 2 h, respectively. The tubes were agitated with a magnetic stirrer at 600 rpm. Initial and final samples of the liquid phase of the reaction tubes were analyzed for methyl acetate, methanol, and water content.

In the second set of experiments the same system was utilized with acetonitrile (3.8 g) as solvent and 0.100 g (1.1 mmol) of dimethyl carbonate. The reactions were performed for 2 h at 100 °C and 600 rpm. Initial samples of the solvent and final samples of each of the liquid phases were analyzed for methyl acetate, dimethyl carbonate, methanol, and water content.

2.2.5. Analytical methods

Acetic acid concentrations from aqueous samples were analyzed on a Waters HPLC system using a Bio-Rad Aminex HPX-87H column (7.8 × 300 mm) at 60 °C. Phosphoric acid (1.5 mmol/L at 0.6 mL/min) was used as an eluent. Quantification was done by UV detection at 210 nm using an external standard.

Reactions carried out in acetonitrile were analyzed by gas chromatography (GC) on an Agilent 6890N system equipped with a CP-PoraPLOT Q column (25 m length × 0.32 mm internal diameter, 10 μm film, 2.5 m particle trap) and a flame ionization detector. Helium was used as carrier gas. An injection size of 1 μL was used with a split ratio of 20. The injector temperature was 200 °C. The column was initially at 60 °C and a 10 °C/min temperature ramp was used up to 150 °C followed by a second ramp of 20 °C/min up to 240 °C. Methanol, DMC and methyl acetate were identified by comparison with known standards. Reactions using DMC as solvent and reagent were analyzed in the same GC system using an HP-Innowax column (30 m length × 0.25 mm internal diameter, 0.25 μm film). Injection and detector conditions were maintained. The column temperature program was maintained at 60 °C for 0.5 min, and then a 10 °C/min temperature ramp was used up to 220 °C with a final holding time of 5 min. Methyl acetate, dimethyl carbonate, methanol and byproducts were identified by mass spectrometry (MS). Karl Fischer titrations (Metrohm 831 KF coulometer) were used for the quantification of water concentration in the samples.

2.2.6 Thermodynamic data

The standard enthalpy and the standard Gibbs energy of formation of the components involved in the reactions were obtained from reported data, [25-28] and are shown in Table 2.2.

The integrated form of the van't Hoff equation was used to correlate the temperature dependence of the chemical equilibrium constant (eq 1), and calculate the values at the operation temperature.

$$\ln\big(K(T)\big) = \frac{\Delta H_r^0 - \Delta G_r^0}{R * T^0} - \frac{\Delta H_r^0}{R}\left(\frac{1}{T}\right) \qquad \text{(Eq. 1)}$$

Table 2.2. Thermodynamic data of pure substances involved in the reactions.

Substances	State	$\Delta H_f°$ (kJ mol^{-1})	$\Delta G_f°$ (kJ mol^{-1})	ref.
Dimethyl carbonate	liquid	-613.78	-464.23	[25]
Water	liquid	-285.83	-237.14	[28]
Methanol	liquid	-239.1	-166.6	[28]
Acetate	aqueous	-486	-369.3	[28]
Bicarbonate	aqueous	-692	-586.8	[28]
Methyl carbonate	aqueous	-598.69*	-620.13	[26]
Methyl acetate	liquid	-442.79	-328.39	[27]

*Using a pK_a of 1.7 [29] to calculate the dissociation of methyl hydrogen carbonate to the methyl carbonate anion.

The assumptions used for the thermodynamic calculations are constant ΔH_r^0 because of the relatively small temperature interval considered (293-373 K); the system is pseudohomogeneous, so that the quaternary ammonium group behaves as if it is dissolved in DMC; the reaction has reached equilibrium when it is stopped.

Other components such as water, methyl acetate, and methanol in dimethyl carbonate are not at standard conditions, so the real interactions between these three components in DMC are considered. These interactions are represented as the activities a_i for each component, and calculated with the UNIFAC model. In this model, the size and surface of the molecules are described with the volume parameter r and the area parameter q. These parameters were calculated from molecular structure information and compared with reported data (Table 2.3).

Table 2.3. UNIFAC values of r_i and q_i.

Component	r_i	q_i	ref.
Methyl acetate	2.8042	2.5760	[27]
Water	0.9200	1.4000	[27]
Methanol	1.4311	1.4320	[27]
Dimethyl carbonate	3.048	2.816	[30]

The activity coefficient (γ_i) was calculated using the UNIFAC model[31, 32] and then the values were used to correct the equilibrium constant, K, calculated by the Gibbs reaction energy (eq 1). The molar-based chemical equilibrium constant K_x is related to the activity-based chemical equilibrium constant K as shown in eq. 2.

$$K = K_x * K_\gamma \qquad \text{(Eq. 2)}$$

K_γ is the activity coefficient quotient. This was used for the calculation of the apparent equilibrium constant K_x, (eq 3 and 4).

$$K_{x,R.2} = K_{R.2} \frac{\gamma_{DMC} * \gamma_{QAc}}{\gamma_{MeAc} * \gamma_{QMeCO_3}} \quad \text{(Eq. 3)}$$

$$K_{x,R.5} = K_{R.5} \frac{\gamma_{H_2O} * \gamma_{QMeCO_3}}{\gamma_{MeOH} * \gamma_{QHCO_3}} \quad \text{(Eq. 4)}$$

The assumptions for the calculation of the activity coefficients were the following: the methyl carbonate, acetate and bicarbonate anions have the same change in Gibbs energy when changing from an aqueous solution to a salt in DMC, so $\gamma_{QMeCO3}/\ \gamma_{QAc} = 1$; and the activity coefficient for the solvent (γ_{DMC}) is 1. The group contributions for the UNIFAC model are obtained from the literature.[31] The activity coefficients were assumed to be constant within the studied range, and were calculated at the maximum concentrations of methyl acetate, methanol, and water.

The resulting values of K_x were used to calculate the change in the chemical equilibrium of the reactions. The equilibrium amounts were used to calculate yield (moles of methyl acetate per mole acetate in) and selectivity (moles of methyl acetate per mole of methanol) at equilibrium for the system at different initial amounts of DMC and water. The amounts (n) of methyl acetate and methanol are calculated from a system of equations in which eqs 3-11 were solved simultaneously. Equations 7-11 represent material balances for the conserved groups: carbonate, methyl, acetate, quaternary ammonium and hydroxyl groups, respectively.

$$K_{x,R.2} = \frac{n_{MeAc} * n_{QMeCO_3}}{n_{DMC} * n_{QAc}} \quad \text{(Eq. 5)}$$

$$K_{x,R.5} = \frac{n_{MeOH} * n_{QHCO_3}}{n_{H_2O} * n_{QMeCO_3}} \quad \text{(Eq. 6)}$$

$$2n_{DMC_{in}} = 2\, n_{DMC} + n_{QMeCO_3} + n_{QHCO_3} + n_{MeAc} \quad \text{(Eq. 7)}$$

$$n_{DMC_{in}} = n_{DMC} + n_{QMeCO_3} + n_{QHCO_3} \quad \text{(Eq. 8)}$$

$$n_{QAc_{in}} = n_{QAc} + n_{MeAc} \quad \text{(Eq. 9)}$$

$$n_{QAc_{in}} = n_{QAc} + n_{QHCO_3} + n_{QMeCO_3} \quad \text{(Eq. 10)}$$

$$n_{H_2O_{in}} = n_{H_2O} + n_{MeOH} \quad \text{(Eq. 11)}$$

2.3. Results and Discussion

2.3.1 Role and stability of the quaternary ammonium group

The role of the quaternary ammonium group and the acetate source were studied for methyl acetate and byproduct (methanol) formation. The resin Dowex Marathon MSA in the chloride and acetate forms, potassium acetate (KAc), tetramethylammonium acetate ($Me_4N^+Ac^-$), tetrabutylammonium acetate ($Bu_4N^+Ac^-$), and tetrabutylammonium chloride ($Bu_4N^+Cl^-$) were used. A qualitative inspection showed that the solubility of the compounds in DMC differs considerably. Tetrabutylammonium chloride dissolves in DMC, while the other compounds

dissolve poorly (especially $Me_4N^+Ac^-$). The result is a solid-liquid system for potassium acetate, tetramethylammonium acetate, and the Dowex MSA resin, while tetrabutylammonium acetate yields a monophasic liquid system. The higher hydrophobicity of the butyl groups in tetrabutylammonium acetate might be the cause of the higher solubility in DMC. The solubilities improve with increasing temperature, which might increase the rate of the reactions. Experiments were performed at 60 °C to investigate the reactivity at low temperatures, at which the hydrolysis of DMC can be avoided.

The results prove for the first time the alkylation of a quaternary ammonium acetate salt with DMC to produce methyl acetate. Other researchers have used tetrabutylammonium chloride and K_2CO_3 as catalyst for the esterification of carboxylic acids with DMC.[33] In our experiments, we start directly with the carboxylate form of the quaternary ammonium group for the alkylation. A novelty is that, besides strong anion exchange resins,[14] we can use liquid quaternary ammonium salts (ionic liquids) for acetate recovery and as catalytic agent.

Table 2.4 shows the final concentration of methanol, methyl acetate, and water for each of the experiments (average of triplicates) after 20 h reaction at 60 °C with DMC as both solvent and alkylating agent. The initial concentration of water in DMC was 0.0120 mmol of H_2O/g of DMC, and initially there is no methyl acetate or methanol. The blanks and KAc experiments result in no methanol or methyl acetate formation. This indicates a positive correlation between the hydrolysis of DMC and the presence of the quaternary ammonium group. Methanol is formed in the presence of the quaternary ammonium cation. As a comparison, Dowex Marathon MSA chloride form and KAc experiments were performed with similar amounts of water (0.034-0.047 mmol of H_2O/g total), but no methanol is formed in the case of the KAc. This suggests that reaction R.6 (Figure 2.2) does not take place.

Table 2.4. Reaction of DMC as solvent with different quaternary ammonium materials at 60 °C for 20 h[a]

Quaternary ammonium material/acetate source	Final water (mmol/g total)	Final methanol (mmol/g total)	Final methyl acetate (mmol/g total)	Yield (mmol methyl acetate/mmol acetate in)	Selectivity (mmol methyl acetate/ mmol methanol)
Blank	0.012 ± (6×10^{-4})	0	0	-	-
Potassium acetate	0.047±0.014	0	0	-	-
Tetramethylammonium acetate	0.023±0.001	<0.0016	0.0031± (5×10^{-5})	0.035 ±(9×10^{-4})	>2
Dowex Marathon MSA acetate/chloride	0.034± 0.003	0.014 ± 0.001	0.012±(9×10^{-4})	0.21 ± 0.01	0.85±0.08
Dowex Marathon MSA chloride	0.039±0.001	0.030 ± (9×10^{-4})	0	-	-
Tetrabutylammonium acetate	0.011±0.003	0.089± 0.01	0.054±0.01	1.17 ± 0.02	0.60±0.02
Tetrabutylammonium chloride	0.0081±(6×10^{-4})	0.046± 0.01	0	-	-

[a]Initial anion amounts were 0.04 mmol/g total, and 0.08 mmol/g total in case of tetramethylammonium acetate

These experiments show that the change in yield depends on the cation and the alkyl groups of the quaternary ammonium materials. The yield of methyl acetate formation (per mole of acetate supplied) increases in the order K<Me_4N< Dowex MSA<Bu_4N. The reason might be

the change of solubility of the functional group in DMC for each of these compounds, making them a better catalyst. For tetrabutylammonium acetate the yield is 17% higher than the maximum amount on the basis of the stoichiometry of reaction R.2 (Figure 2.2). Based on the equations considered, there is no clear explanation for this higher yield. Furthermore, on the basis of acetate input the water concentration at the end is lower (0.008-0.011 mmol of H_2O/g total) than the initial water content in DMC (0.012 mmol of H_2O/g total).

The selectivity (moles of methyl acetate per mole of methanol) for the tetramethylammonium acetate is above 2, which means that there is more methyl acetate than methanol formation. The reason can be the reduction of the side reaction (responsible for the methanol formation) at 60 °C, R.5 (Figure 2.2). This reduction can be caused by the low concentration of methyl carbonate anion (probably in the same range as methyl acetate, 0.0031 mmol/g) and water (~0.01 mmol/g) which affects the equilibrium of R.5, and in this case reduces the hydrolysis.

Table 2.5. Reaction of DMC as solvent with different quaternary ammonium materials at 100 °C for 2 h[a]

Quaternary ammonium material/acetate source	Final water (mmol/g total)	Final methanol (mmol/g total)	Final methyl acetate (mmol/g total)	Yield (mmol methyl acetate/mmol acetate in)	Selectivity (mmol methyl acetate/ mmol methanol)
Blank	0.0087 ±9E-4	0	0	-	-
Potassium acetate	0.038±0.003	0	0	-	
Tetramethylammonium acetate	0.027±0.002	0.028 ±0.005	0.026±0.004	0.29 ±0.02	0.95±0.04
Dowex Marathon MSA ® acetate/chloride	0.066± 0.015	0.045±0.006	0.028±0.004	0.56 ± 0.02	0.62±0.09
Dowex Marathon MSA ® chloride	0.073±0.011	0.027±0.003	0	-	-
Tetrabutylammonium acetate	0.0043±0.001	0.057±0.003	0.038±0.001	1.18 ± 0.04	0.65±0.01
Tetrabutylammonium chloride	0.0045±8E-4	0.062±0.001	0	-	-
Dowex Marathon MSA ® acetate	0.042±0.01	0.051±0.002	0.048±0.002	0.73 ± 0.02	0.95±0.04
Dowex Marathon MSA ® acetate (6 h)	0.142±0.012	0.083±0.006	0.045±0.003	0.84 ± 0.01	0.54±0.01

[a]Initial anion amounts were 0.03-0.04 mmol/g total, 0.08 mmol/g total for tetramethylammonium acetate, and 0.06-0.07 mmol/g total for Dowex Marathon MSA fully loaded

As a next step, the change in the reactivity was studied at 100 °C during a reaction time of 2 h. The results (Table 2.5) confirm that there is no methanol formation in the absence of the quaternary ammonium groups, even at this temperature. They also show a reduction in the selectivity in the experiments with tetramethylammonium acetate and Dowex Marathon MSA acetate/chloride in comparison with the experiment at 60 °C. Interestingly, for tetramethylammonium acetate the selectivity is 0.95±0.04, which indicates that the same amounts of methanol and methyl acetate are formed. For Dowex MSA acetate/chloride the selectivity is 0.62±0.09. The resin was not completely in the acetate form since it was loaded in a batch mode. Interestingly, the selectivity of the experiment is close to the ratio between acetate and chloride present in the resin, which is 0.79 acetate form/chloride form. This is in accordance with the previous result, which indicates that the chloride form of the quaternary ammonium

group formed methanol from DMC, and supports the importance of having the quaternary ammonium group fully loaded with a carboxylate anion. A completely loaded Dowex MSA acetate resin reacts with DMC with a yield of 0.73±0.02 and a selectivity of 0.95±0.04 (Table 2.5). After reaction, the resin was dried and further introduced in water. The formation of carbon dioxide (according to gas bubble formation) and absence of methanol (<0.004 mmol/g) in water is consistent with the resin being in the bicarbonate form after reaction, and with methanol being formed in the alkylation reaction due to the hydrolysis of the methyl carbonate anion. An additional experiment with completely loaded Dowex MSA acetate resin was performed for 6 h in which a higher yield, 0.84±0.01, and a lower selectivity 0.54±0.01 are obtained. The higher yield demonstrates that the reaction does not reach equilibrium at 2 h. The explanation for the lower selectivity might be extra hydrolysis of DMC with the quaternary ammonium group as catalyst after the equilibrium is reached.

As in the previous experiments, the yield in the tetrabutylammonium acetate experiment is higher (by 18%) than in the theoretical. There is no clear explanation for this higher methyl acetate formation. Besides the methyl acetate formation, there are several side products formed. Tetrabutylammonium acetate can react with DMC and participate in Hoffman elimination reactions.[20] Figure 2.3 shows the GC-MS of the compounds formed during the different experiments at 100 °C. Tetrabutylammonium acetate forms side products such as butyl methyl carbonate and dibutyl methylamine. For this reason, it is not recommended to use this type of quaternary ammonium group in the alkylation reactions with DMC.

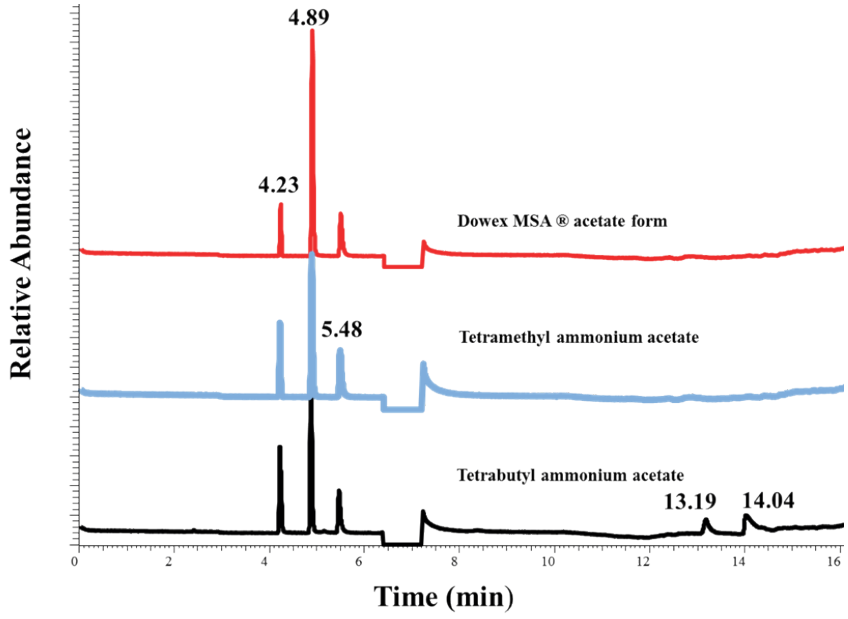

Figure 2.3. GC-MS of the different quaternary ammonium groups after reaction in DMC at 100 °C. Peaks: 4.23 carbon dioxide/butene, 4.89 methyl acetate, 5.48 methanol, 6.5-7.5 solvent (DMC), 13.19 butyl methyl carbonate, and 14.04 dibutyl methylamine

2.3.2 Reactivity of the methyl carbonate anion

In section 2.3.1, we suggested that the source of methanol is the hydrolysis of the methyl carbonate anion. For this reason, we studied the reactivity of the methyl carbonate anion, the possibility of avoiding its hydrolysis (R.5, Figure 2.2), and the second methylation of acetate using methyl carbonate (R.4, Figure 2.2). Reactions of tetramethylammonium acetate with triethylmethylammonium methyl carbonate (50% in 2:3 m/m methanol:water) in acetonitrile and methanol as solvent were performed. Not even traces of methyl acetate are detected (Figure 2.4). At the same conditions of temperature and water content, DMC reacts with tetramethylammonium acetate to produce methyl acetate. The reason can be that the reaction takes place via the methoxycarbonylation and not methylation at 100 °C. Other researchers have shown that the methyl carbonate anion of a phosphonium catalyst does not have any carbonylating activity,[34] which supports this hypothesis. Another reason can be that methanol hinders the second methylation reaction by reducing the nucleophilicity of the acetate anion. An alternative to prove if the methanol hinders the second methylation is to reduce the amount of water in the reaction. The reduction of the water concentration can avoid the hydrolysis of the methyl carbonate anion, and enable the second methylation reaction.

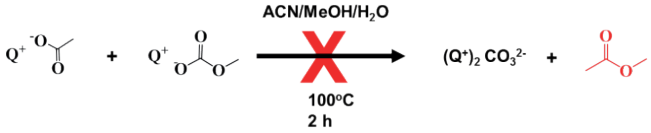

Figure 2.4. Methylation of acetate with a methyl carbonate anion at 100 °C for 2 h.

A decrease of initial amount of water is an alternative to avoid the hydrolysis of the anion. However, the prevention of the hydrolysis reaction (R.5, Figure 2.2) depends on the stability of the quaternary ammonium methyl carbonate. The quaternary ammonium methyl carbonate compound is a stable compound at our operation temperature. The methyl carbonate anion is reported to be stable at temperatures below 170-180 °C.[20] However, it is basic enough (K_b in water is 10 times larger than for acetate) to catalyze its hydrolysis producing bicarbonate and methanol. The hydrolysis is more feasible, both kinetically and thermodynamically, than the direct decomposition of the methyl carbonate anion.[20, 29] The hydrolysis reaction of methyl carbonate is so fast that no methylcarbonic acid is detected, and only methanol and bicarbonate. The hydrolysis occurs in the presence of a polar organic solvent or stoichiometric amount of water.[29]

In our reaction, an excess of DMC is used to create a pseudoequilibrium in which full conversion of acetate produces methyl acetate and probably an equimolar amount of quaternary ammonium methyl carbonate (before hydrolysis). In this situation, the mole amount of methyl carbonate anion is the same as the amount of functional sites of the anion exchange resin (for Dowex Marathon MSA 1.1 equiv/L). This indicates that for achieving an equimolar amount of water the resin has to be dried down to 0.028 g of water/g of dry resin, if the added solvent is completely dry.

Drying this type of resin is a not a simple procedure because of its hydrophilic nature. Dowex Marathon MSA is a macroporous styrene-polyvinyl benzene resin. In the chloride form the water content is between 56-66%. The presence of the charged groups converts it into a hydrophilic material. The ion exchange resins holds water in its pores as an integral part of the polymer structure. The higher the cross-linking the lower the water content. The maximum cross-

linking is close to values of 10-15% otherwise the structure becomes too hard and dense. It is reported that for acidic (cation exchange) macroporous styrene-divinylbenzene resins an effective water removal procedure is heating in an oven at 110 °C for more than 10 h. At this condition, the moisture content has been reduced to 0.03 g of water/g of dry resin, and a further methanol percolation can reduce the water content to 0.01 g of water/g of dry resin.[35, 36] Drying at high temperatures (>100 °C) is not an alternative because of the decomposition of the quaternary ammonium groups, as discussed previously. We anticipate that a water content of 0.028 g of water/g of resin in our resin will entirely hydrolyze the methyl carbonate anion to methanol and bicarbonate. In section 3.4, we study the theoretical requirements for avoiding the hydrolysis of the methyl carbonate anion and influence the reaction equilibrium.

2.3.3 Consumption of dimethyl carbonate

The consumption of DMC was measured to relate it to the product and byproduct formation. Experiments using acetonitrile as solvent were performed to quantify DMC consumption. In this experiment, tetramethylammonium acetate and DMC (2 mol of DMC:1 of mol acetate) were reacted in anhydrous acetonitrile at 100 °C for 2 h. The consumption of DMC is 0.76 (moles DMC/moles acetate in) which is higher than the amount needed for the observed methyl acetate formation (yield of 0.12). The observed methyl acetate:methanol molar ratio for this reaction is 0.50. The low ratio indicates that there are side reactions. One observed side reaction is the hydrolysis of acetonitrile to acetamide. In other attempts to measure the consumption of dimethyl carbonate, experiments with tetrahydrofuran and cyclopentylmethyl ether as solvents were performed. In these reactions, tetramethylammonium acetate and Dowex MSA in acetate form were reacted with DMC (3 mol of DMC:1 mol of acetate) in each of the solvents at 100 °C for 2 h with no success. The formation of methyl acetate in these reactions is too low to quantify the ratio between reactant consumption and products. A theoretical study of the chemical equilibrium of the reactions was performed to identify the conditions required for high yield and selectivity.

2.3.4 Chemical equilibrium of the reactions

From the previous experiments, we have evidence that the alkylation with DMC (R.1+R.3 or R.2, Figure 2.2) and the hydrolysis of the methyl carbonate anion in the presence of water (R.5) are the reactions that proceed at 100 °C. Also, we suggested that a low concentration of water (~0.03 g of water/g of dry resin) is sufficient to hydrolyze the methyl carbonate anion and that an excess of DMC is needed for a high yield of reaction. In this section, we explore the equilibrium of the reaction system R.2 and R.5, and the theoretical conditions needed for high yield and selectivity. The reaction system R.1, R.3, and R.5 should give the same results if the products of R.1 do not reach significant equilibrium concentrations. These products indeed seem to be high Gibbs energy intermediates.

Table 2.6. Calculated values of standard enthalpies and Gibbs energies of reaction at standard conditions, and of reaction equilibrium constants at 100 °C.

Reaction	$\Delta H^{\circ}_{r,i}$ (kJ mol^{-1})	$\Delta G^{\circ}_{r,i}$ (kJ mol^{-1})	K^{373K}
R.2	58.3	-115	1.05
R.5	-46.6	104	0.95

Table 2.6 shows the standard enthalpy and Gibbs energy of reaction for reactions R.2 and R.5 (Figure 2.2) at standard conditions, and the equilibrium constant at 100 °C. These values were used in eqs 3 and 4 for the calculation of the theoretical value of K_x as discussed in

section 2.2.6. The theoretical chemical equilibrium was used to predict the trend in the yield and selectivity of the alkylation reaction as a function of the amount of DMC at different water contents at 100 °C (Figure 2.5 and 2.6). Figure 2.5 shows that an excess of DMC is needed to achieve a high yield of methyl acetate, especially at water concentrations below 0.01 g of water/g of resin. The water concentration has a strong effect on the yield and on the selectivity of the reactions. A water content of 0.04 g of water/g of resin increases the yield of reaction from 0.80 (for 0.01 g of water/g of resin) to 0.90 with a DMC excess of 2 mol of DMC_{in}/ mol of $acetate_{in}$. At a DMC excess above 50 mol of DMC_{in}/ mol of $acetate_{in}$ the yield is calculated to be higher than 0.99, and there is no variation with the water content. Our experiments were performed with 275 mol DMC_{in}/ mol $acetate_{in}$, and a water concentration in the resin of ~0.08 g water/g resin (assuming that water in the reaction comes entirely from the resin), shown in Figure 2.6. The lower yield (0.74-0.83) suggest that after 2 and 6 h the reaction has not reached equilibrium, and that a more complicated model is required to predict the reaction course in detail.

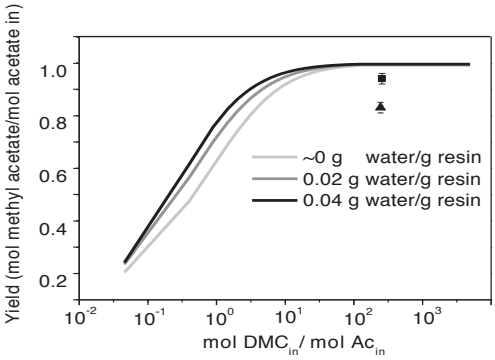

Figure 2.5. Calculated equilibrium of the alkylation reaction in relation to excess of DMC at different initial water concentrations at 100 °C. The highest initial water concentration (0.04 g of water/g of resin) corresponds to 1.6 mol of water/ mole of initial acetate (Ac_{in}). Experimental data: ■ 0.84 ± 0.01 Dowex MSA-acetate form (6 h) ; ▲0.73 ± 0.02 Dowex MSA-acetate form (2 h).

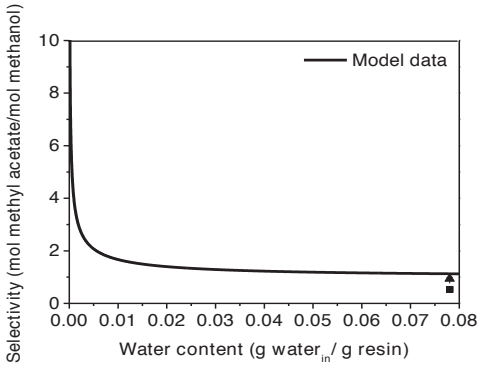

Figure 2.6. Calculated selectivity at equilibrium of methyl carbonate anion hydrolysis reaction R.5 in relation to the water concentration with an excess of DMC (250 mol of DMC_{in}/mol of Ac_{in}) at 100 °C. Experimental data: ■ 0.54 ± 0.01 Dowex MSA-acetate form (6 h) ; ▲0.95 ± 0.04 Dowex MSA-acetate form (2 h).

Figure 2.6 shows that the water concentration in the resin would have to be lower than 0.005 g of water/ g of resin to avoid the hydrolysis of half the methyl carbonate anion (selectivity equal to 2). To achieve this low water concentration is difficult, as discussed previously. Even if this can be achieved, the concentration of the methyl carbonate anion is too low to expect any further alkylation reaction (considering that the reaction at 100 °C is a direct methylation). In this case, the amount of DMC consumed per mole of methyl acetate produced (and MeOH) is 1:1. Experimentally, the selectivities are lower than predicted.

2.4. Conclusion

In this chapter, the methanol (byproduct) formation during the alkylation of acetate with dimethyl carbonate was reduced to about 1 mol of methanol/mol of methyl acetate. It was concluded that the quaternary ammonium group has a strong effect in the reaction selectivity, and that quaternary ammonium salts (ionic liquids) are also suitable. A molar yield of 0.84 mol of methyl acetate/ mol of $acetate_{in}$ was obtained with an anion exchange resin at 100 °C. Furthermore, to achieve a low byproduct formation (methanol) the quaternary ammonium group has to be previously fully converted into the carboxylate form. Otherwise, the remaining chloride or bicarbonate form of the quaternary ammonium group can hydrolyze the DMC when the reaction is proceeded. The water concentration and the excess of DMC have a strong effect on the yield of the alkylation reaction. According to equilibrium calculations, an initial ratio 50 mol of DMC_{in}/ mol of $acetate_{in}$ is needed to have a yield higher than 0.98 in a reaction medium with or without water. In the presence of water, a yield of 0.99 might be achieved with an initial ratio of 24 mol of DMC_{in}/ mol of $acetate_{in}$. The maximum theoretical selectivity of the system at high water concentration (>0.08 g of water/g of resin) is 1.1 mol of methyl acetate /mol of methanol, and it is not possible to perform a second alkylation with methyl carbonate. The reasons are the hydrolysis of the methyl carbonate anion and the absence of carbonylating reactivity of the methyl carbonate anion. As a result, the large-scale feasibility of alkylation can be compromised by a low yield on DMC, especially for products such as methyl acetate. In these cases, a further recycling of the methanol for DMC production or the utilization of other green methylating agents should be considered. In further chapters, different alternatives for the application of this technology for the recovery and ester production from carboxylates produced by anaerobic digestion (carboxylate platform) are considered.

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2.6. Nomenclature

$\Delta G_{f,i}$ = Gibbs energy of formation of component *i* [kJ mol^{-1}]
ΔG_r = Gibbs energy of reaction [kJ mol^{-1}]
$\Delta H_{f,i}$ = enthalpy of formation of component *i* [kJ mol^{-1}]
ΔH_r = enthalpy of reaction [kJ mol^{-1}]
K = activity-based chemical equilibrium constant
K_x = mole fraction-based chemical equilibrium constant
K_γ = activity coefficient ratio
n = amount [mmol]
T = temperature [K]
q_i = area parameter of component *i*
r_i = volume parameter of component *i*
x_i = molar fraction of component *i* in the liquid phase
a_i = activity coefficient of component *i* in the liquid phase

Superscript

in = initial
0 = standard state

Abbreviations

Ac = acetate
DMC = dimethyl carbonate
HPLC = high-performance liquid chromatography
KAc = potassium acetate
MeOH = methanol
MeAc= methyl acetate
$MeCO_3^-$ = methyl carbonate anion
NBu_4 = tetrabutylammonium
NMe_4 = tetramethylammonium
Q^+ = quaternary ammonium group
R = reaction
UNIFAC = universal quasichemical functional group activity coefficients

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Chapter 3

Recovery and Esterification of Aqueous Carboxylates by using CO_2-expanded Alcohols with Anion Exchange

Abstract

The recovery of carboxylic acids from fermentation broth is one of the main bottlenecks for the industrial production of bio-based esters. This study proposes an alternative for the recovery of carboxylates produced by fermentations at pH values above the pK_a of the carboxylic acid. In this approach, the aqueous carboxylate anion is recovered using anion exchange, followed by desorption and esterification with CO_2-expanded alcohols. Using CO_2-expanded methanol, we achieved a high desorption yield at 10 bar of CO_2 and 20 °C. An ester yield of 1.03 ± 0.07 mol methyl acetate/ $acetate_{in}$ was obtained for the combined desorption-esterification at 5 bar of CO_2 and 60 °C. The proposed process has low chemicals consumption and low waste production. The proposed process works, with a lower yield, for other carboxylates (e.g. lactate and succinate) and alcohols (e.g. ethanol).

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3.1 Introduction

Many carboxylic acids can be produced by bacterial fermentation. The most efficient bacterial fermentation methods for producing carboxylic acids require a titration with base to maintain a neutral pH, because the pK_a values of the acids are normally 3-5.[1, 2] The result is a carboxylate solution at a pH above the pK_a of the carboxylic acid. Some reported methods to recover carboxylates from these carboxylate solutions are shown in Table 3.1.

Table 3.1. Reported schemes for the recovery of carboxylates from fermentation broth at pH > pK_a.

Primary Recovery	Concentration	Purification (Regeneration)	Salt co-produced	Ref.
Carboxylate precipitation	Water evaporation	Protonation with H_2SO_4	$CaSO_4$	3
		Ketonization	$CaCO_3$	4
Protonation with H_2SO_4 or CO_2	Extraction with tertiary amine	Thermal decomposition	$CaCO_3$	5, 6
		Esterification	$CaCO_3$	7-9
	Adsorption	Desorption e.g. with MeOH	$CaSO_4$ or $CaCO_3$	10-12
Monopolar electrodialysis	Bipolar electrodialysis	Water removal/ nanofiltration	NaOH	13
Membrane electrolysis	Extraction	Esterification	none	14, 15
Protonation with cation exchange resin	Desorption with HCl	Precipitation or water evaporation (Regeneration by thermal decomposition of $MgCl_2$)	$MgCl_2$	16, 17
Anion exchange resin	Desorption with NaCl or H_2SO_4	Water evaporation or crystallization	NaCl or Na_2SO_4	18, 19
	Desorption with MeOH (EtOH) + H_2SO_4	Esterification	Na_2SO_4 or $CaSO_4$	10, 20
	Alkylation	Distillation	$NaHCO_3$	21, 22

Traditional recovery of carboxylic acids from this carboxylate solution coproduces stoichiometric amounts of waste inorganic salt and/or is energy intensive. The reason is that at this pH the acid is dissociated, and the primary recovery uses mainly electrostatic interactions (e.g. precipitation, electrodialysis, anion/cation exchange), or protonation of the carboxylate anion. Precipitation and protonation of the acids traditionally involve the formation of stoichiometric amount of salts as waste, while electrodialysis requires high amounts of energy.

Anion exchange resins are used to recover carboxylates because of the high affinity of the resin's quaternary ammonium group for the dissociated form of the acid.[23, 24] In the traditional anion exchange process, the main drawback is related to desorption of the carboxylate from the anion exchange resin. This desorption process involves adding an extra chemical (e.g. NaCl, H_2SO_4) which produces a stoichiometric amount of salt waste.[19, 25] Another option is to use methanol and H_2SO_4 to protonate the carboxylate anion, and then the carboxylic acid is esterified using the remaining H_2SO_4 as catalyst.[10, 19, 20] Unfortunately, in this case there is also a stoichiometric amount of salt produced as waste.

To avoid the salt waste co-production, we have explored the direct downstream transformation of carboxylate salts,[21, 22] by coupling anion exchange to an alkylation using dimethyl carbonate (DMC), which produces a methyl ester and regenerates the resin into the bicarbonate form. The bicarbonate liberated upon ion exchange should be used during the fermentation for pH control, to be not counted as waste. Carbonate and bicarbonate anions have

been used as neutralizing agents in fermentation with favorable results.[26] Additionally, some bacterial fermentations required carbonate species as carbon source besides carbohydrates to achieve high yields.[27] The alkylation reaction proceeds with high yield of methyl ester on carboxylates but with modest selectivity with respect to DMC.[28] The modest selectivity becomes a limiting factor for using this technology to produce non-expensive esters such as methyl acetate.

A new option for the direct downstream transformation is to use methanol and carbon dioxide. As DMC can be formed from methanol and carbon dioxide,[29-31] we wondered if it might be possible to use methanol and carbon dioxide for the desorption of the carboxylate from the anion exchange resin, and to subsequently produce a methyl ester. It has been reported that at 30 bar of CO_2 and 170 °C, alkali metal salts of carboxylates in methanol can be converted into esters with a molar yield of 0.81.[32]

These CO_2/alcohol systems at relatively low pressures ($<P_c$ (CO_2)) are known as gas-expanded liquids, and have been studied in detail for esterification, alkylation and carboxylation reactions, amongst others.[33] The addition of CO_2 to the alcohol makes it possible to tune the polarity of the system, and as a consequence, control the solubility of solutes.[34]

The aim of this study is to explore the effect of protonating a carboxylate anion recovered by an anion exchange resin with a CO_2-expanded alcohol, and to further esterify the carboxylic acid. Our option clearly differs from methods in which CO_2 pressure is applied to aqueous carboxylate solutions in order to facilitate transfer of carboxylate to an extractant or adsorbent phase.[35, 36] In our approach, the starting point is loading an anion exchange resin (Q^+) with a carboxylate, such as acetate (Ac^-) (R.1).

$$NaAc_{(aq)} + Q^+HCO_3^- \leftrightarrow NaHCO_{3\,aq)} + Q^+Ac^- \quad \text{R.1}$$

Then, we use a CO_2/alcohol system for the desorption of the carboxylates from the anion exchange resin with subsequent esterification (R.2).

$$Q^+Ac^- + MeOH + CO_2 \leftrightarrow Q^+HCO_3^- + MeAc \quad \text{R.2}$$

The overall stoichiometry is the combination of R.1 and R.2 (R.3).

$$NaAc_{(aq)} + MeOH + CO_2 \leftrightarrow NaHCO_{3\,(aq)} + MeAc \quad \text{R.3}$$

In this chapter, we study the effect of the CO_2 pressure on the desorption of acetate in methanol and ethanol; the effect of water on the protonation and esterification steps; and the application of the technology for other carboxylates produced by fermentation, *e.g.* lactate and succinate.

3.2 Material and Methods

3.2.1. Materials

Potassium acetate (≥99.9%), Dowex Marathon MSA resin (type I; macroporous, chloride form), methyl acetate (≥99.9%), anhydrous methanol (≥99.8%), succinic acid (≥99%), dimethyl succinate (≥99%), monomethyl succinate (≥95%), lactic acid (≥90%), methyl lactate (≥97%), and anhydrous ethyl acetate (≥99.8%) were from Sigma-Aldrich, and acetic acid (≥99%) from J.T. Baker B.V. Ethanol extra dry/absolute (≥99.5%) was from Fischer Scientific. Carbon dioxide (≥99.8%) as compressed gas was from Linde. Amberlyst15 hydrogen form (4.7 meq/g by dry weight, Serva Heildelberg) was washed with methanol and dried at 60 °C in an oven before use. Aqueous solutions were prepared by diluting with deionized water from a Milli-Q water purification system (Millipore).

3.2.2. Resin Preparation and adsorption

The adsorption experiments were performed with potassium acetate, sodium succinate and sodium lactate solutions to mimic fermentation broth.[37] Column elution was used to convert the resin Dowex Marathon MSA from the chloride form to the acetate, succinate, lactate or bicarbonate form. The resin was washed at 2 mL min^{-1} with potassium acetate, sodium bicarbonate, sodium succinate or sodium lactate solution (20 g L^{-1}), until the concentration of chloride in the outlet was below 9 mg L^{-1} and the absorbance at 210 nm at the outlet of the column was constant. Outlet samples were colorimetrically analyzed for chloride concentration. The resin was washed 3 times in a batch with 50 mL deionized water, filtered at 20 mbar using Millipore Steriflip 60 µm nylon net filtration unit, washed 3 times with 30 mL methanol, filtered using the same system, and dried in an oven at 60 °C for 16 h. The elemental composition of the surface of the resin was measured in triplicate using X-ray photoelectron spectroscopy (XPS), and the presence of water in the resin in duplicate by thermogravimetric analysis (TGA).

3.2.3. Desorption with a carbon dioxide expanded alcohol

The desorption of acetate from the resin was performed in a 50 mL Büchi glass stirred autoclave reactor. The reactor was equipped with a magnetically driven four blade impeller controlled by an overhead motor, a thermocouple for temperature control, a pressure sensor, a pressure relief valve, a nitrogen and carbon dioxide inlet, reagent addition and sampling ports.

The experiments were performed adding 0.5-1 g of Dowex MSA-acetate (2.2 mmol acetate per g dry resin) to 30 g of anhydrous methanol (or ethanol). Then, the reactor was flushed with N_2 to achieve inert atmosphere. Agitation was at 600 rpm, and a pressure of 5 bar of N_2 was maintained (control experiment). For the other experiments, it was flushed 5 more times with CO_2, and then the pressure was set to the desired value (2, 5 or 10 bar of CO_2). The reactor was repressurized with CO_2 until constant pressure. The experiments were performed for 4 h in duplicate. Liquid samples were obtained at the set pressure. Initial samples of the solvent, and final samples were analyzed for the specific methyl esters, carboxylic acid and water content on weight basis of alcohol.

3.2.4. Esterification reactions

Esterification reactions were carried out in closed glass tubes in a Greenhouse Plus Parallel Synthesizer (Radleys). The experiments were performed in duplicate. In a typical experiment, 4

g of a solution of 2% or 4% w/w of acetic acid in methanol was added to the reaction tubes. A catalyst was added to different reaction tubes (0.06 g of dried Amberlyst15 hydrogen form or 4 μL of 96 %w/w H_2SO_4). The tubes were flushed with N_2 to have an inert atmosphere. The conditions were kept at 60 °C and agitated with a magnetic stirrer at 600 rpm for 4 h. Final samples were analyzed for methyl acetate, acetic acid and water content.

For the simultaneous desorption and esterification reactions, a similar procedure as explained in section 2.3 was followed. The difference was the addition of 0.5 g of pre-washed Amberlyst15 in a separate chamber in the reactor to catalyze the esterification reaction. The reaction was performed at 60 or 78 °C for 4 h. Final samples were analyzed for the methyl esters, carboxylic acids and water content.

3.2.5 Recycle of the resin

The resin Dowex Marathon MSA was washed with deionized water and converted from chloride bicarbonate form by the column elution technique described in section 3.2.2. Then the resin was washed 3 times with 30 mL of deionized water, and the excess water was removed with a vacuum filter (20 mbar). The adsorption experiments were performed in batch, in which 1.5 g of wet resin was added to 30 g of a 10 g L^{-1} solution of potassium acetate. The batch was kept for 16 h, in which initial and final liquid samples were taken, and analyzed by HPLC (section 3.2.6). The mixture was filtered and the resin was washed 3 times with 30 mL with deionized water, 3 times with methanol, and dried at 60 °C for 3 h. The desorption experiments were performed using the simultaneous desorption-esterification method described in section 2.4. The liquid samples were analyzed for methyl acetate as described in section 2.6. The Dowex Marathon MSA resin was recovered and washed 3 times with 30 mL deionized water, and the excess water was removed with a vacuum filter (20 mbar). The resin was then reused in the next adsorption batch. The procedure was repeated until 5 consecutive adsorption and desorption steps were performed.

3.2.6. Analytical Methods

Dimethyl carbonate, methyl acetate, ethyl acetate, dimethyl succinate, methyl lactate and acetic acid were analyzed by gas chromatography (GC) using a ZB-WAXplus column (20 m length × 0.18 mm internal diameter, 0.18 μm film) and a flame ionization detector (FID). Injection and detector conditions were maintained. Liquid samples were conditioned with formic acid and anisole as internal standard. The sample (0.5 μL) was injected at 200 °C with a split flow of 30 mL min^{-1}. The oven temperature was maintained at 60 °C for 10 min, then a 10 °C min^{-1} temperature ramp was used up to 200 °C. Succinic acid, methyl succinate and lactic acid concentrations were analyzed on a Waters HPLC system using a Bio-Rad Aminex HPX-87H column (78 × 300 mm) at 60 °C. Phosphoric acid (1.5 mmol L^{-1} at 0.6 mL min^{-1}) was used as an eluent. Water content was measured by Karl Fischer titration (Metrohm 831 KF coulometer).

The elemental analysis of the anion exchange resin was carried out using an X-ray Photoelectron Spectrometer (Thermo Fisher Scientific K_α model). A monochromatic Al K_α X-ray source was used with a spot size of 400 μm at a pressure of 10^{-7} mbar. A constant pass energy of 200 eV for the survey and 50 eV for the high-resolution region was used. The flood gun was turned on during the measurement in order to compensate the potential charging of the surface. The peak position was adjusted based on the internal standard C 1s peak at 284.8 eV, with an accuracy of ± 0.05 eV. *Avantage* processing software was used to analyze all spectra, and the peak fitting was done on the basis of mixed Lorentzian-Gaussian function.

Thermogravimetric analysis (TGA) measurements were performed with a TA Instruments thermo gravimetric analyzer from RT to 150 °C. The heating rate was 10 °C min^{-1} and the purge gas was air.

3.3. Results and Discussion

3.3.1 Characterization of the anion exchange resin used for the recovery of acetate

In the proposed process, the acetate anion is recovered from the fermentation broth (at pH > pK_a) using an anion exchange resin. A quaternary ammonium anion exchange resin (Dowex Marathon MSA provided in Cl^- form) is used because at this pH (7.7) electrostatic interactions are needed to bind acetate. The loading of acetate to the resin was 0.043 g acetate/ g of wet resin. The surface composition of the resin loaded with acetate was measured with XPS and compared with the chloride and bicarbonate form of the resin (Table 3.2). The bicarbonate form of the resin is obtained upon regeneration of the resin using the proposed method (as mentioned in (R.2)). For this reason, the variation in the composition between chloride, acetate and bicarbonate on the resin was measured.

Table 3.2. X-ray photoelectron spectroscopy analysis of dried Dowex Marathon MSA resin.*

Resin Counter-ion	Surface atomic composition (%)			
	C	O	N	Cl
Chloride	82.6 ± 0.3	5.4 ± 0.2	6.3 ± 0.3	5.6 ± 0.1
Acetate	77.3 ± 0.8	18.5 ± 1.4	2.7 ± 2.1	Not detectable
Bicarbonate	79.3 ± 0.8	12.9 ± 1.6	4.8 ± 0.5	Not detectable

* Relative constitution as C, O, N, and Cl.

Table 3.2 presents the surface atomic composition of the dried resin in the chloride, acetate and bicarbonate form. Results clearly show that there is no chloride detectable after loading the resin with acetate or bicarbonate using the column elution technique, which is in good agreement with the chloride and UV measurements in the outlet of the column (section A.3.1). The absence of chloride in the acetate and bicarbonate resins confirms the success of the reactions. Furthermore, oxygen is present (~5 to ~18%) in all samples. The detection of oxygen in the chloride form of the resin might be associated to surface contaminations as suggested by C-O and C=O contributions in the XPS C1s spectrum (section A.3.2.2). In addition, water can be strongly adsorbed to resin, even at a pressure of 10^{-7} mbar during the XPS analysis. After all, ion-exchange resins are highly hydrophilic as also shown by our TGA results, which were performed on the chloride, bicarbonate and acetate forms. The thermogravimetric curves reveal a degradation step within 150 °C both in the wet and dry resin with values of 65-68% w/w and 5-8% w/w, respectively.

Nevertheless, the oxygen composition significantly increases upon the addition of acetate and bicarbonate, which is again supporting the anion exchange reactions.

We further note that the presence of adsorbed water is important for the further desorption and esterification steps. The variation in the nitrogen content is related to the non-homogeneous distribution of the quaternary ammonium group on the resin surface.[38] This is observed in the acetate sample in which the nitrogen atomic composition is 2.7±2.1%, for which the measurements varied in the range of 4.2% (similar as the bicarbonate form) to 1.2%. In another set of samples (Table A.3.2), the nitrogen compositions of the acetate and bicarbonate form of the resin were fluctuating from 3.2 to 5.7%.

Once the target carboxylate is bound to the resin, desorption of the carboxylate from the anion exchange resin has to overcome the strong binding energy of the electrostatic interactions between the carboxylate and the quaternary ammonium group of the resin. To solve this problem, a new approach for the desorption of the carboxylate using CO_2-expanded alcohols is explored.

3.3.2. Desorption of acetate with CO_2-expanded methanol

The innovative step in the process is the desorption of the acetate from the anion exchange resin. The acetate anion is desorbed from the resin using CO_2-expanded methanol. Table 3.3 shows the effect of CO_2 pressure on the desorption of acetate. At low CO_2 pressures (2-10 bar) a high recovery yield (mol acetic acid/mol $acetate_{in}$) ranging from 0.55-0.79 is observed. In contrast, a 0.38±0.05 mol acetic acid/$acetate_{in}$ desorption yield was found at a CO_2 pressure of 10 bar in water (Table A.3.5).

Table 3.3. Desorption of acetate from an anion exchange resin with CO_2-expanded methanol at 20-22 ºC with a resin loading of 3.4 %w/w dry resin/ methanol.

Equilibrium CO_2 pressure (bar)	Final water (mmol/g solvent)	Desorption (mol acetic acid/mol $acetate_{in}$)
0	0.30±0.04	0
2.12	0.35±0.04	0.55 ±0.09
5	0.37±0.07	0.72 ±0.02
10	0.38±0.05	0.79 ±0.04

With this desorption, the anion exchange resin might be converted into the methyl carbonate or bicarbonate form (R.4 and R.5), and the acetate is protonated.

$$Q^+Ac^- + MeOH + CO_2 \leftrightarrow Q^+MeCO_3^- + HAc \quad \text{R.4}$$

$$Q^+Ac^- + H_2O + CO_2 \leftrightarrow Q^+HCO_3^- + HAc \quad \text{R.5}$$

The high solubility of carbon dioxide in methanol (Table 3.4) enhances the desorption of acetate from the anion exchange resin. This allows the utilization of a much lower CO_2 pressure than in water to protonate the carboxylate anion. Other low CO_2 pressure research has been conducted in water in which CO_2 and amines are used for the recovery of acetic acid.[8] In that approach, aqueous calcium acetate is protonated using CO_2, and the formed acetic acid is bound to tributylamine. The amine complex is extracted using a water insoluble alcohol. Downsides of that approach are the losses of extractant and CO_2 dissolving in the aqueous phase, and the requirement of hydrophobic alcohols (butanols to octanols) to extract acid. In contrast, using the proposed method we can get the acetic acid dissolved in hydrophilic alcohols such as methanol, which enables more interesting esterification reactions.

Table 3.4. Solubility of carbon dioxide (10 bar) in different solvents at 25 ºC [39, 40]

Solvent	Mole fraction	Mass Fraction
Water	0.00592	0.0144
Methanol	0.0772	0.1030
Ethanol	0.1110	0.1065

In the case of methanol and acetate, the reactions considered are: the protonation of the acetate bound to the resin via the formation of the methyl carbonate anion[41] (from MeOH and CO_2, (R.4)); the protonation by the formation of bicarbonate anion (R.5); the hydrolysis of the

methyl carbonate anion (R.6); the formation of dimethyl carbonate (DMC) from the methyl carbonate anion and methanol (R.7); and the conversion of the hydroxide to the bicarbonate form of the resin (R.8). During the experiments, DMC was detected in low concentrations. Because of the low concentrations detected, DMC might play no role as an alkylating agent in a reaction with acetate.

As a result, the formed acetic acid (protonated acid) is in solution with methanol and CO_2. The next downstream process step might be a recovery (e.g. distillation) of the protonated acid, an esterification of the acid or another reaction step. In this chapter, we explore the integration of the desorption in CO_2-expanded methanol with an esterification reaction (R.9). Once the system is at equilibrium, an excess of methanol and CO_2 might direct the equilibrium to the products' (ester and water) formation.

In the next section, we compare different reactor configurations for the integration of the desorption and esterification steps. Furthermore, the requirements of catalyst and the effect of the CO_2 and methanol excess in the shift of the desorption and esterification equilibrium are studied.

3.3.3. Integration of esterification with CO_2-expanded methanol desorption

The esterification of acetic acid with methanol is a well-studied topic.[42-45] It has been reported that CO_2 can improve the molar yield of esterification reactions from 0.64 to 0.72-0.80 (without catalyst).[43] However, the reaction kinetics are not improved, and the time to reach equilibrium is long (>20 h). For our system, preliminary experiments demonstrated that the reaction is too slow and that a catalytic agent is required. Catalytic agents that are commonly used are H_2SO_4, strong cation exchange resins (with sulfonic acid groups) and zeolites.[42, 45, 46] Some other carboxylic acids are sufficiently strong acids to catalyze their own esterification reaction. The type of catalyst, the reaction temperature, the CO_2 pressure used and the stability of the catalyst and anion exchange resin are factors that determine optimal reactor(s) configuration. The different reactor(s) configuration that are considered: consecutive 2-compartments; simultaneous 1-compartment; and simultaneous 2-compartments (Fig. 3.1). These reactor(s) configurations are studied to determine the effect of integrating the desorption and esterification steps.

Our experiments were performed using the simultaneous 1-compartment system and the consecutive 2-compartment systems. Experiments with a simultaneous 2-compartment system are more difficult to implement on lab scale, but we expect the degree of conversion to be similar as for the 1-compartment system at the same operating temperature for both compartments and high recycle rates. The main results are shown in Table 3.5.

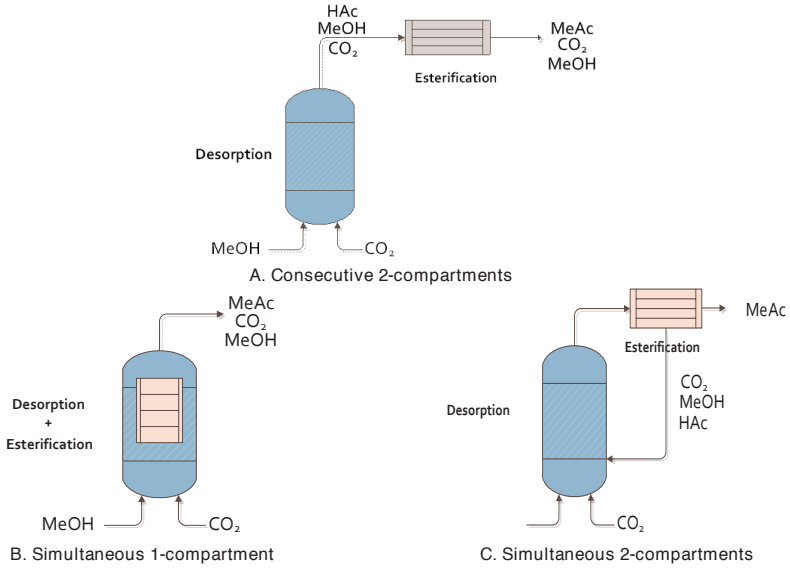

Figure 3.1. Options for process integration for the desorption and esterification steps.

Table 3.5. Effect of the catalyst on the esterification of acetic acid with methanol at 60 ºC for 4 h at different process configurations.

Experiment	Process configuration	Solution	Esterification Equilibrium CO_2 pressure (bar)	Catalyst[a,b]	Final water (mmol/g solvent)	Yield (mol methyl acetate/mol $acetate_{in}$)
1	Only esterification	0.4 %w/w HAc in MeOH	0	none	Not available	0
2	Only esterification	0.4 %w/w HAc in MeOH	0	H_2SO_4	Not available	0.86±0.02
3	Only esterification	0.2 %w/w HAc in MeOH	0	H_2SO_4	0.06±0.02	0.76±0.02
4	Only esterification	0.4 %w/w HAc in MeOH	0	Amberlyst	0.27±0.02	0.81±0.02
5	Only esterification	0.2 %w/w HAc in MeOH	0	Amberlyst	0.12±0.01	0.85±0.02
6	Consecutive	Desorbed effluent CO_2-expanded protonation (10 bar)	0	H_2SO_4	0.60±0.03	0.87±0.02
7	Simultaneous	3.3 %w/w Dowex MSA acetate form in MeOH	5	none	0.40±0.06	0
8	Simultaneous	3.3 %w/w Dowex MSA acetate form in MeOH	5	Amberlyst	0.39±0.07	0.58±0.07

[a.] 0.08 % w/w H_2SO_4. [b.] 1.4 %w/w dry Amberlyst 15.

It can be observed that the maximum methyl acetate yield achieved is 0.87, which is the same as reported in literature with different catalyst systems.[42, 45, 47] The simultaneous desorption and esterification process configuration presented a yield of 0.58±0.07 mol methyl acetate per mole of $acetate_{in}$. This value is comparable to the overall yield of the consecutive configuration which the desorption step yield is 0.79±0.03 mol of acetic acid per mole of $acetate_{in}$, and the further esterification reaction is 0.87±0.02 mol methyl acetate per mole of $acetic\ acid_{in}$, which gives an overall yield of 0.68 mol of methyl acetate per mole of $acetate_{in}$.

Envisaged advantages and disadvantages vary for the process integration options shown in Figure 3.1. For example, the 2-compartments options can potentially operate at individual optimum conditions for desorption and esterification. A major advantage of the simultaneous options (1- and 2- compartments) is an equilibrium shift of the desorption step to the product side by the consumption of acetic acid during esterification. This should allow the utilization of lower CO_2 pressures. On the other hand, a heterogeneous acid catalyst will be desired, because otherwise the acid catalysts' anion (e.g. sulfate) can exchange in the anion exchange resin in the desorption compartment. The main disadvantage of the simultaneous 1-compartment option is that this heterogeneous acid catalyst will have to be separated from the anion exchange after this resin has been fully desorbed.

3.3.4. Effect of water on the simultaneous desorption and esterification of acetate with CO_2-expanded methanol

Generally, water counteracts esterification. In our system, water is introduced to the reaction with the utilization of resins (anion and cation exchange) in each of the systems. Water has been largely removed from both resins by washing them with methanol and drying it in an oven at 60 °C. At industrial scale this would be done in a different way but it might still be an expensive step because of energy and equipment requirements. For this reason, the effect of a higher initial water concentration on the desorption and esterification of acetate with CO_2-expanded methanol has been studied.

It can be advantageous for an industrial process if merely filtering the resin would remove water to a sufficient extent. A comparison between the yields obtained with a dry (methanol dried) and wet resin (filtered) are presented in Table 3.6. The wet resin was obtained after washing the resin a couple of times with deionized water and the water was filtered off while using a vacuum pump (10 mbar). The esterification reactions were performed without CO_2 since we expected a small effect of CO_2 on the esterification at this low concentration (0.02 mmol acetic acid per g). As mentioned earlier, the amounts of adsorbed water were found to be 68-71% for wet resin and 7-8% for dry resin.

The desorption of acetate from the anion exchange resin decreases from 0.79 to 0.50 mol of acetic acid/ mol of $acetate_{in}$ when changing from a dry to a wet resin. It seems that the desorption equilibrium with methanol is more favorable (R.4), and it is easily affected by the presence of water (R.5 and R.6). Esterification of acetic acid with methanol is not affected by a water content of 1.95 ± 0.14 mmol g^{-1} at a lower initial acetic acid concentration (~1.5 mg acetic acid per g solution). The reason is that the concentration of acetic acid in this treatment is lower than in the others, and the excess methanol improves the yield until almost full conversion of methyl acetate. However, in the consecutive desorption and esterification the total methyl acetate yield is reduced from 0.68 to 0.48 in the presence of the wet resin. Interestingly, for the simultaneous desorption and esterification the total desorption is only slightly affected by the increase in water content (yield decreases from 0.66-0.57), but the overall ester yield is reduced from 0.58 ± 0.07 to 0.37 ± 0.02 mol of methyl acetate/mol of $acetate_{in}$. For both systems, the extra water present in the reaction medium (coming from the different ion exchange resins) affects the esterification equilibrium and reduces the methyl acetate formation. The concentration of water introduced to the system by the anion exchange resin is 20 times higher in the case of the wet resin (3.3 mmol water/g solvent), in comparison to the dry resin (0.16 mmol water/g solvent). In general terms, the overall yield might be improved by the removal of water from the system, but also by using a higher excess of methanol to push the equilibrium to the products. To increase the esterification

yield, esterification may be performed as reactive distillation or reactive SMB chromatography.[48, 49]

Table 3.6. Effect of water on the desorption and esterification using 0.02-0.04 mmol/g acetic acid with methanol for 4 h.

Exp.	Process config.	Resin[c] (Dowex MSA) pretreat-ment	Desorption equilibrium CO_2 pressure (bar)	Temp (°C)	Catalyst [a,b]	Final water (mmol/g solvent)	Total Desorption yield[f]	Yield[g]
9	Desorption	Dry	10	20	none	0.42 ±0.03	0.79 ±0.04	-
10	Desorption	Wet	10	20	none	1.90 ±0.40	0.50 ±0.01	-
11	Esterification	Dry[d]	-	60	H_2SO_4	0.60 ±0.03	-	0.87 ±0.02
12	Esterification	Wet[e]	-	60	H_2SO_4	1.95 ±0.14	-	0.97 ±0.01
9+11	Consecutive	Dry	exp. 9 & 11	exp. 9 & 11	exp. 9 & 11	0.60 ±0.03	0.79 ±0.04	0.68 ±0.03
10+12	Consecutive	Wet	exp. 10 & 12	exp. 10 & 12	exp. 9 & 11	1.95 ±0.14	0.50 ±0.01	0.48 ±0.01
13	Simultaneous	Dry	5	60	Amberlyst	0.39 ±0.07	0.66 ±0.07	0.58 ±0.07
14	Simultaneous	Wet	5	60	Amberlyst	3.42 ±0.5	0.57 ±0.01	0.37 ±0.02

[a.] 0.1 % w/w H_2SO_4.[b.] 1.4 %w/w dry Amberlyst 15. [c]Dry resin (8 %w/w water) and wet resin (68 %w/w water).[d.] Effluent exp. 9. [e.] Effluent exp. 10. [f.] (mol MeAc + mol HAc)/mol $acetate_{in}$. [g.] mol MeAc/ mol $acetate_{in}$.

3.3.5. Desorption and esterification with other carboxylates: lactate and succinate

The yield of the desorption and esterification of acetate can be improved using a higher excess of methanol to push the equilibrium further. In this section, we decreased the amount of resin from 3.4 to 1.7 % w/w dry resin Dowex MSA/ methanol to increase the methyl carboxylate yields. Table 3.7 shows that under these conditions the yield of methyl acetate formation increased to completion (1.03 ± 0.07). The higher excess of methanol improves the reaction. However, it decreases the overall productivity of the process and increases costs of ester recovery by methods such as distillation. This might compromise the process feasibility, especially for low-priced products such as methyl acetate. The same ratio of resin and methanol was used for the desorption and esterification of succinate and lactate. These two carboxylates are attractive platform chemicals because of their chemical functionality and valuable derivatives.

Table 3.7. Simultaneous desorption and esterification of acetate, succinate and lactate with CO_2-expanded methanol at 60 °C and 5 bar CO_2. [a,b]

Carboxylate	Time (h)	mmol carboxylate/ g dry resin	Final water (mmol/g solvent)	Final acid (mmol/ g solvent)	Yield monoester[c]	Yield diester[d]
Acetate	4	2.2	0.31 ± 0.12	0.0034 ± 0.0005	1.03 ± 0.07	-
Succinate	4	1.8	0.20	0.0013	0.02	<0.04
Succinate	20	1.8	0.32 ± 0.04	0.0005 ± 0.0001	0.017 ± 0.003	0.18 ± 0.03
Lactate	4	2.0	0.16 ± 0.05	0.004 ± 0.001	0.70 ± 0.02	-

[a.] 1.7 %w/w dry resin Dowex Marathon MSA / methanol. [b.] 1.4 %w/w dry Amberlyst 15. [c.] mol methyl carbonxylate/mol $carboxylate_{in}$. [d.] mol dimethyl carboxylate/mol $carboxylate_{in}$

Table 3.7 shows that the desorption and esterification of succinate with CO_2-expanded methanol is possible with a modest yield of 0.18 mol dimethyl succinate/mol $succinate_{in}$ at 60 °C and 5 bar of CO_2. From the residual amount of succinic acid (0.0006 mmol g^{-1}) and methyl succinate (yield of 0.01 mol monoester/mol $carboxylate_{in}$) in the methanol solution, it seems that most of the dicarboxylate anion is still bound to the resin. Apparently, 5 bar CO_2 pressure is not enough to protonate the two carboxylate groups of succinate and push it out of the resin. Moreover, an increase in the yield for the esterification for 20 h suggests that there is room for optimization of catalyst, temperature, and reaction time. It has been reported that for the esterification of succinic acid with ethanol a major difference on the rate in diethyl succinate formation is achieved with different cation exchange resins as catalyst.[50]

A yield of 0.70 mol methyl lactate/mol $lactate_{in}$ is observed for the desorption and esterification of lactate at 60 °C and 5 bar of CO_2. The yield of methyl lactate is higher than reported[51] for the esterification of lactic acid (0.4 mol of methyl lactate/mol lactic acid) at a lower excess of methanol (5 mol methanol/mol lactic acid) in comparison with our excess (~460 mol methanol/mol lactic acid).

It would be interesting to explore the utilization of this method for other industrial relevant carboxylates such as propionic acid, 3-hydroxypropionic acid, levulinic acid, itaconic acid and 2,5-furandicarboxylic acid (FDCA).

3.3.6. Stability and regeneration of the anion exchange resin

Dowex Marathon MSA resin maintained its performance after five reuse cycles in a regeneration step with ethyl chloride at 100 °C.[21] The conditions used in our new method with CO_2-expanded alcohols are at lower temperature (60 °C) than in previously reported studies,[21, 22] which might improve the stability and regenerability of the resin, because quaternary ammonium groups suffer deamination under long term exposure to high temperatures. Decoupling desorption and esterification steps in a consecutive system such as described in Figure 3.1 also provides the option to perform the anion exchange at ambient temperatures.

Table 3.8. Performance of Dowex Marathon MSA in cycles of 16 h of adsorption of potassium acetate (RT) and 4 h of desorption + esterification (60 °C) in CO_2-expanded methanol

Process step	Cycle				
	1	2	3	4	5
Adsorption (g acetate/g wet resin)	0.059	0.055	0.056	0.061	0.068
Desorption + esterification (mol methyl acetate/ mol acetate in)	1.01	1.12	1.00	0.92	1.00

Table 3.8 shows that the resin performs similarly in 5 successive adsorption- desorption + esterification cycles. The adsorption capacity remains 0.060 ± 0.005g acetate/ g wet resin and the desorption + esterification yield remains 1.01 ± 0.07 mol methyl acetate/mol $acetate_{in}$, also in line with previous experiments (Table 3.7). The resin was exposed to a total experimental time of 100 h, however a longer period is necessary to evaluate its long term stability.

3.3.7. Perspectives for other CO_2-expanded alcohols: ethanol as example

In previous sections, we demonstrated that CO_2-expanded methanol can be used for the desorption and esterification of carboxylates from a strong anion exchange resin. The main advantage of this method is the high solubility of CO_2 in methanol. CO_2 has also a high solubility in other alcohols such as ethanol (Table 3.4). Ethanol is a suitable chemical because it is a non-

expensive, bio-based and produced worldwide. Moreover, the produced ethyl carboxylates compounds are industrially interesting products. Ethyl acetate and ethyl lactate have several industrial applications.[52]

Table 3.9. Simultaneous desorption and esterification of acetate with CO_2-expanded ethanol at 5 bar CO_2 for 4 h

Process Step	Temperature (°C)	Catalyst[a]	Dry Dowex MSA-acetate in ethanol (% w/w)	Final water (mmol/g solvent)	Total desorption yield[b]	Yield[c]
Desorption	20	None	3.5	0.16±0.01	0.50±0.03	-
Desorption and esterification	78	Amberlyst	3.5	0.27±0.04	0.71±0.02	0.55±0.02
Desorption and esterification	78	Amberlyst	1.7	0.30±0.15	0.87±0.05	0.67±0.04

[a.] 1.4 %w/w dry Amberlyst 15. [b.] mol (EtAc+HAc)/mol $acetate_{in}$. [c.] mol ethyl acetate/mol $acetate_{in}$.

Table 3.9 shows the results for desorption and esterification of acetate with CO_2-expanded ethanol at 5 bar. The desorption yield at 20 °C is 0.50 ± 0.03, which is lower than the amount achieved with methanol (0.72 ± 0.02). A lower rate with a higher alcohol is expected because of steric effects and slower diffusion. Besides, at similar mass concentrations the molar excess of alcohol decreases. Similar results were reported for the transesterification of ethylene carbonate with different alcohols, in which the yield decreases with an increase of the carbon atoms of the alcohol.[53] This indicates that a higher pressure is required for CO_2-expanded ethanol to achieve higher desorption yields. As in the methanol case, the desorption yield increases when a simultaneous esterification occurs. The desorption increases to 0.71 ± 0.02 mol (HAc + MeAc)/ mol $acetate_{in}$ with an esterification yield of 0.55 ± 0.02 with an excess of ethanol of 3.5% w/w $acetate_{in}$/ethanol. A further excess of ethanol (1.7% w/w $acetate_{in}$/ethanol) increases the esterification yield to 0.67 ± 0.01, which is in accordance with reported esterification data.[54]

The method might be applicable for a range of other alcohols such as butanol, benzyl alcohol, isoamyl alcohol, and geraniol. These alcohols can be used to produce esters such as butyl butyrate, benzyl acetate, isoamyl acetate and geranyl acetate, which are important in the solvent, fragrance and flavor industry.[55] The specific process conditions to achieve high conversion depend on each scenario and industry.

Recovery and esterification of carboxylates from fermentation broth still has to be tested. Sorption studies using carboxylates from actual fermentation on the current resin[37] indicate that contaminating anions, which are fermentation-specific, will have to be dealt with. Furthermore, other impurities (*e.g.* solid impurities and inorganic anions) might affect the long term stability and regeneration of the resin. The effect of these impurities in the feasibility of the process and the regeneration of the resin has to be study in detail for each application. In some cases, an extra conditioning step of the resin (to remove the impurities) might be needed in between each of the cycles .

Additionally, the high dilution of the produced esters (0.1-0.3 %wt) complicates their purification. In the case of methyl acetate, the ester can be concentrated at least to its azeotrope with methanol (81.3 wt%) by distillation. For dimethyl succinate and methyl lactate, having boiling points higher than methanol, no such azeotrope exists and recovery become a bottleneck. A higher concentration of the esters in CO_2-expanded alcohols would facilitate ester recovery. Currently, we are exploring the limits of achieving a higher concentration of esters (using

changes in alcohol excess and CO_2 pressure), and studying their recovery including excess solvent recycle.

3.4. Conclusions

This chapter has presented a new method for the recovery and esterification of carboxylates using CO_2-expanded alcohols. Using this method, the carboxylates are recovered using an anion exchange resin, and CO_2-expanded alcohol is used for the desorption and subsequent esterification of the carboxylates. The main advantages are: no stoichiometric waste production, low pressures of CO_2 needed and integration of the unit operations. Using CO_2 -expanded methanol, we achieved a desorption yield of 0.79 mol acetic acid/ $acetate_{in}$ at 10 bar of CO_2, and an ester yield of 1.03 mol methyl acetate/ $acetate_{in}$ in the combined desorption-esterification at 5 bar of CO_2 and 60 °C. The method might be applied for the recovery of different carboxylates produced by fermentation at pH > pK_a, such as lactate (0.70 methyl lactate/$lactate_{in}$) and succinate (0.18 dimethyl succinate/$succinate_{in}$), however has to be improved further, especially for dicarboxylates such as succinate. Moreover, a lower yield of 0.67 mol of ethyl acetate/ mol $acetate_{in}$ was obtained with CO_2-expanded ethanol. The method is versatile and can be optimized with respect to the reactor configuration, catalyst, CO_2 pressure, alcohol excess, temperature and reaction time, depending on the specific application.

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A.3. Supporting Information

A.3.1 Loading of the resin with acetate, succinate and lactate

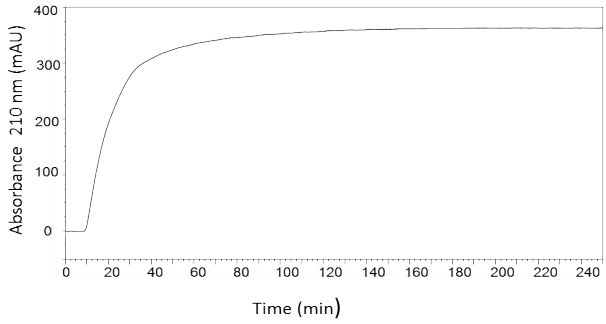


Figure A.3.1. Loading of Dowex MSA (~5 g wet resin) with 2 mL/min of a solution of potassium acetate (10 g/L).

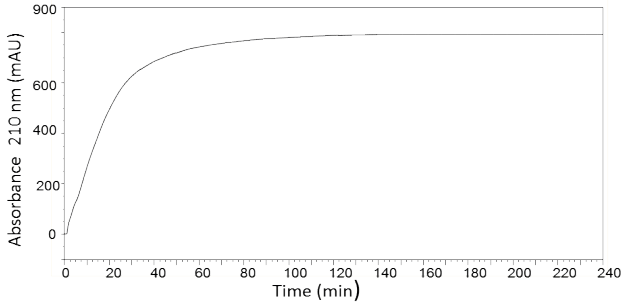


Figure A.3.2. Loading of Dowex MSA (~5 g wet resin) with 2 mL/min of a solution of sodium succinate (20 g/L).

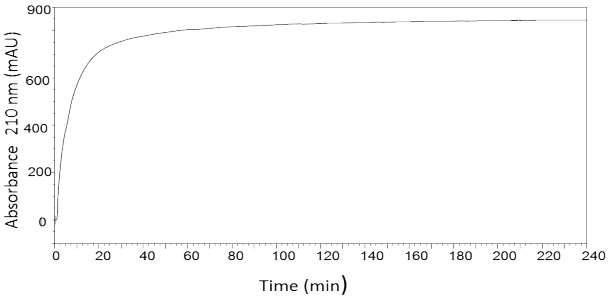


Figure A.3.3. Loading of Dowex MSA (~5 g wet resin) with 2 mL/min of a solution of sodium lactate (20 g/L).

A.3.2 X-Ray photoelectron spectroscopy (XPS) of the anion exchange resin

A.3.2.1 Surface composition of Dowex Marathon resin with different counter-ions

Table A.3.1 X-ray photoelectron spectroscopy analysis of Dowex Marathon resin*

Resin Counter-ion	Condition of the resin	Surface atomic composition (%)			
		C	O	N	Cl
Chloride	wet	75.57 ± 0.08	14.94 ± 1.99	5.06 ± 0.86	3.36 ± 1.42
Chloride	dry	82.62 ± 0.26	5.40 ± 0.21	6.25 ± 0.26	5.57 ± 0.02
Acetate	dry	77.31 ± 0.76	18.45 ± 1.42	2.66 ± 2.14	Not present
Bicarbonate	dry	79.33 ± 0.78	12.88 ± 1.59	4.8 ± 0.52	Not present
Recycle (MeOH+ CO_2)	dry	79.33 ± 0.78	14.39 ± 0.17	6.06 ± 0.31	0.42

*Relative constitution as C, O, N and Cl

Table A.3.2 X-ray photoelectron spectroscopy of preliminary Dowex Marathon resin loaded in batch mode (not a complete anion exchange)

Resin Counter-ion	Condition of the resin	Surface atomic composition (%)			
		C	O	N	Cl
Chloride	dry	81.7 ± 2.4	6.0 ± 1.4	6.2 ± 0.7	6.1 ± 1.3
Acetate	dry	83.7 ± 0.1	7.2 ± 0.3	5.7 ± 0.2	3.5 ± 0.1
Bicarbonate	dry	78.7 ± 0.5	15.6 ± 1.5	3.2 ± 0.8	2.4 ± 0.5

*Relative constitution as C, O, N, Cl

Table A.3.2 shows that on a batch process the resin is not fully exchanged, and some remaining chloride anion are bounded to the resin.

A.3.2.2 Deconvolution of C peak

The aim with de analysis of the deconvolution of the carbon peak is to analyze the type of the C bonds present at the resin surface. The deconvolution of the C peaks was done by keeping the C-C bond as internal standard at 284.8 eV.

Table A.3.3 Percentage of C-C, C-O and C=O bonds from the high resolution spectra*

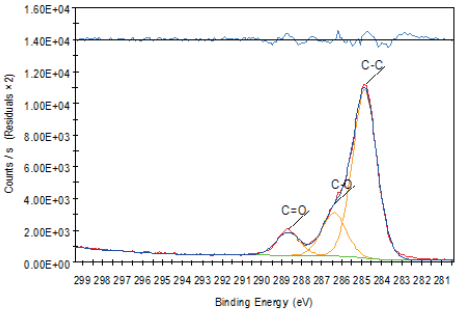
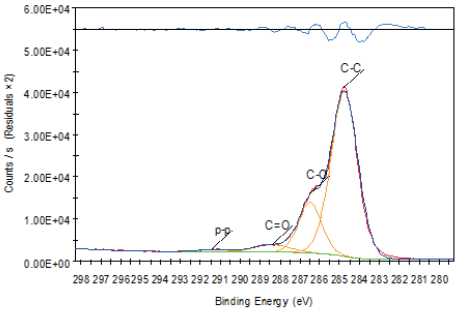
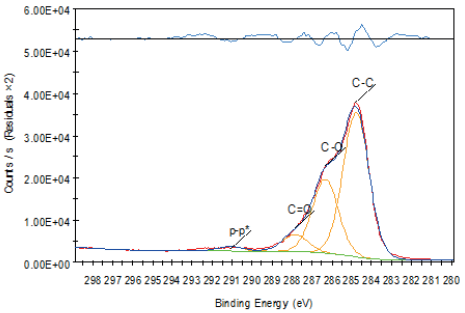
Resin Counter-ion	Condition of the resin	%C-C	%C-O	%C=O	**%π – π†**
Chloride	wet	41.0	34.2	18.2	6.7
Chloride	dry	57.6	34.6	6.3	1.5
Acetate	dry	71.5	18.5	9.9	Not observed
Bicarbonate	dry	74.1	20.0	4.6	1.4
Recycle (MeOH+ CO_2)	dry	60.1	30.82	7.2	1.9

*The fitting was done on representative spot for each sample.
†The π–π bond is calculated and represents the presence of the aromatic ring in the resin structure.

The deconvolution of the C peak shows three type of bonds for all the samples: C-C, C-O and C=O. Except for the acetate sample, all the other samples have the %π – π† transition, typical of the presence of aromatic rings. The wet chloride resin presents a lower amount of C-C (40.97) in comparison with the dry resin (57.63), but a higher amount of C=O (18.18) in comparison with the other samples. This might be because the water strongly binds to the resin, and for this reason the adsorbed water was further quantify with TGA. The C-C values increase for the

acetate and bicarbonate resin in comparison with the chloride form of the resin. Moreover, the acetate form has a higher value of C=O (9.92) compared to the bicarbonate form (4.57).

Table A.3.4. X-ray photoelectron spectroscopy spectra

Resin Counter-ion	Condition of the resin	High Resolution Spectra of C peak
Chloride	dry	
Acetate	dry	
Bicarbonate	dry	
Recycle (MeOH+ CO_2)	dry	

A.3.3 Thermogravimetric analysis (TGA) of the resin for detection of water content

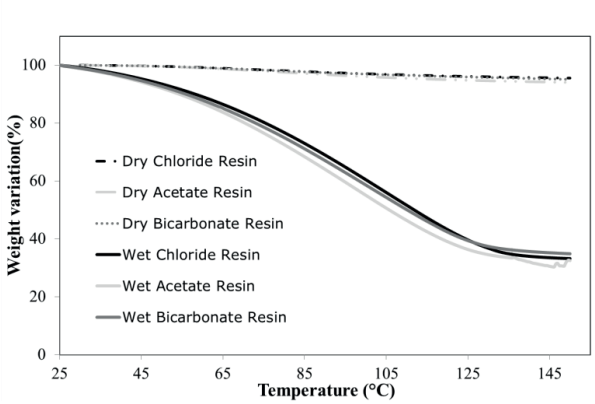


Figure A.3.4. Thermogravimetric analysis of the resin in chloride, acetate and bicarbonate form.

A.3.4 Desorption of acetate with water and carbon dioxide

Table A.3.5 Desorption of acetate from an anion exchange resin with CO_2 at 10 bar in water at 20-22 °C with a resin loading of 3.4 %w/w dry resin/water

Equilibrium CO_2 pressure (bar)	Desorbed acetic acid (mg/g)	Desorption (mol acetic acid/mol $acetate_{in}$)
10.1±0.1	1.23±0.48	0.38±0.05

Chapter 4

Esters Production via Carboxylates from Anaerobic Paper Mill Wastewater Treatment

Abstract

Some carboxylic acids can be formed from wastewater components using anaerobic mixed culture fermentation. The main challenge for their industrial production is their recovery from dilute aqueous solution. In this chapter, an option is proposed for the recovery and esterification of carboxylates produced by anaerobic digestion at a pH above the pK_a. The carboxylates (acetate, propionate, butyrate, valerate and lactate) are recovered using a strong anion exchange resin in the bicarbonate form. The wastewater pH and the presence of other inorganic anions have a strong effect on the total loading on the resin. Calcium, which is present in paper mill wastewater, can cause precipitation problems, especially at high pH. The resin was regenerated and methyl esters were produced using 5 bar CO_2-expanded methanol at 60 °C. Esters yields ranged from 1.08 ± 0.04 mol methyl acetate/ mol of $acetate_{in}$ to 0.57 ± 0.02 mol methyl valerate/ mol of $valerate_{in}$.

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4.1. Introduction

The decrease in the availability of natural resources and environmental impact of oil-based products has led to recovery of valuable compounds from waste streams. One of the main limitations for their recovery is the heterogeneous and dilute nature of the waste streams. Several techniques have been developed to recover or break down this waste stream in an efficient way.[1] Some of the techniques to produce high value products from waste streams are the enzymatic conversion of biomass into five and six carbon-sugars (sugar platform), biomass conversion into syngas (syngas platform) and biomass conversion into short chain organic acids (carboxylates platform).[2, 3]

The carboxylate platform aims to convert organic feedstock (often derived from agricultural or industrial waste) into short chain carboxylates as platform chemicals. In this process, mixed cultures of microorganisms are used under anaerobic conditions.[4] This anaerobic mixed-culture digestion is a well-known technique used to treat wastewater and recover methane for energy utilization. Since the energy density of methane is low, other alternatives such as the production of carboxylic acids and alcohols have been developed.[5] The main advantages of anaerobic wastewater treatment (in comparison with aerobic treatments) are: lower energy demand, lower microbial biomass production and lower nutrient requirement. During anaerobic digestion the microbial community is selected by the process conditions. The organic matter in the wastewater is broken down into water soluble products such as carboxylate salts, while methanogenesis is inhibited.[6] These produced carboxylate salts are difficult to recover as carboxylic acids because strong ionic interactions have to be overcome. Therefore, this recovery is a bottleneck for valorizing wastewater.

Different separation techniques have been developed for carboxylates recovery.[7-9] Additionally, some technologies focus on the conversion of water soluble carboxylates to other products that might be easier to recover from the aqueous stream. Such technologies are for example: production of polyhydroxyalkanoates (PHA)[10] and medium chain fatty acids (MCFA).[11, 12] However, the separation and purification of the PHA and MCFAs still represent important processing costs that compromise industrial implementation.[11, 13, 14] For example, the main advantage that has been reported for MCFA production is an easier extraction in comparison to short chain carboxylates. However, the pK_a of these acids is lower than the pH (5.5-7.0) used in the chain elongation reactor,[15, 16] which means that the majority of the molecules are in the dissociated form and their hydrophobic characteristics cannot be entirely exploited. As a consequence, the process presents similar separation difficulties as other carboxylates produced by fermentation at pH above the pK_a. Therefore, alternative techniques such as membrane electrolysis have been developed to separate these MCFAs.[17] However, these techniques are energy intensive, and further improvement is needed for their industrial implementation. Other approaches include the utilization of ionic liquids for the recovery of carboxylic acids at low pH,[18, 19] or the utilization of weak anion exchange resin combined with a desorption with methanol and hydroxide.[20]

To avoid the difficulties involved in the traditional separation of carboxylates (high energy consumption and high waste coproduction), an integrated recovery and protonation of the carboxylates salt was developed. With this method, the carboxylates are recovered using a strong anion exchange resin in the bicarbonate form. Consequently, the carboxylates that are bound to the resin are desorbed and protonated using CO_2-expanded methanol. The advantages of this method are: high solubility of CO_2 in the alcohol (low operating CO_2 pressures needed) and no

stoichiometric waste salt production, if liberated bicarbonate is used to control pH of anaerobic digestion. The next separation steps of the desorbed carboxylic acid from the alcohol might involve distillation, esterification or crystallization (by tuning the acid solubility in the alcohol using CO_2). Furthermore, regenerated resin can be reused in the next adsorption step. The method has been experimentally validated with individual solutions of acetate, succinate and lactate, using either methanol or ethanol as alcohol.[21]

However, it is not clear yet if such a method would work with real wastewater. The current chapter aims to recover and esterify carboxylates (acetate, propionate, lactate, butyrate and valerate) from an anaerobic treated paper mill wastewater stream. The paper industry generates large amounts of waste with high moisture content.[22] In this chapter, recycled paper industry wastewater was treated anaerobically for the production of carboxylate salts (pH above the pK_a). Consequently, the carboxylates are recovered with an anion exchange resin, and desorption-esterification is performed with CO_2-expanded methanol.

4.2. Material and Methods

4.2.1 Acidified Paper Mill Wastewater

Paper mill wastewater was obtained from Eska Graphic Board (Hoogezand, the Netherlands). The wastewater originates from their paper recycling process in which no chemical pulping, bleaching or chemical deinking was performed. This paper recycling process used mechanically disrupting, sorting and pH maintenance by CaO addition for the treatment of the recycled paper. This industrial wastewater contains ~25 g COD/L, and 20%w/w of the total COD (chemical oxygen demand) was so-called volatile fatty acids, according to supplier. This stream was treated in a pilot plant anaerobic plug flow reactor where the remaining COD was converted into volatile fatty acids (yield 60-70%w/w). The hydraulic retention time (HRT) of the anaerobic reactor was 6 h, and the solid retention time (SRT) was 4 days. The volatile fatty acids were concentrated in a storage vessel (HRT of 6 days) to 70-80% w/w of the total COD. Samples of the acidified wastewater were taken from the storage vessel of the pilot plant, and were analyzed (after removal of solid particles by microfiltration) for determination of acetate, propionate, butyrate, valerate, nitrate, phosphate, sulfate, chloride, bicarbonate, calcium concentration and total COD.

Mimicked acidified wastewater was prepared dissolving acetic acid, propionic acid, butyric acid, valeric acid, lactic acid, sodium chloride, sodium phosphate, sodium nitrate and sodium sulfate in deionized water (Milli-Q). The pH was then adjusted to 5.1 with sodium hydroxide.

4.2.2 Other Materials

All the chemicals were analytical grade: potassium acetate (≥99.9%), Dowex Marathon MSA resin (type I; macroporous, chloride form), methyl acetate (≥99.9%), anhydrous methanol (≥99.8%), methyl propionate (≥99%), methyl butyrate (≥99%), methyl valerate (≥95%), methyl lactate (≥97%) (Sigma-Aldrich), acetic acid (≥99%), butyric acid (≥99%) and lactic acid (1M) from JT. Baker B.V. Propionic acid (≥99%) and valeric acid (≥99%) were obtained from Merck. Compressed carbon dioxide (≥99.8%) was used directly (Linde Group). Amberlyst15 (Serva, Heildelberg) hydrogen form (4.7 mEq/g by dry weight) was washed with methanol and dried at 60 °C in an oven before used. All the aqueous solutions were prepared by diluting the different

inorganic salts and the carboxylic acids to the required concentration using deionized water from a Milli-Q purification system.

4.2.3 Resin Preparation

Dowex Marathon MSA was supplied in the chloride form (Sigma-Aldrich). It was converted from the chloride form to the bicarbonate form by column elution technique. In this preparation, the resin was washed with constant flow (2 mL/min) of sodium bicarbonate solution (20 g/L), until the absorbance at 210 nm at the outlet of the column was constant. The resin was washed with a constant flow (2 mL/min) of deionized water (50-100 bed volumes), until the absorbance at 210 nm at the outlet of the column remained constant. The resin was converted to the bicarbonate form because this is the form in which the resin is regenerated after desorption with methanol and carbon dioxide.

For the desorption experiments, the resin was further washed 3 times with 50 mL deionized water. The excess water was removed using a vacuum filter, Millipore Steriflip 60 µm nylon net filtration unit, at 20 mbar. Subsequently, the resin was washed 3 times with 30 mL methanol and filtered with the same system. Finally, the resin was dried in an oven at 60 °C for 16 h.

4.2.4 Recovery of carboxylate by column sorption

A weighed amount of anion exchange resin (5 g of wet resin chloride form (65-68 % w/w water)) was placed in an adjustable height Omnifit glass column (1 cm of internal diameter x 15 cm height). Breakthrough experiments were performed in a Thermo Scientific Dionex Ultimate 3000 system. Carboxylate solutions were pumped through the column at 2 mL/min and 25 °C. Fractions of 2 mL were collected. Feed samples and collected fractions were analyzed for carboxylates and inorganic anions (sulfate, nitrate, phosphate and chloride).

4.2.5 Batch ion exchange experiments

Batch ion exchange experiments were performed with and without carbon dioxide. The experiments without carbon dioxide were performed in bottles with 60 mL of calcium acetate (2.68 g/L) to which different amounts of wet resin (Dowex Marathon MSA) in the bicarbonate form were added (from 1 to 5 g or resin). The bottles were shaken for 16 h at 22 °C and 225 rpm. A control experiment was performed at the same conditions with resin in chloride instead of bicarbonate form. Samples were collected at 0 h and 16 h, and were analyzed immediately for total CO_2, dissolved calcium, acetate and pH.

The experiments with CO_2 pressure were performed in 50 mL Büchi glass stirred reactor (see section 2.6). In a typical experiment, approximately 30 g solution of calcium acetate (2.68 g/L) or wastewater was added to the reactor. Then, 0.75 g of resin (Dowex Marathon MSA) for acetate solution or 1.75 g of resin for wastewater in the bicarbonate form was added to start the recovery step. The experiment was kept for 16 h at 1-3 bar of CO_2 (depending of the experiment), at 20-22 °C and an agitation of 200 rpm. Samples were collected and analyzed using the same procedure as before. The loading of acetate was calculated by the difference between the liquid concentration of acetate before and after the batch experiment.

4.2.6 Desorption and esterification with carbon dioxide expanded methanol

Desorption batch experiments were performed in a 50 mL Büchi glass stirred autoclave reactor, which was equipped with a magnetically driven four blade impeller controlled by an

overhead motor, thermocouple for temperature control, pressure sensor, pressure relief valve, nitrogen and carbon dioxide inlet, reagent addition and sampling ports.

During a typical experiment, 0.5 g of dry Dowex MSA (loaded as described in section 2.3) was added to 30 g of anhydrous methanol. As catalyst for the esterification, 0.5 g of dry Amberlyst15 was added to the mixture in a separate compartment in the reaction. The reactor was flushed 5 times with carbon dioxide, and then the pressure was set to 5 bar of CO_2. The reactor was repressurized with carbon dioxide until the pressure was constant. The experiments were performed for 4 h at 60 °C in duplicate. Liquid samples were obtained at the set pressure. Initial samples of the solvent, and final samples were analyzed for methyl acetate, methyl propionate, methyl butyrate, methyl valerate, methyl lactate and the inorganic anions (chloride, phosphate, nitrate and sulfate).

4.2.7 Analytical Methods

Methyl acetate, methyl butyrate, methyl valerate and methyl lactate were analyzed by gas chromatography (GC) using a ZB-WAXplus column (20 m length × 0.18 mm internal diameter, 0.18 µm film) and a flame ionization detector (FID). Injection and detector conditions were maintained. Liquid samples were conditioned with anisole as internal standard. The sample (1 µL) was injected at 200 °C with a split flow of 30 mL/min. The oven temperature was maintained at 60 °C for 10 min, then a 10 °C/min temperature ramp was used up to 200 °C. Methyl propionate was analyzed by gas chromatography (GC) on an Agilent 6890N system equipped with a CP-PoraPLOT Q column (30 m length × 0.32 mm internal diameter, 10 µm film) and a flame ionization detector. Helium was used as carrier gas. An injection size of 1 µL was used with a split ratio of 20. The injector temperature was 200 °C. The column was initially at 150 °C and kept for 5 min, followed by a temperature ramp of 10 °C/min until 220 °C. Total acetic acid, propionic acid, butyric acid, valeric acid and lactic acid concentrations were analyzed on a Waters HPLC system using a Bio-Rad Aminex HPX-87H column (78 × 300 mm) at 60 °C. Phosphoric acid (1.5 mmol/ L at 0.6 mL/min) was used as an eluent. Phosphate (Hach-Lange LCK349), sulfate (Sigma-Aldrich MAK132), nitrate (Hach-Lange LCK339), total chemical oxygen demand (Hach-Lange LCK914), calcium (Hach-Lange LCK327), potassium (Hach-Lange LCK328), carbon dioxide (Hach-Lange LCK388), and chloride concentration (Sigma-Aldrich MAK023) were determined spectrophotometrically using the specific test kit.

The inorganic ions in initial wastewater samples were analyzed with a Metrohm ion-chromatography system using an A Supp 5/150/4.0 column for anion analysis and a C4 Cation 150/4.0 column for cation analysis. The system consists of two independent modules for the separate detection of anions and cations; a Metrohm 818 anion and 883 cation system and a conductivity detector. The eluents used for separation in the columns were: 3.2 mmol/L Na_2CO_3 and 1 mmol/L $NaHCO_3$ (0.7 mL/min) for the cation system, and 3 mmol/L HNO_3 (0.9 mL/min) for the anion system, respectively. The anion system requires chemical suppression of background signal exchanging Na^+ by H^+. The background signal was lowered to 1 µS/cm by the Metrohm Surpessor Module (MSM) and a CO_2 stripper. The MSM was regenerated by a 50 mmol/L H_2SO_4 solution.

4.3. Results and Discussion

4.3.1 Wastewater characterization

Recycled paper wastewater was treated anaerobically to produce a stream that was rich in carboxylates. The wastewater contains a high amount of calcium, since the paper industry uses calcium oxides in the process to control the pH and removal of ink particles. Sodium is present in the wastewater, since sodium hydroxide was used to control the pH during anaerobic digestion in the pilot plant. The analyzed anions that were detected in the wastewater are carboxylates: acetate, butyrate, propionate, valerate and lactate, and the inorganic anions: chloride and phosphate. The measured concentrations of these anions are shown in Table 4.1. Calcium, sodium and potassium are the main cations present in the wastewater, but 5 mEq/L of an unknown cation is needed to close the charge balance of the measured anions and cations. The pH of the wastewater is 5.1.

Table 4. 1. Characterization of the acidified paper mill wastewater

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Calcium	323.2	Acetate	839±9
Sodium	175.5	Propionate	279±4
Potassium	172.15	Butyrate	377±9
		Valerate	186±3
		Lactate	19±0
		Chloride	297
		Phosphate	71.29
Total cations	28.16 mEq/L	Total anions	33.20 mEq/L

The soluble COD content of this substrate was 3310 mg/L. The accumulated COD of the carboxylic acids is 2155 mg/L, which is around 65% of the total soluble COD. This suggest that other organic components might be present such as glucose, ethanol or soluble lignin.[23] The wastewater obtained from Eska comes from the treatment of recycled paper with mechanical disruption, sorting and pH maintenance by CaO addition. As a result, the wastewater does not contain extra chemicals from pulping and bleaching, but it might contain ink and sizing additives and complex organic structures like lignin. Typical inorganic additives used during the paper making process comprehend: magnesium, silica, calcium, sodium, aluminum, barium, zinc, potassium, ammonium, titanium, sulfate, chloride, carbonate and phosphate.[24] Total suspended solid (TSS) and volatile suspended solids (VSS) concentrations were 0.05 g/L for both determinations, according to supplier. Additionally, microfiltration was performed before the anion exchange process to prevent fouling of the bed. Although microfiltration could not remove all the particles, the amount remaining did not seem to affect the experiments.

The characterization of the wastewater was used to prepare carboxylates mixtures and mimicked wastewater mixtures for column experiments. In these experiments, the effect of the different inorganic/organic anions was studied in detail.

4.3.2 Recovery of the carboxylates by anion exchange resin

Sorption studies were done using a mixture of carboxylates, a mixture of carboxylates with inorganic anions, and the paper mill wastewater. The concentration of the mimicked mixtures was adjusted to the values reported in Table 4.1. The pH was adjusted with sodium hydroxide. Fig. 4.1 and 4.2 show the elution profiles of the carboxylates as breakthrough curves for the mimicked mixture and the wastewater (pH 5.1). The resin used is Dowex Marathon MSA with

bicarbonate as counter-ion, and was prepared as described in Section 4.2.3. The bicarbonate form of the resin is used because this is the form after desorption with methanol and carbon dioxide (Section 4.3.5).

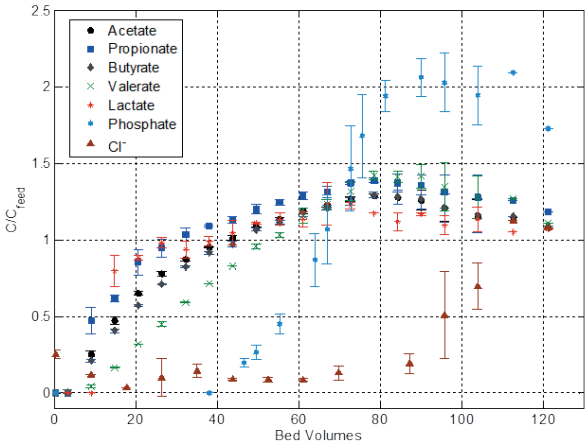

Figure 4.1. Breakthrough curves, mimicked mixture of wastewater at room temperature. (C, effluent concentration; C_{feed}, feed concentration). Average values of duplicate experiments.

Figure 4.1 shows that the breakthrough of acetate, propionate and butyrate occurs at 9 bed volumes, and shows a spread sorption front. Figure 1 suggests that the selectivity of valerate is higher than the selectivity of other carboxylates. A reason might be that at this pH (5.1), a 30% valeric acid (un-dissociated form) is also present, which is similarly removed by the resin. Valeric acid is more hydrophobic than other lower chain carboxylic acids (Table 4.2), which caused a higher interaction and higher removal of valeric acid in comparison with the other carboxylates. Additionally, there is a higher loading capacity (1.67 mEq carboxylates per g wet resin) for all the carboxylates at pH 5.1 in comparison with the loadings of fully dissociated carboxylates (pH 7) (1.13 mEq carboxylates per g wet resin), which are summarized in Table 4.3 The loading per anion was determined by numerical integration of the total amount of anion retained by the resin. The capacities obtained are higher than the reported values of ~0.8 mEq carboxylates per g wet resin (assuming a water content in their resin of 60 %w/w and taking their best performance at pH 6.5, 1.4 mmol per g dry resin) in batch operation for recovering of carboxylates from anaerobic treated grape pomace wastewater.[20]

Table 4.2. Dissociation constant and partition coefficient of carboxylic acids.[25]

Carboxylic acid (PubChem CID)	pK_a	Log P
Acetic acid (176)	4.76	-0.17
Lactic acid (612)	3.86	-0.72
Propionic acid (1032)	4.88	0.33
Butyric acid (264)	4.82	0.79
Valeric acid (7991)	4.84	1.39

The carboxylates showed chromatographic peaking at 50 BV, resulting in an effluent concentration higher than the feed concentration. This is caused by the higher affinity of the

inorganic anions to the resin in comparison with the carboxylates. The inorganic anions compete for the exchange sites already occupied by the carboxylates, which results in carboxylate desorption. As a consequence, there is an overshooting of the carboxylates with the breakthrough of phosphate followed by the overshooting of phosphate after the breakthrough of chloride.

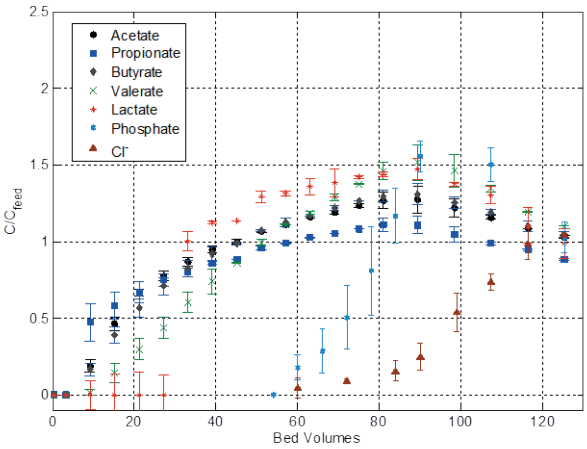

Figure 4.2. Breakthrough curves for anions from acidified paper mill wastewater at pH 5.1. (C, effluent concentration; C_{feed}, feed concentration)

Figure 4.2 shows the breakthrough curve for the different anions from the wastewater at pH 5.1. As in the mimicked wastewater experiment, the breakthrough of the carboxylates (excluding valerate) is at 9 BV, and the breakthrough of valerate is at 15 BV. There is an overshooting of the carboxylates and phosphate similar as for the mimicked mixture (breakthrough of phosphate and chloride). A main difference in the wastewater is the presence of calcium as counter-ion, which leads to the possible precipitation of calcium carbonate. During the sorption experiment, there is an increase of the effluent pH to 8 because of the liberation of bicarbonate from the resin (counter-ion of the resin, Section 4.2.3). The increase of the pH shifts the carbon dioxide equilibrium to the formation of carbonate, which might cause precipitation of calcium carbonate (solubility of calcium carbonate is 0.12 g/mL). Additionally, there was an increase in the pump pressure to 15 bar during the interval at pH 8, which suggests a change in equilibrium caused by calcium. Thereafter, the pressure starts to decrease until 3 bar, and it is attributed to the re-solubilization of calcium carbonate with the decrease of the pH.

Table 4.3 shows a comparison between the characteristics observed in the mimicked mixture and the paper mill wastewater.

Table 4.3. Comparison of sorption of a mimicked mixture and wastewater at pH 5.1.

Mimicked mixture	Paper mill wastewater
Inorganic anions are preferably retained	Inorganic anions are preferably retained
Overshooting of all anions except chloride	Overshooting of all anions except chloride
Valerate seems to be more selective than the other organic anions	Valerate seems to be more selective than the other organic anions
Breakthrough of chloride at about 80 BV	Breakthrough of chloride at about 80 BV
Breakthrough of phosphate at about 47 BV	Breakthrough of phosphate at about 60 BV
Sharper peak of phosphate C/C_{feed} = 2.0	Peak of phosphate C/C_{feed} = 1.6
Loading capacity 1.47 ± 0.03 (mEq/g wet resin)	Loading capacity 1.76 ± 0.08 (mEq/g wet resin)

Table 4.4 shows the recovery and loading of carboxylates and inorganic anions from the separation with Dowex Marathon MSA at pH 5.1. The obtained total loading capacity of anions is higher for the wastewater than for the carboxylate and mimicked mixture. As shown in a later section, the reason might be that other impurities such as Ca^{2+} in the wastewater affect the equilibrium of bicarbonate, and promote the adsorption of the carboxylates. Moreover, the loading of carboxylates at 120 BV is higher in the carboxylate mixture (1.50 mEq/g wet resin) than in the mimicked mixture (0.12 mEq/g wet resin) or wastewater (0.17 mEq/g wet resin) because of the overshooting, competition and displacement of the carboxylates from the resin. In most cases, the carboxylate anions that were once adsorbed to the resin are displaced by inorganic anions, which have a higher affinity to the resin. This is especially observed in the values of the mimicked carboxylates (Table 4.4), in which the amount of acetate and propionate bound to the resin is in the same order of magnitude (or negative values) as the standard deviation (measurements error). For the mimicked mixture and wastewater, the amounts of carboxylates that were loaded on the resin are comparable.

Table 4.4. Loading capacity of Dowex Marathon MSA bicarbonate form for the recovery of carboxylates and inorganic anions at pH 5 at 120 bed volumes (BV).

Carboxylate	Amount loaded to resin (mEq/g wet resin)		
	Carboxylate mixture	Mimicked carboxylate and inorganic anions	Wastewater
Acetate	0.95+0.03	0.059 ± 0.065	0.060 ± 0.022
Propionate	0.12*	-0.070 ± 0.029	0.079 ± 0.005
Butyrate	0.26+0.01	0.033 ± 0.016	0.019 ± 0.011
Valerate	0.14+0.02	0.028 ± 0.006	0.010 ± 0.001
Lactate	0.025+0.002	0.000 ± 0.044	0.000 ± 0.010
Chloride	-	1.019 ± 0.119	1.125 ± 0.084
Sulfate	-	0.253 ± 0.00	0.447 ± 0.005
Phosphate	-	0.001 ± 0.000	0.003 ± 0.004
Nitrate	-	0.017 ± 0.001	0.018 ± 0.000

*No repetition

Because of overshooting, the resin is loaded mainly with chloride anions (for mimicked mixture and wastewater) at the end of the experiments (120 BV). To avoid the displacement of the carboxylates from the resin, the column has to be operated at a lower retention time. At 40 BV, the carboxylate concentration reaches the feed concentration ($C = C_{feed}$), in which 1/3 of the resin is in the carboxylate form, 1/3 in the inorganic anion form and 1/3 in the original bicarbonate form. The calculated loading capacity considers the total carboxylates and carboxylic acids adsorbed to the resin. The reason is that at pH 5.1 there might be additional adsorption of the undissociated acid form (for example, by hydrophobic bonding with the resin), which improves the capacity. In the following section, experiments with the wastewater at pH 7 are used to compare them with experiments at pH 5.1.

4.3.3 Effect of pH on the recovery of the carboxylates from wastewater

The change of feed pH has a strong effect on the recovery of carboxylates from wastewater. At pH close to the pK_a, carboxylates are removed by both ionic and hydrophobic interactions with the resin. At a higher pH, the hydrophobic interactions are weak in comparison with the ionic interactions for small molecules such as the carboxylates acetate, propionate, butyrate, lactate and valerate. The pH of the wastewater was increased to 7 and 12 to analyze the change in selectivity and total change in recovered carboxylates. The wastewater changed drastically of

color with the change in pH (Appendix, Figure A.4.2). This might be caused by the ink products present in the wastewater coming from recycled paper. A breakthrough experiment was performed for the wastewater solution at feed pH 7, but the pressure rapidly increased to ~40 bar and the experiment was stopped. The reason of the pressure increase is assumed to be obstruction of the column material because of precipitation of calcium carbonate, especially at higher pH value in the column (Appendix, Figure A.4.3). This was confirmed by a column experiment of the wastewater at pH 7 using the resin initially in the hydroxide form. In this experiment, the effluent pH increased until 12, but no increase in pressure was observed (Appendix, Figure A.4.4). Breakthrough experiments were performed for the wastewater solution at pH 12, and a rapid increase of the pressure (~40 bar) was observed after 20 BV (Appendix, Figure A.4.5) in which the experiment was stopped. At this point, the resin achieved saturation of carboxylates and it was used for further desorption-esterification (Fig. 4.3).

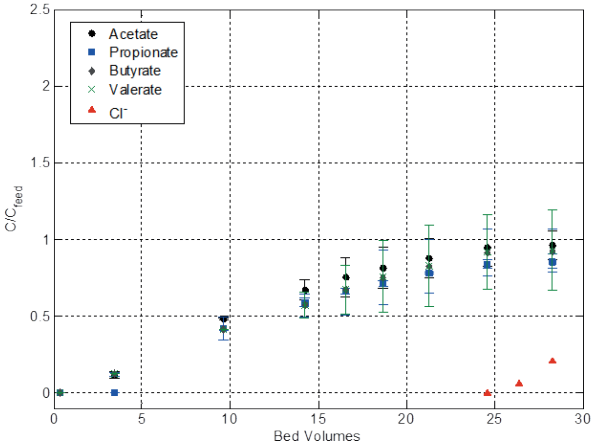

Figure 4.3. Breakthrough curves for anions from acidified paper mill wastewater at pH 12. (C, effluent concentration; C_{feed}, feed concentration). The concentration of the other anions (lactate, phosphate, sulfate) are below detection limits during the operation at 30 BV. Lactate is below detection limits during 20 BV of the experiment.

At feed pH 12, blockage of the resin by the formation of calcium carbonate was confirmed by reduction of calcium concentration at the effluent of the column. At high pH, the dissociation equilibria of carbonic acid and bicarbonate shift to carbonate, which then precipitates with calcium (Section 4.3.4). This might become a difficulty in the case of wastewaters with high content of calcium and with a pH close to the pK_a of carbonate and bicarbonate. Therefore, these equilibrium reactions were studied in more detail to avoid precipitation of calcium carbonate.

4.3.4 Precipitation of calcium carbonate during the recovery of carboxylates with a strong anion exchange resin in the bicarbonate form

Batch experiments were used to confirm the occurrence of calcium carbonate precipitation. Hence, experiments with a calcium acetate solution and wastewater were performed in which the carboxylates were recovered using the anion exchange resin in the bicarbonate form. Different amounts of resin were used, and the results are shown in Table 4.4.

Table 4.4. Precipitation of calcium carbonate in batch with Dowex Marathon MSA in bicarbonate form with 60 mL of calcium acetate solution (2.68 g/L), initial pH 7.42, $Ca^{2+}{}_{initial}$: 682 mg/L

Amount of wet resin (g)	Final pH	Loading of acetate (total g acetate on resin)	Final Ca^{2+} (mg/L)
Control*	7.23±0.02	0.024±0.01	656±9
1	6.59±0.04	0.040±0.01	525±4
2	6.58±0.03	0.060±0.01	480±4
3	6.56±0.02	0.072±0.01	379±7
5	6.76	0.087±0.01	271

*Control: Dowex Marathon MSA in chloride form, 1 g

There is a decrease in the calcium concentration with an increase of the amount of resin. With more exchange between acetate and bicarbonate, more bicarbonate is released into the solution, which results in a pH increase. At higher pH, bicarbonate is converted into carbonate, and contributes to the precipitation of calcium carbonate (reduction in final Ca^{2+} concentration). As calcium carbonate precipitates, there is a further decrease in pH due to the consumption of carbonate ions. The equilibria reactions that are considered are expressed in equations R.0-R.6.

	CO_2 (g)		↔		CO_2 (aq)		R.0
CO_2 (aq)	+	H_2O	↔		H_2CO_3		R.1
	H_2CO_3		↔	HCO_3^-	+	H^+	R.2
	HCO_3^-		↔	CO_3^{2-}	+	H^+	R.3
	$CaCO_3$ (s)		↔	CO_3^{2-}	+	Ca^{2+}	R.4
	HAc		↔	Ac^-	+	H^+	R.5
$Q^+HCO_3^-$	+	Ac^-	↔	Q^+Ac^-	+	HCO_3^-	R.6

From the equilibrium reactions (R.0-R.6), it can be seen that the occurrence of precipitation in the calcium acetate-bicarbonate resin system can be controlled by shifting the equilibria to carbonic acid formation, which lowers the pH. At higher CO_2 pressures, the equilibria are pushed to the formation of the more soluble species: bicarbonate and carbonic acid. To avoid precipitation, batch experiments were performed with different CO_2 pressures and Dowex MSA in the bicarbonate form for a calcium acetate solution and paper mill wastewater at pH 5.1 (Table 4.5).

Table 4.5. CO_2-pressurized batches for the recovery of acetate from a calcium acetate solution (2.68 g/L, initial pH 7.42, $Ca^{2+}{}_{initial}$: 685 mg/L) and paper mill wastewater (initial pH 5.27, $Ca^{2+}{}_{initial}$: 321 mg/L) using 1.75 g of Dowex Marathon MSA in the bicarbonate form

Solution	$CO_{2\,eq}$ Pressure (bar)	Final pH	Loading of carboxylate (total g carboxylate in resin)	Final Ca^{2+} (mg/L)
Calcium acetate	2.84-3.00	5.72±0.10	0.018±0.01	681±3
Calcium acetate	1.00	5.96	0.021±0.01	683.7
Wastewater	1.15	6.02±0.03	0.025±0.01	329±31

Table 4.5 shows that there is no decrease in the calcium concentration at the end of each of the batches with CO_2. This confirms that the precipitation can be avoided, and that the equilibria can be affected by using pressurized CO_2 in the system. However, higher CO_2 pressures result in higher bicarbonate concentration in solution which reduces the exchange of acetate (lowering the removal capacity of the resin). As can be observed, the carboxylate loading is lower for the calcium acetate batch at ~3 bar CO_2 pressure than at 1 bar CO_2 pressure, which is caused by the competition with extra bicarbonate anions in solution. The CO_2 partial pressure can be controlled

in the adsorption column and released after the column operation to permit the precipitation of $CaCO_3$. Furthermore, precipitated $CaCO_3$ can be reused in the anaerobic digestion for pH control as proposed by others.[26]

4.3.5 Desorption and ester production with CO_2-expanded methanol

In previous chapter, we demonstrated that CO_2-expanded alcohols can be used for the desorption and esterification of carboxylates (acetate, lactate and succinate) from a strong anion exchange resin.[21] However, the application of this method has to be proven for desorption of carboxylates recovered from wastewater. For this reason, the resin-bound carboxylates from paper mill wastewater (Section 4.3.2 and 4.3.3) were used to achieve desorption and esterification of acetate, propionate, butyrate, lactate and valerate from the anion exchange resin with CO_2-expanded methanol. The results are shown in Table 4.6 for a carboxylate solution and paper mill wastewater.

Table 4.6. Desorption and esterification of carboxylates recovered from paper mill wastewater at 5 bar of CO_2 and 60 °C for 4 h

Adsorption		Desorption + esterification Yield (mol methyl ester/ carboxylate$_{in}$)				
Wastewater	pH	Methyl acetate	Methyl propionate	Methyl Butyrate	Methyl lactate	Methyl valerate
Carboxylate solution	5.5	1.02±0.11	0.60±0.09	0.47±0.04	0.76±0.18	0.41±0.04
Carboxylate solution	7	0.86±0.08	0.63±0.03	0.42±0.04	0.34±0.07	0.34±0.03
Carboxylate solution[a]	7	1.08±0.04	0.65±0.02	0.58±0.03	1.07±0.05	0.57±0.02
Paper mill wastewater	5.1	0.89±0.04	0.41±0.02	0.46±0.03	n.d.[b]	0.43±0.02
Paper mill wastewater	12	0.88±0.04	0.57±0.02	0.56±0.03	n.d.	0.46±0.02

[a.] Desorption + esterification reaction for 16 h instead of 4 h. [b.] n.d: not detected

Table 4.6 shows that the desorption method is effective for the five different carboxylates studied. High methyl ester yields are obtained for the smaller carboxylates, and the yield decreases with the increase in molecular size. This result is comparable to results in other studies, which concluded that the reactivity of the carboxylic acids was controlled by steric factor with an increase in alkyl chain length.[27] Additionally, longer reaction times (16 h shown in Table 4.6) increase the yield for all the methyl esters, thus indicating that the system did not achieve equilibrium after 4 h.

The carboxylate solution does not contain inorganic anions, and as a result there is a higher carboxylate loading on the resin in comparison with wastewater experiments (Section 4.3.2 and 4.3.3), which affects the desorption-esterification step. This is especially noticeable in the methyl lactate case, in which the loading on the resin is low (0.013 mEq/g dry resin), and as a consequence the amount of methyl lactate produced, with the paper mill wastewater, is below the detection limit.

In this chapter, it has been demonstrated that the recovery of carboxylates from wastewater and further desorption and esterification with CO_2-expanded methanol is an option for valorization of wastewater. However, the methyl esters still have to be recovered from the methanol and carbon dioxide mixture. Development of this separation is required to assess the

applicability of the overall method. The current concentration of about 4 mg total methyl esters per g methanol will have to be increased.

Moreover, the integration of the recovery and purification steps to the process is an important factor that has to be studied in detail. For example, the bicarbonate solution produced after the adsorption of the carboxylates might be recycled to the anaerobic digestion for pH control. It would be interesting to study the effect of this recycle on the mixed culture fermentation and on the spectrum of carboxylates produced. Several researchers have studied the effect of addition of CO_2, removal of carboxylate, and ratio of metal cation used on the amount and type of carboxylate produced.[11, 28-30]

4.4. Conclusions

Paper mill wastewater was treated in an anaerobic mixed culture fermentation, and the produced carboxylates were recover by an anion exchange resin. The carboxylate loading is higher (1.67 mEq /g wet resin) for carboxylates loaded at pH 5.1 in comparison with pH 7 (1.13 mEq carboxylates/ g wet resin). $CaCO_3$ precipitation can be avoided in the column by controlling the CO_2 pressure. The resin was regenerated and esters were obtained with yields from 1.08 ± 0.04 mol methyl acetate/ mol of $acetate_{in}$ to 0.57 ± 0.02 mol methyl valerate/ mol of $valerate_{in}$ at 5 bar of CO_2-expanded methanol and 60 °C.

4.5. Acknowledgements

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A.4. Supporting Information

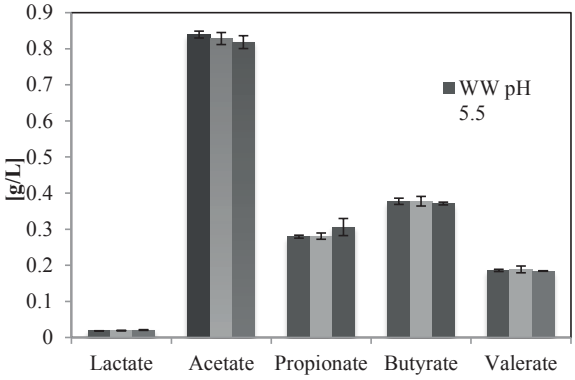


Figure A.4.1. Analysis of carboxylate concentration in the paper mill wastewater (WW) at pH 5.5, 7.13 and pH 12 (removal of precipitate by centrifugation).

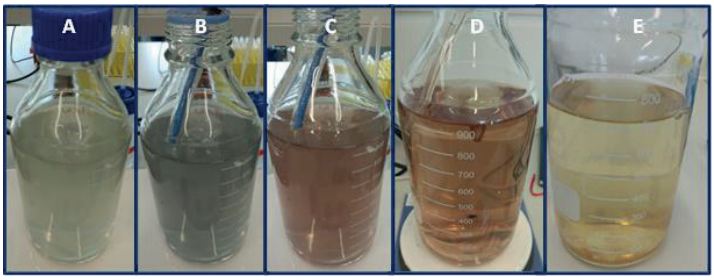


Figure A.4.2. Change of color of the paper mill wastewater at different pH values. A) pH 5.37; B) pH 7; C) pH 9.95; D) pH 11; and E) pH 12.

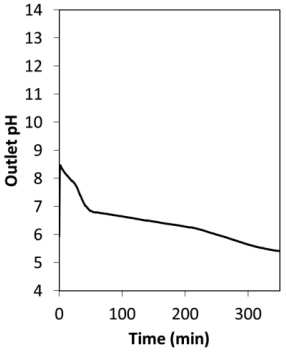


Figure A.4.3. Raw data of a breakthrough experiment of the paper mill wastewater at pH 5.1 with the resin in the bicarbonate form.

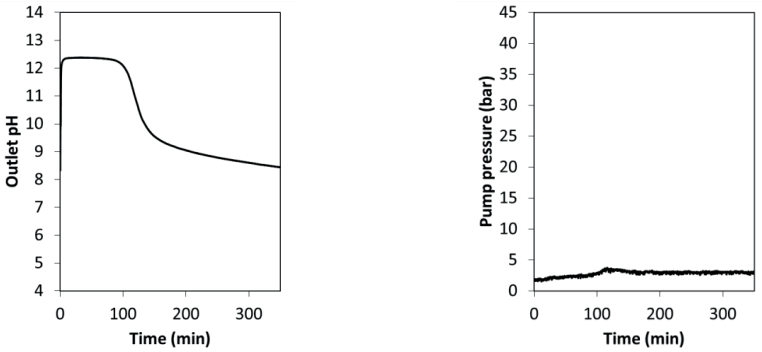


Figure A.4.4. Raw data of a breakthrough experiment of the paper mill wastewater at pH 7 with the resin in the hydroxide form.

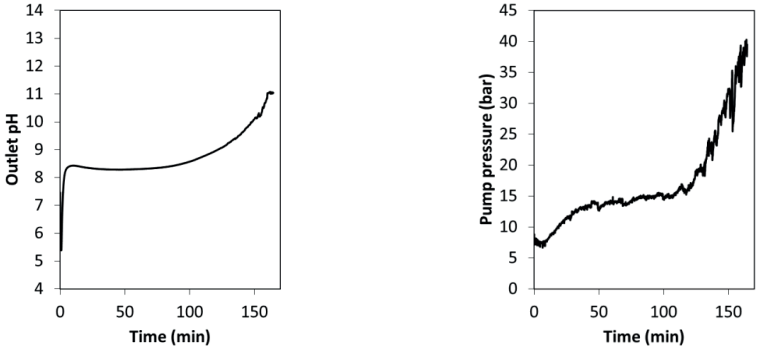


Figure A.4.5. Raw data of a breakthrough experiment of the paper mill wastewater at pH 12 with the resin in the bicarbonate form.

Chapter 5

Recovery of acetate by anion exchange with consecutive CO_2-expanded methanol desorption: A model-based approach

Abstract

Production of bio-based carboxylates is commonly hindered by the high costs of the downstream processing. In a previous work, we developed a new method to recover carboxylates salts using anion exchange resins. The carboxylates are subsequently desorbed and upgraded using CO_2-expanded alcohol. In this chapter, a model to describe this new method is developed. The model consists of equilibrium parameters for both the adsorption and desorption step. The calculated parameters are: for the adsorption $K_{Cl^-}^{Ac^-} = 0.125$, $K_{Cl^-}^{HCO_3^-} = 0.206$ and $K_{OV,HAc} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$, and for the desorption $pK_{MeCO_3^-}^{Ac^-} = 3.71$. The maximum experimental concentration of acetic acid obtained in CO_2-expanded methanol is 0.427 mol/kg (20 g/L_{MeOH}) at an operating pressure of 31 bar. The model represents the expected trends for all species, and can be used to design a multicolumn system for the recovery and upgrading of carboxylates.

5.1. Introduction

Bio-based production of carboxylic acids via fermentation is a route to a wide variety of chemicals.[1] Examples of carboxylic acids that can be fermented from renewable materials, and for which large scale production exists, are acetic acid, citric acid, lactic acid, and itaconic acid.[2] Commercial production of carboxylic acids by fermentation is only possible if the recovery from the aqueous solution is efficient.

Some fermentation methods to produce carboxylic acids (concentrations 2-100 g/L) require titration with a base to maintain neutral pH, and as a result produce a carboxylate salt.[2] Traditional recovery of carboxylic acids from these carboxylate salts involves high energy consumption and waste co-production. One method to capture carboxylates from a dilute solution is to use strong anion exchange resins. Anion exchange resins are used to recover carboxylates because of the high affinity of the positively charged functional group. To avoid the use of strong mineral acids during desorption, a novel process for the recovery of carboxylic acid using the strong anion exchange resins and desorption with CO_2-expanded alcohols was developed.[3] At the end, the resin is regenerated to the bicarbonate form and the carboxylic acid dissolves in the CO_2-expanded alcohol solution for further processing (e.g. ester formation).

The main advantages of the method are: high solubility of CO_2 in the alcohol, no stoichiometric waste salt production (if the liberated bicarbonate is reused to control the pH of the fermentation), and integration with further downstream steps such as esterification, distillation or crystallization. The method was tested to work with different alcohols and carboxylates recovered from aqueous solutions and paper mill wastewater. However, the main limitation of the method is the high dilution of the produced carboxylates and esters (0.1-0.3 wt.%) after desorption/esterification.[3, 4] A higher concentration of products in the CO_2-expanded alcohol solution would facilitate the further purification. However, no theoretical or empirical data are available to predict the maximum concentration achievable in desorption at a given amount of methanol and CO_2. For these reasons, a model that can predict the equilibrium concentration of carboxylate desorption using CO_2-expanded methanol is needed. In this paper, acetic acid is used as example for the determination of the model parameters. Acetic acid is one of the carboxylic acids that can be produced via fermentation. It is industrially used in the synthesis of vinyl acetate, cellulose acetate, and other acetate esters.[5]

To predict the maximum achievable concentration during desorption, the current research aims to develop an equilibrium model for both the adsorption of aqueous acetate and chloride to a strong anion exchange resin in the bicarbonate form and subsequent desorption of acetic acid with CO_2-expanded methanol. After desorption with CO_2-expanded methanol, the resin is regenerated to the bicarbonate form. In this chapter, chloride is used as model anion to study the effect of impurities in the system. The equilibrium model is used to check the maximum concentration of acetate achievable in the CO_2-expanded methanol solution. Furthermore, an equilibrium dispersive model is used to model the transport through the column during adsorption and desorption. This mathematical model is needed for the design of a multicolumn system for the continuous recovery of carboxylates from diluted streams.

5.2. Theory

5.2.1 Ion exchange and adsorption equilibrium

In this study, recovery of acetate from a dilute aqueous solution at pH above the pK_a is performed using a strong anion exchange resin with a quaternary ammonium functional group (Type I). In addition to exchange of the acetate ion with the counter-ion of the resin's functional group, adsorption of the un-dissociated acetic acid to the resin backbone occurs. For this reason, the adsorption mechanism of acetic acid at a pH above the pK_a is described by ion exchange (equation 6) and adsorption (equation 8). The counter-ion of the functional group is chloride, and the interaction with acetate and bicarbonate (regenerated version of the resin) is studied. Additionally, the dissociations of all the species involved in the recovery of acetate are represented, and shown by the equilibrium reactions in Table 5.1, in which γ and m are the activity coefficient and molality in the aqueous phase, and q is the molality in the wet resin phase.

Table 5.1. Equilibrium expression and constants for the adsorption of acetate to a strong anion exchange resin.

Process	Equilibrium Expression	Eq.	Parameter	Ref.
Acetic acid dissociation $HAc \leftrightarrow H^+ + Ac^-$	$K_{a,1} = \frac{\gamma_{H^+} \cdot m_{H^+} \cdot \gamma_{Ac^-} \cdot m_{Ac^-}}{\gamma_{HAc} \cdot m_{HAc}}$	(1)	$pK_{a,1} = 4.76$	6
Water dissociation $H_2O \leftrightarrow H^+ + OH^-$	$K_w = \gamma_{H^+} \cdot m_{H^+} \cdot \gamma_{OH^-} \cdot m_{OH^-}$	(2)	$pK_w = 14$	7
Bicarbonate dissociation $CO_2 + H_2O \leftrightarrow H_2CO_3$	$K_{H_{CO_2}} = \frac{\gamma_{H_2CO_3} \cdot m_{H_2CO_3}}{f_{CO_2}}$	(3)	$pK_{H_{CO_2}} = 2.77$	7
$H_2CO_3 \leftrightarrow H^+ + {HCO_3}^-$	$K_{CO_2,1} = \frac{\gamma_{H^+} \cdot m_{H^+} \cdot \gamma_{HCO_3^-} \cdot m_{HCO_3^-}}{\gamma_{H_2CO_3} \cdot m_{H_2CO_3}}$	(4)	$pK_{CO_2,1} = 3.6$	7
${HCO_3}^- \leftrightarrow H^+ + {CO_3}^{2-}$	$K_{CO_2,2} = \frac{\gamma_{H^+} \cdot m_{H^+} \cdot \gamma_{CO_3^{2-}} \cdot m_{CO_3^{2-}}}{\gamma_{HCO_3^-} \cdot m_{HCO_3^-}}$	(5)	$pK_{CO_2,2} = 10.3$	7
Acetate Ion Exchange $Q^+Cl^- + Ac^- \leftrightarrow Q^+Ac^- + Cl^-$	$K_{Cl^-}^{Ac^-} = \frac{q_{Ac^-}}{q_{Cl^-}} \cdot \frac{\gamma_{Cl^-} \cdot m_{Cl^-}}{\gamma_{Ac^-} \cdot m_{Ac^-}}$	(6)	to be fitted	
Bicarbonate Ion Exchange $Q^+Cl^- + HCO_3^- \leftrightarrow Q^+HCO_3^- + Cl^-$	$K_{Cl^-}^{HCO_3^-} = \frac{q_{HCO_3^-}}{q_{Cl^-}} \cdot \frac{\gamma_{Cl^-} \cdot m_{Cl^-}}{\gamma_{HCO_3^-} \cdot m_{HCO_3^-}}$	(7)	to be fitted	
Acetic Acid Adsorption $Q^+Cl^- + HAc \leftrightarrow Q^+Cl^- \cdots HAc$	$K_{OV,HAc} = \frac{q_{HAc}}{\gamma_{HAc} \cdot m_{HAc}}$	(8)	to be fitted	

Ion exchange equilibria are described by a homogeneous mass action model, equation 6 and 7. This originates from the common approach to treat the process like a reversible chemical reaction.[8] The exchanger is assumed to be a homogeneous phase, and non-idealities for the liquid phase are taken into account by introducing activity coefficients.[9]

In this study, the activity coefficients for neutral species in solution are considered ideal (γ_{HAc} and $\gamma_{H_2CO_3} = 1$), since the deviation from ideality in aqueous systems is small and the error in

the calculation is not significant.[10] For electrolyte solutions, deviations from ideality, even at low concentrations, can be important because of strong ion interactions with other ions, solvent and exchange resin. To quantify solution non-idealities, Debye-Hückel or Pitzer like models are generally used.[11] In this study, the activity coefficients for acetate, bicarbonate, carbonate, chloride, proton, hydroxide and sodium acetate in the water phase are calculated by the modified Debye-Hückel model of Truesdell and Jones (equation 9).[7, 12]

$$log\,\gamma_i = \frac{-Az_i{}^2 I^{0.5}}{1 + Ba_i I^{0.5}} + b_i \mathrm{I} \qquad \text{(Eq. 9)}$$

The ionic strength, I, is calculated as equation 10, where z_i is the charge of ionic species.

$$I = \frac{1}{2}\sum_i m_i z_i^2 \qquad \text{(Eq.10)}$$

The fermentation broths that we consider have an acetate concentration < 0.5 mol/kg, in which the Truesdell-Jones model is valid.[12] The parameters used for the activity coefficient model are reported in Appendix A.5.1 (Table A.5.1 and Table A.5.2).

The activity coefficients in the resin phase are resin dependent, and the simultaneous calculation of the activity coefficient and equilibrium constant exhibits a disturbing interdependence.[9] For this reason, it was assumed that the activity coefficients of the acetate, bicarbonate and chloride ions in the resin phase are approximately the same, leading to equations 6 and 7 without activity coefficients in the resin phase.

For the non-dissociated acetic acid species, the adsorption is described through the linear region of the isotherm by a constant ($K_{OV,HA}$), equation 8.

All the parameters are calculated at 25 °C and 1 atm CO_2 and for this reason the fugacity coefficient (for the adsorption step) is assumed to be 1. The results of the batch adsorption experiments are used to calculate the selectivity and distribution coefficient for acetate, bicarbonate and acetic acid, respectively. The calculated parameters are further used to describe the effect of pH on the acetate and bicarbonate recovery. This information is used to model the recovery of the ions with the anion exchange resin at different pH and concentrations.

To solve the system, additional assumptions and mass balances are implemented:

- Electroneutrality in the liquid phase is assumed during all the experiments.

$$m_{H^+} + m_{Na^+} = m_{Cl^-} + m_{Ac^-} + m_{HCO_3^-} + 2 \cdot m_{CO_3^{2-}} + m_{OH^-} \qquad \text{(Eq. 11)}$$

- The difference between inlet molalities and aqueous equilibrium molalities is assumed to be in the resin phase for each species i. In which W_{resin} is the mass of resin added in the liquid phase, and $W_{solution}$ is the mass of the solution, which are assumed to be constant. $q_{in,i}$ is the initial value of each species on the resin, which is $q_{in,i} = 0$, for most components except for one component in which $q_{in,i} = q_{max}$.

$$m_{in,i} + q_{in,i}\frac{W_{resin}}{W_{solution}} = m_{eq,i} + q_{eq,i}\frac{W_{resin}}{W_{solution}} \qquad \text{(Eq. 12)}$$

5.2.2 Desorption equilibrium

The anion exchange resin is regenerated using CO_2-expanded methanol as described in our previous publications.[3, 4] However, in the current study no catalyst is used for the formation of

esters, because the aim is to study the desorption equilibrium (without esterification). As a result, the desorption with CO_2-expanded methanol is described by five equilibrium reactions: the transfer of CO_2 from the gas to the methanol phase, the formation and deprotonation of methyl carbonic acid, the ion exchange of methyl carbonate with acetate and the protonation to acetic acid. Table 5.2 shows the equilibrium reactions considered in our desorption model.

Table 5.2. Equilibrium expressions and constants for the CO_2 expanded methanol desorption of acetate.

Process	Equilibrium Expression	Eq.	Parameter	Ref.
Methyl carbonic acid formation $MeOH + CO_2 \leftrightarrow MeCO_3H$	$K_1 = \frac{\gamma_{HMeCO_3} \cdot m_{HMeCO_3}}{\gamma_{MeOH} \cdot m_{MeOH} \cdot f_{CO_2}}$	(13)	$pK_1 = 3.21$	13
Methyl carbonic acid dissociation $MeCO_3H \leftrightarrow MeCO_3^- + H^+$	$K_{ACA} = \frac{m_{H^+} \cdot m_{MeCO_3^-} \cdot \gamma_\pm^2}{\gamma_{HMeCO_3} \cdot m_{HMeCO_3}}$	(14)	$pK_{ACA} = 5.73$	13
Ion Exchange $Q^+Ac^- + MeCO_3^- \leftrightarrow Q^+MeCO_3^- + Ac^-$	$K_{MeCO_3^-}^{Ac^-} = K_\gamma \frac{q_{MeCO_3^-}}{q_{Ac^-}} \cdot \frac{m_{Ac^-}}{m_{MeCO_3^-}}$	(15)	to be fitted	
Acetic acid dissociation $HAc \leftrightarrow H^+ + Ac^-$	$K_m = \frac{\rho_{MeOH} \cdot m_{H^+} \cdot m_{Ac^-} \cdot \gamma_\pm^2}{\gamma_{HAc} \cdot m_{HAc}}$	(16)	$pK_m = 9.63$	14

In table 5.2, CO_2 dissolution in methanol and acid formation were combined (equation 13).[13] The fugacity is calculated by equation A.5.1 (Appendix A.5.2). The acetic acid dissociation in methanol was described using the published dissociation constant[14] (equation 16), and converted to molality with ρ_{MeOH}.

For simplicity, the activity coefficients of neutral species are again taken as unity ($\gamma_{HMeCO_3}, \gamma_{HAc}, \gamma_{MeOH}$). The mean ionic activity coefficient, $\gamma_\pm$, is estimated using equation 17, which is the first term of Pitzer's model, as proposed by others,[13] and used in equation 14 and 16. This term of the Pitzer model includes the electrostatic far field interactions between ions, but does not represent the specific binary, near-field interactions between pairs or ternary interactions (Ac^-, $MeCO_3^-$ and H^+), which are not reported elsewhere.

$$ln\gamma_\pm = -A\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + 1.67 \cdot ln\left(1 + 1.2\sqrt{I}\right)\right] \quad \text{(Eq. 17)}$$

A is the Debye-Hückel parameter; which is estimated as proposed by Gmehling et al. (2012).[15]

$$A(T) = 1.8248 \cdot 10^6 \frac{kg^{0.5}}{mol^{0.5}} \frac{\sqrt{\frac{\rho_{solv}}{(kg/L)}}}{\left(\frac{T}{(K)}\epsilon_r\right)^{1.5}} \quad \text{(Eq. 18)}$$

Where ρ_{solv} is the density of methanol (0.786 kg/L), T is the temperature in K (298 K) and ϵ_r is the relative dielectric constant of methanol (33.05).

As previously, ion exchange equilibria for the batch experiments are described by a homogeneous mass action model. Since the mean activity coefficients of ions in the methanol phase are calculated by equation 17, the activity coefficients of acetate and methyl carbonate in methanol are equal. Furthermore, the activity coefficients of acetate and methyl carbonate on the resin phase are assumed to be the same. These assumptions lead to $K_\gamma = 1$ in equation 15. In this study, the mass action law model is derived to express the equilibrium concentration of acetic

acid in methanol as a function of CO_2 pressure and the methanol/resin ratio. The concentration of anions in both phases are expressed in terms of acetic acid concentration, CO_2 pressure and methanol/resin ratio. Finally, the parameter $K_{MeCO_3^-}^{Ac^-}$ is determined from experimental data to model the ion exchange between acetate and methyl carbonate. Electroneutrality in the liquid phase is assumed in the batch calculations (equation 19), and the amount of each component bound to the resin is calculated as stated in equation 12.

$$m_{H^+} = m_{Ac^-} + m_{MeCO_3^-} \quad \text{(Eq. 19)}$$

5.2.3 *Dispersive model*

The performance of a chromatographic column depends on factors that belong to two broad categories: equilibrium and dispersive factors. The equilibrium factors for our system have been described in Section 5.2.1 and 5.2.2. In this section, a term describing axial dispersion is included in the mass balance of the mobile phase, and the bed porosity is included.[16, 17] In the model, the effect of several parameters are lumped into the dispersion coefficient D_{app}. The lumped parameter D_{app} includes peak broadening effects caused by the fluid dynamics of the packing (axial dispersion) and all other mass transfer effects. Using these assumptions, the differential mass balances for the liquid phase of all components are given by equation 20.

$$\frac{\partial m_i}{\partial t} = D_{app}\frac{\partial^2 m_i}{\partial x^2} - u_{int}\frac{\partial m_i}{\partial x} - \frac{1-\varepsilon}{\varepsilon}\left(\frac{\partial q_i}{\partial t}\right) \quad \text{(Eq. 20)}$$

Here, the required parameters are the dispersion coefficient (D_{app}), the interstitial velocity (u_{int}) and the bed porosity (ε). The bed porosity is determined by residence time distribution experiments with potassium chloride and dextran as discussed in section 5.3.5.1. It is further calculated using three characteristic times: the time of a tracer that enters the particles (t_{KCl}), the time of a tracer that should not enter the particles ($t_{Dextran}$) and the time of a tracer without column (dead volume until detector) ($t_{detector}$). In a typical experiment, $t_{KCl} = 130$ s, $t_{detector} = 38$ s, and $t_{Dextran} = 117$ s.

$$t_0 = t_{KCl} - t_{detector} \quad \text{(Eq. 21)}$$

$$t_{0,int} = t_{Dextran} - t_{detector} \quad \text{(Eq. 22)}$$

$$\varepsilon_t = t_0\frac{\dot{V}}{V_c} \quad \text{(Eq. 23)}$$

$$\varepsilon = t_{0,int}\frac{\dot{V}}{V_c} \quad \text{(Eq. 24)}$$

Were $\dot{V}$ is the flow rate and V_c is the packed volume of the column, and calculated from the packed length and the internal diameter of the column. The interstitial velocity (u_{int}) is calculated from the operating flow rate ($\dot{V}$), the column internal cross-sectional area (A_c) and the extraparticle void fraction (ε) as:

$$\mathrm{u_{int}} = \frac{\dot{V}}{A_c \cdot \varepsilon} \quad \text{(Eq. 25)}$$

The dispersion coefficient (D_{app}) is calculated by moment analysis of an injection of potassium chloride and their relation with the van Deemter plot, and assumed to be the same for all components. The first two moments were calculated directly by numerical integration as:

$$\tau = \frac{\int_0^\infty m(t) \cdot t \, dt}{\int_0^\infty m(t) dt} \quad \text{(Eq. 26)}$$

$$\sigma^2 = \frac{\int_0^\infty m(t) \cdot (t-\tau)^2 \, dt}{\int_0^\infty m(t) dt} \quad \text{(Eq. 27)}$$

And the height equivalent to a theoretical plate (HETP) is calculated by the two moments and the column length (L_c) as:

$$\text{HETP} = \frac{\sigma_{col}^2 \cdot L_c}{\tau_{col}^2} \quad \text{(Eq. 28)}$$

Exploiting the connection between the apparent dispersion coefficient and the second moment, the dispersion coefficient can be calculated as proposed by others.[17] This apparent dispersion coefficient is used directly for the adsorption experiments. In the case of the desorption experiments, the apparent dispersion coefficient is calculated by fitting it to the experimental data.

$$D_{app} = \frac{HETP \cdot u_{int}}{2} \quad \text{(Eq. 29)}$$

For the solid phase, the differential mass balance for each component is given by equation 30.

$$\frac{\partial q_i}{\partial t} = k(m_i - m_i^{eq}) \quad \text{(Eq. 30)}$$

From which the m_i^{eq} is given by the specific equilibrium equation (Section 5.2.1, equation 12) and k for ion exchange is considered to be an instantaneous reaction (assumed to be $1000 \cdot s^{-1}$). An additional required parameter is the total capacity of the resin (q_{max}), which is used to close the resin mass balance. The resin q_{max} is obtained experimentally as explained in section 5.3.5.2.

The assumptions for all the experiments are:

- The feed is homogeneous so that the concentration of each species at the inlet is equal to $m_{i,feed}$ at all times.
- The apparent dispersion coefficient is equal for all species.
- The concentration of carbonate and carbonic acid are negligible at these conditions.

The initial and boundary conditions are:

- At time zero, the concentration of the binding component (acetate and chloride for adsorption, methyl carbonate for desorption) in the liquid phase throughout the column is zero.
- The concentration of bicarbonate (for adsorption) and acetate (for adsorption and desorption) was given a small initial concentration (0.01 mmol/kg) to avoid division by zero.
- The concentrations at the inlet were increased from zero to the feed value by using a step function.
- At the outlet boundary, a zero gradient of the liquid concentration was assumed.

- For adsorption, the resin phase was initially assumed to be fully loaded with bicarbonate and this is equal to q_{max}.
- For desorption, the methyl carbonic acid inlet concentration is assumed to be constant at the operating pressure of 31 bar CO_2. This was calculated with equation 13 and the result is shown in Table A.5.3.
- For desorption, the resin phase was initially assumed to be fully loaded with acetate (acetate loading) or with acetate, chloride and bicarbonate in which acetate is loaded with a ratio of 0.14· q_{max}.

The additional required equations necessary to solve the system are the thermodynamic equilibrium that is used as calculated in Section 5.2.1 and 5.2.2. The simulation is done in COMSOL Multiphysics as explained in Section 5.3.7, in which the molalities are converted to mol/L to be solved in the software using the density of water (1 kg/L) and methanol (0.786 kg/L), respectively.

5.3. Materials and Methods

5.3.1 Materials

Sodium bicarbonate was purchased from J.T. Baker. Anhydrous potassium acetate (99%), methanol (≥99.9 %), dextran blue and anhydrous methanol (≥99.8%) were obtained from Sigma-Aldrich. Potassium chloride (>99.5%) was purchased from Merck. Carbon dioxide (≥99.8%) was supplied by Linde as compressed gas. The strong anion exchange resin (Dowex Marathon MSA, macroporous) in the chloride form was purchased from Sigma Aldrich. The nominal total exchange capacity is at least 1.1 eq/L (wet basis). All aqueous solutions were prepared with deionized water from a Milli-Q water purification system (Millipore). Deionized water was used from a Milli-Q purification system.

5.3.2 Adsorption batch experiments

Adsorption experiments were performed in 50 mL flasks with 1 g of wet resin (chloride form) added to 10 mL aqueous solutions of a carboxylate salt/carboxylic acid at different concentrations. Sodium acetate solution concentrations were between 0.006-0.72 mol/kg (0.5-60 mg/$g_{solution}$), acetic acid between 0.012-3.66 mol/kg (0.7-180 mg/$g_{solution}$) and sodium bicarbonate between 0.006-0.34 mol/kg (0.5-28 mg/$g_{solution}$). The flasks were then shaken at 200 rpm and 25 °C for about 18 h in which it is assumed that equilibrium was reached. Each experiment was performed in duplicate. The pH of the samples before and after the reaction was measured. After the reaction each system was filtered using a Millex-GV Syringe Filter Unit and acetic acid, bicarbonate and chloride concentration in the liquid phase were quantified (section 5.3.6).

5.3.3 Resin preparation for batch desorption

Column elution was used to convert the resin to the bicarbonate form. Fresh resin in the chloride form was hydrated in a beaker with deionized water for 30 min. The resin was then filtered under vacuum for 2 min in a glass filter. The hydrated resin was weighed and tightly packed in an Omnifit glass column (1 cm internal diameter, 15 cm height) and the column was placed in a Dionex Ultimate 3000 HPLC (Thermo Scientific). The resin was sequentially washed with 2 mL/min deionized water for 30 min, 4 mL/min sodium bicarbonate (20 g/L) for 240 min, then with 4 mL/min of deionized water for 240 min, and finally is converted to the acetate form with a solution of 0.10 mol/kg (10 g/L) potassium acetate at 2 mL/min. The absorbance of the

outflow was continuously measured with the internal VWD-3400RS UV-Visible detector, and 2 mL samples were taken at 40 min intervals with the AFC-3000 automatic fraction collector. The last sample was analyzed for acetate concentration (section 5.3.6). The breakthrough curve was constructed using the online measured absorbance and final sample acetate concentration, and the resin capacity for acetate was calculated by integration. The resin was removed from the column and washed 3 times with 50 mL deionized water and filtered at 20 mbar using Millipore Steriflip 60 μm nylon net filtration unit. The washing-filtering procedure was repeated two times with 30 mL of methanol and one time with 30 mL of anhydrous methanol. The resin was dried in an oven at 60 °C for 4 h to remove residual water and allow to cool in a desiccator.

5.3.4 Desorption batch experiments

Desorption experiments were performed at varying CO_2 pressures and methanol to resin ratios. CO_2 pressures of 2.1, 5, 10 and 20 bar and methanol to dry resin ratios of 5, 10, 15, 20, and 25 g/g were used. The desorption of acetate from the resin was performed by adding 0.5-2 g of resin (dry) and the required mass of anhydrous methanol in a 50 mL Büchi glass stirred autoclave. The vessel was equipped with a magnetically driven four blade impellers, an overhead motor, a pressure sensor, a pressure relief valve, a carbon dioxide inlet, and a sampling port. The reactor was flushed 4 times with CO_2. Agitation was set to 250 rpm and then CO_2 was added until the pressure stabilized at the desired value. The experiments were performed for 4 h in duplicate. Final pressure and temperatures (20-22 °C) were recorded. Liquid samples were obtained at the set pressure and analyzed for acetic acid concentration (section 5.3.6).

5.3.5 Dynamic experiments

5.3.5.1 Dispersion and porosity determination

Hydrated resin was packed in an Omnifit glass column (15 cm height x 1 cm internal diameter). A 20 μL tracer pulse of aqueous potassium chloride (3 mol/L) was added at a constant flow (0.15- 6 mL/min) to the system with (resin in chloride form) and without column at 20-22 °C. The mean time of passage (τ) and variance (σ^2) of the system with the column were calculated by numerical integration of the conductivity response, and used for the determination of total porosity as explained in section 2.3. The particle porosity was measured in the system by repeating the experiment with 6.6 g/L of dextran blue as tracer.

5.3.5.2 Total resin capacity

The total anion exchange capacity of the resin was determined based on the ASTM D2187-94 Standard method-Test H. The method consists of the conversion of a sample to the chloride form using a concentrated solution of hydrochloric acid. The sample was washed with water and isopropanol. Elution of chloride from non-salt-splitting group was done using ammonium hydroxide. The sample was changed to the chloride form again washing it with sodium chloride (50 g/L) and the subsequent elution of chloride from salt splitting group was performed using sodium nitrate. Determination of chloride in the separate eluents was done by titration with silver nitrate (0.1 mol/L).

5.3.5.3 Adsorption dynamic experiments

An Omnifit glass column (1 cm internal diameter x 15 cm height) was used, with approximately 5 g of wet resin in the chloride form (~60 %wt/wt water). The dispersion of the column was measured as mentioned in section 5.3.5.1. The column was converted to the

bicarbonate form with a solution of 0.24 mol/kg (20 g/L) sodium bicarbonate (section 5.3.3). Dynamic experiments were performed in a Thermo Scientific Dionex Ultimate 3000 system. Carboxylate solutions were pumped through the column at 0.3 and 2 mL/min and 25 °C. The carboxylate inlet solutions contained acetate 14.2 mmol/kg (0.84 g/L) and chloride 9 mmol/kg (0.32 g/L) at a pH of 5 or 7.6 Fractions of 2 mL were collected. Feed samples and collected fractions were analyzed for acetate and chloride, and pH, conductivity and absorbance (210 nm) were measured online.

5.3.5.4 Desorption dynamic experiments

After an adsorption experiment, the column was washed with Milli-Q water (4 mL/min) until the conductivity was below 0.007 mS/cm. Then, the column was washed with methanol (2 mL/min) for 30 min. The desorption dynamic experiments were performed in a modified Thermo Scientific Dionex Ultimate 3000 system. The system was modified with a high-pressure pre-mixing vessel to equilibrate the methanol with 10 bar of carbon dioxide during ~30 min. A back-pressure was installed after all sensors to the modified system to assure that the pressure remained above the set-point of the pre-mixing vessel (10 bar). The methanol/carbon dioxide solution was pumped through the column at 1.5 mL/min at 20-22 °C. Fractions of 2 mL were collected. Collected fractions were analyzed for acetic acid as explained in section 5.3.6, and absorbance (210 nm) was measured online.

5.3.6 Analytical methods

The concentration of total acetate in the systems was evaluated using a Waters HPLC system equipped with a UV/Visible Detector (Waters 2489) and a Refractive Index Detector (Waters 2414) for both water and methanol samples. The column used was the Bio-Rad Aminex HPX-87H column (7.8 × 300 mm). A mobile phase of phosphoric acid (1.5 mmol/L) was used in isocratic mode at 0.6 $mL \cdot min^{-1}$. The injection volume was 10 μL and the duration of the run was 30 min, the column temperature was 60 °C and the detection was at 210 nm. The experimental aqueous acetate and acetic acid concentration were determined using the total acetate measurement, the experimental pH and equation 1. The methanol samples were diluted 10 times to avoid deterioration and interference with the column material. Chloride concentrations (Sigma-Aldrich MAK023) were determined spectrophotometrically using the Sigma Aldrich MAK023 test kit in 96 well plates. Total carbonate was measured as carbon dioxide with a Hach-Lange LCK388 kit, which includes all carbonate species (carbonate, bicarbonate and carbon dioxide).

5.3.7 Regression and model calculations

The determination of the parameters from each set of equations was done by minimizing the sum of mean squared error of the total acetate (chloride concentration for the bicarbonate experiment) with MATLAB® optimization algorithm *fminsearch*. The objective functions were the set of equilibrium equations that were solved in a separate MATLAB® function using the built-in nonlinear solver *fsolve*.

The dynamic model was implemented on the COMSOL Multiphysics platform (v5.2a, Comsol Inc., Burlington, MA). Equations for a one-dimensional dispersion and ion exchange were solved with a variable time step with a mesh size of $2 \cdot 10^{-4}$ m.

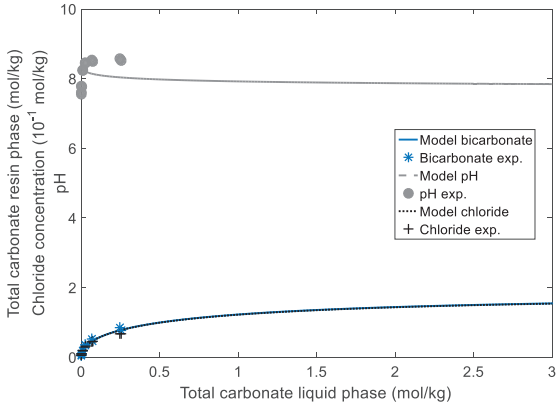
5.4 Results and Discussion

5.4.1 Parameters for the ion exchange adsorption equilibrium model

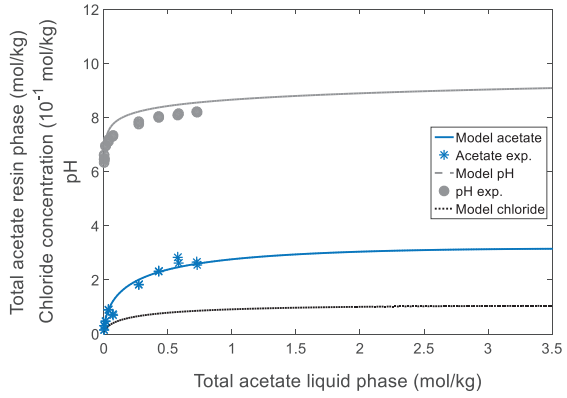
Figure 5.1 shows the isotherms for acetate, acetic acid and bicarbonate with the corresponding model. The maximum loading obtained was 169 mg/g (wet resin in chloride form) for acetate and 120 mg/$g_{wet\ resin}$ for acetic acid. Thus, the resin shows a lower capacity for acetic acid than for acetate. The bicarbonate isotherm does not reach a plateau because of low solubility of sodium bicarbonate (~1.3 mol/kg at 20 °C). The loading obtained for bicarbonate is 49 mg/$g_{wet\ resin}$. The total exchange capacity (q_{max}) was 1.9 mEq/$g_{wet\ resin}$, and measured as explained in section 5.3.5.2. Some of the reported loading for the adsorption of acid species with a quaternary group resin are: 24 mg/g_{resin} for acetic acid with a Sepra SAX resin (silica matrix, quaternary amine group, 0 % water), 66 mg/g_{resin} for the Sepra ZT SAX resin (polymeric matrix with quaternary amine group, 0 % water), and 41.2 mg/$g_{wet\ resin}$ on the A26OH resin (polystyrene matrix, quaternary ammonium group).[18-20] In these reported values, the type of the functional group of the resin leads to different interactions of the functional group with the acid at the low pH experiments.[21] For the acetate recovery (pH above the pK_a), the obtained capacities are comparable with reported values, 28 mg/$g_{wet\ resin}$ (IRA-910 chloride form) and 112 mg/$g_{wet\ resin}$ (IRA-910 hydroxide form).[22] Experiments reported in dry resin basis were converted to wet basis assuming 60 %wt. water content.

Figure 5.1 shows that the model follows the experimental values for chloride, bicarbonate, acetate and pH. The pH in all the experiments is lower than the pH of the feed solutions (data not shown), because chloride is a weaker base than bicarbonate and acetate. For acetic acid, which binds to the resin by hydrogen bonding,[2] this was an indication that ion exchange also occurs, confirmed by the chloride release (Figure 5.1.c). The model could describe this behavior and the change of pH with an average error of 10.6% for total carbonate, 5.22% chloride and 4.92% for pH in the bicarbonate model (Figure 5.1.a); 5.6% acetate and 4.0% for the pH in the acetate model (Figure 5.1.b); 4.4% acetic acid, 9.6% for pH and a high error of 60% for the chloride in the acetic acid model (Figure 5.1.c). The high chloride error in the acetic acid model is assumed to be due to measurement error at these low concentrations (1- 9 mmol/L).

The selectivity for acetate and bicarbonate over chloride and the overall distribution coefficient of acetic acid were estimated as: $K_{Cl^-}^{Ac^-} = 0.125$, $K_{Cl^-}^{HCO_3^-} = 0.206$ and $K_{OV,HAc} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$. These parameters are comparable with reported values of 0.10 for the selectivity of acetate over chloride (calculated from their reported acetate/hydroxide and chloride/hydroxide selectivity),[23] 0.11 to 0.16 for propionate over chloride and 0.28 to 0.33 bicarbonate over chloride.[24] The selectivity of bicarbonate over chloride is lower than the one reported by others (0.21 compared to 0.23-0.33).[24] The reason is that the equilibrium equation of carbon dioxide to carbonic acid (equation 3) was added independently, and in other reported work[24] both equilibrium equations (equation 3 and equation 4) are included in one apparent equilibrium constant (K_{app}=6.3). The resin supplier reports selectivity of 0.145 for acetate over chloride and 0.272 for bicarbonate over chloride.[25] Our distribution coefficient, of $K_{OV,HAc} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$, for the acid species is higher than reported values with other strong anion exchange resins.[23] The obtained parameters values are used in section 5.4.3 to build the dispersive-equilibrium model for the adsorption step.



(a)



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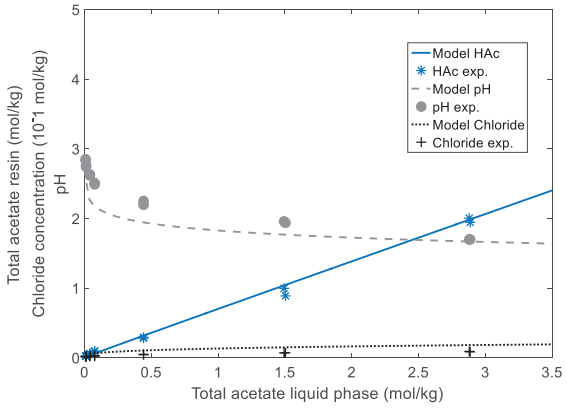


(c)

Figure 5.1. Isotherms for (a) bicarbonate, (b) acetate and (c) acetic acid with Dowex MSA resin in the chloride form, experimental data (dots) and equilibrium model (lines). All experiments were performed with a ratio of 1 g of wet resin to 10 mL of solution.

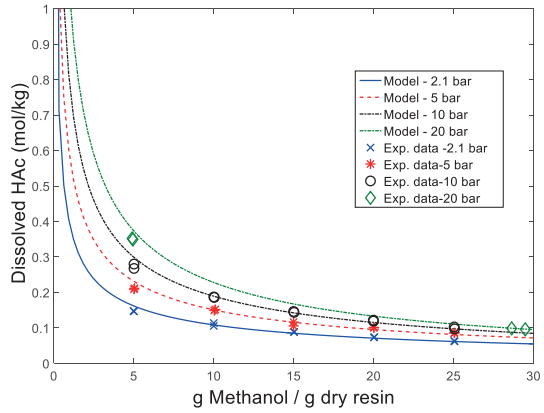
5.4.2 Parameters for the desorption equilibrium model

In this section, the effect of excess methanol and CO_2 pressure in the desorption equilibrium of acetate from the strong anion exchange resin is studied. The aim is to estimate the parameter $K_{MeCO_3^-}^{Ac^-}$ required to describe the equilibrium reactions (as described in section 5.2.2), and calculate the achievable dissolved acetic acid concentration after desorption. A series of batch desorption experiments at different pressures (2-20 bar) and methanol-to-resin ratios (5-25 g methanol/g resin (dry)) were performed with the resin in the acetate form. The equilibrium concentrations of acetic acid were determined for each experiment. The concentration values for the experiments at 2.1 bar CO_2 were used to determine the parameter for the model. The regressed parameter at 2.1 bar $pK_{MeCO_3^-}^{Ac^-}$, is 3.71 at 22 °C.

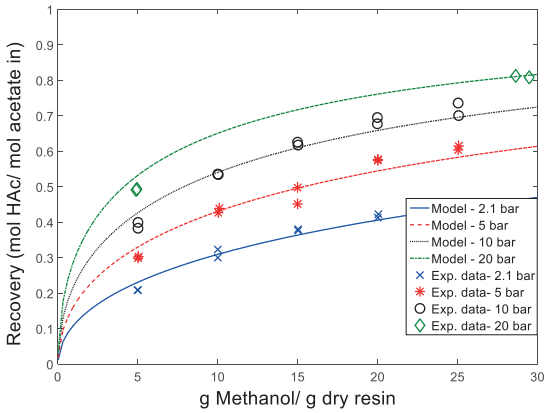
The error for the model at 2.1 bar ranges between 4.7% and 8.3%, with an average of 6.6%. The obtained $pK_{MeCO_3^-}^{Ac^-}$ value was used to predict the equilibrium desorption concentration at different pressures. The error of the predictions ranges from 0.9% to 10.8% with an average of 6.5% and 6.7% for 5 bar and 10 bar of CO_2, respectively. Additional experiments at 20 bar (5 and 30 g methanol per g of resin (dry)) were performed to check the validity of the model at higher pressures. The main deviations occur at high acetic acid concentration, and the reason may be that near-field binary and ternary interactions were not considered for the calculation of the activity coefficient (section 5.2.2), which means that the model for activity coefficient calculations has the same accuracy as a Debye-Hückel model.[15] As well, high acetic acid concentrations imply high concentrations of dissolved CO_2 such that the activity coefficient might deviate and CO_2 might adsorb to the resin like acetic acid does.

In Figure 5.2, the experimental and predicted equilibrium concentrations and recoveries are presented. In Figure 5.2a, the acetic acid equilibrium concentration is plotted as a function of the methanol/resin ratio for the four experimental CO_2 pressures. In Figure 5.2b, the recovery (mol HAc in liquid/mol total acetate originally in resin) is presented as a function of the same variables. As expected, increasing the amount of methanol decreases the concentration of acetic acid but increases its recovery. As m_{MeOH} is constant, the concentration of methyl carbonate increases with CO_2 pressure. The ion exchange equilibrium is then displaced towards the acetate side, hence more acetic acid appears in solution. At 2.1 bar CO_2, reducing the methanol/resin ratio from 25 to 5 increases the dissolved HAc concentration from 0.063 to 0.147 mol/kg, but decreases the recovery (from 49.1 to 22.6%). That represents a 2.3-fold increase in concentration at the expense of a 2.2-fold decrease in recovery. At 5 bar CO_2, for the same decrease in the methanol/resin ratio, the concentration increases 2.47-fold at the expense of a 2.05 fold decrease in recovery. At 10 bar CO_2 the trade-off improves slightly; a 2.72-fold increase in concentration leads to a 2.02-fold decrease in recovery.

The effect of CO_2 pressure on concentration is more pronounced for lower methanol/resin ratios. However, it can be seen that as CO_2 pressure increases, its effect on both concentration and recovery levels off. Higher recoveries deplete the acetate bound to the resin, which in turn requires a larger concentration of methyl carbonate ions to achieve further desorption. The highest recovery achieved in this study is 81% when using 29 $g_{\mathrm{MeOH}}/g_{\mathrm{resin}}$ and 20 bar CO_2. At these conditions, a concentration of acetic acid 0.098 mol/kg (4.6 g of acetic acid/ L methanol) is obtained. This result is in line with Rebecchi et al. (2016), where 1 g of acid was desorbed with 0.2 L of basified ethanol (5 g of acid per L of ethanol).[18]



(a)



(b)

Figure 5.2. Experiments results and model for the desorption equilibrium of acetate with CO_2-expanded methanol at 22 °C. a) Acetic acid concentration as a function of the methanol/resin ratio, b) acetate recovered from a fully loaded resin as a function of the methanol/resin ratio.

In Figure 5.3, the model is used to extrapolate the results to 61 bar CO_2, where it becomes supercritical. The goal is to check the theoretical maximum concentration and recovery that can be achieved in one equilibrium stage. The recovery of acetate is plotted as a function of the equilibrium concentration for different methanol/resin ratios. Isobaric curves are also drawn to allow for a quick estimation of the recoveries and concentrations at different experimental conditions. The values are a useful approximation for design and operation of the column system.

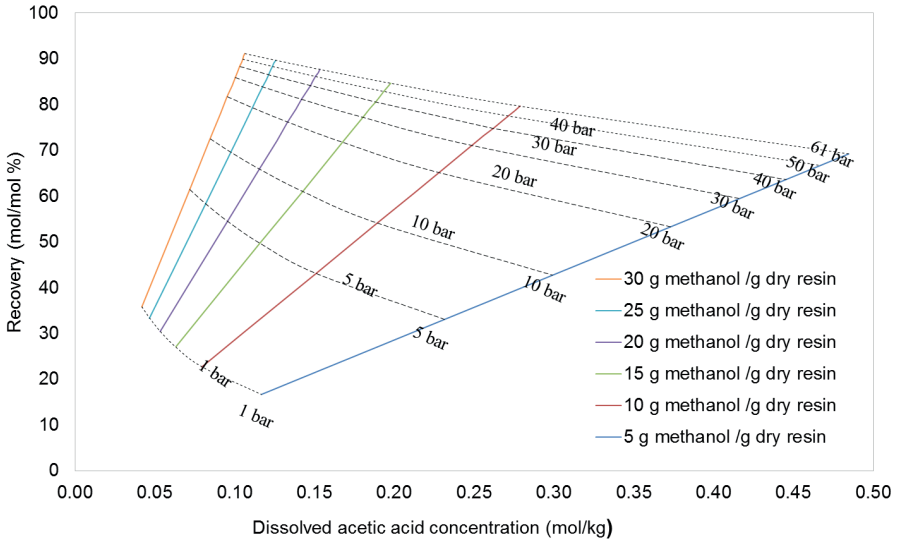


Figure 5.3. Recovery of acetic acid as a function of the equilibrium acetic acid concentration for different methanol/resin ratio. The dotted lines represent isobaric curves.

The highest concentration is obtained at 61 bar, and it is about 0.48 mol/kg (22 g of acetic acid/L of methanol) with a recovery of about 70%. This indicates that this desorption process can be further improved, in comparison with previous reported data.[3, 4] Additionally, a column operation (eventually a multicolumn system) can improve the recovery further, which is studied in section 5.4.3.

5.4.3 Equilibrium dispersive model for adsorption and desorption

Dynamic adsorption experiments were performed at different flows (0.3 and 2 mL/min) and different feed pH (5 and 7.6) with the resin initially in the bicarbonate form. The results are shown in figure 5.4.

Figure 5.4 confirms that chloride is more selective to the ion exchange resin than acetate. This causes an overshooting of acetate after the breakthrough of chloride (Figure 5.4.a), in line with data for recovery of carboxylates from paper mill wastewater.[4] In general, overshooting of an ion occurs when the feed solution contains ions with higher selectivity for the resin group than the overshot ion, resulting in a portion of eluted solution with a concentration of the latter above its feed concentration.[26]

At pH 5, the loading of total acetate to the resin is higher, caused by the additional adsorption of acetic acid to the backbone of the resin. Additionally, a lower elution of bicarbonate at pH 5 than at pH 7 supports the hypothesis that part of the total acetate is removed by hydrophobic adsorption and not by ion exchange.

An equilibrium dispersive model was used to study the behavior of the adsorption to the column in the bicarbonate form. Figure 5.4 shows that the model represents the expected trends for all species. The equilibrium constant (selectivity) of acetate over bicarbonate was calculated from the values obtained of acetate over chloride and bicarbonate over chloride (Section 5.4.1). The model presents deviations caused by the assumptions used to simplify the system, namely:

equal dispersion coefficient for all compounds, all mass transfer effects lumped into the dispersion coefficient, the bed void fraction calculated using dextran blue, and negligible concentrations of carbonate and carbonic acid. The apparent dispersion coefficient was calculated, as mentioned in section 5.2.3, using equation 29. To improve the model, one might use correlations for the lumped dispersion coefficient that take into account diffusion rates into the particles. Bicarbonate was the species that has the highest deviation from the model. Main reasons can be experimental variations caused by measurement errors (inaccuracy of the carbonate measurement method), and the fact that divalent carbonate was not considered in the model.

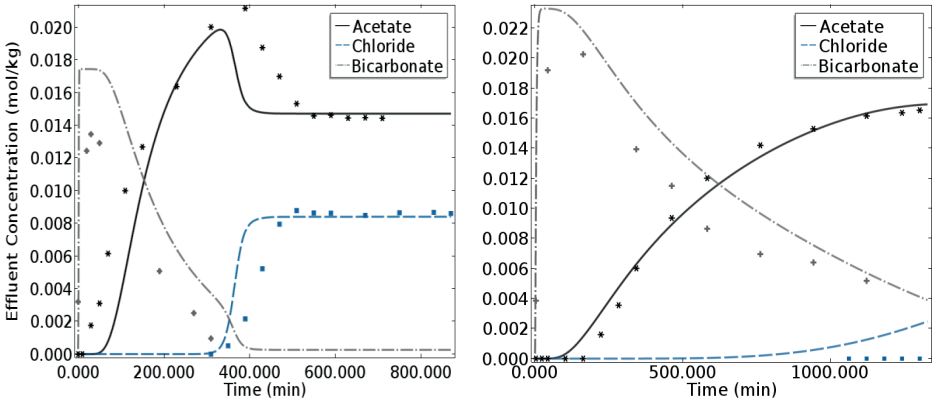


Figure 5.4. Dynamic ion exchange adsorption of acetate and chloride at a flow rate of 2 mL/min and a pH of 5 (a), and a flow rate of 0.3 mL/min and a pH of 7 (b).The feed solution has a concentration of 14.4 mmol/kg of acetate and 8.91 mmol/kg of chloride, the resin was preloaded with bicarbonate. Markers are experimental data, the model is represented by lines.

The dynamic desorption experiments are shown in Figure 5.5. For these experiments, the resin is pre-loaded with an acetate and chloride solution (as in the dynamic adsorption experiments), or fully pre-loaded with acetate. For the resin pre-loaded with acetate and chloride, the resin had all three anions (acetate, chloride and bicarbonate) prior to desorption. The ratio of acetate on the resin compared with the total resin capacity was 0.14. The desorption was performed using CO_2-expanded methanol pre-equilibrated at 10 bar at an operational pressure of 31 bar in the column controlled by the back-pressure. The maximum experimental concentration of acetic acid achieved was 0.427 mol/kg (20 g/L_{MeOH}), which indicates that the CO_2 concentration is dictated by the operation pressure (31 bar) since the maximum expected methyl carbonic acid concentrations are 0.183 mol/kg (at 10 bar of CO_2) and 0.515 mol/kg (at 31 bar of CO_2), calculated from the methyl carbonic acid concentration of the equilibrium reactions (section 5.4.2). All the equilibrium constants (K_{ACA}, $K_{MeCO_3^-}^{Ac^-}$, K_m) were combined to represent the equilibrium as one reaction with a constant of 1.97 (Appendix A.5.5). In this way dissolved ions were not taken into account, which can be justified because their proportion was relatively low.

The CO_2-expanded methanol cannot desorb bound chloride. This is confirmed by the loss of acetate capacity after several adsorption and desorption cycles (Appendix A.5.6). The reason that chloride cannot be desorbed is because of its low pK_m (pK_a of HCl in water is -5.9).[27] To remove the chloride, the resin was additionally regenerated using an aqueous bicarbonate solution.

For the resin loaded with acetate and chloride, the inlet concentration of methyl carbonic acid was assumed to be the ratio of acetate bound to the resin and the concentration of methyl carbonic acid ($0.14 * m_{HMeCO_3}$) at the operating pressure of 31 bar. The reason was that methyl carbonate seemed to exchange not only with acetate, but also with the bicarbonate bound to the resin. This caused a higher consumption of methyl carbonic acid than the expected if only acetate was on the resin. To prove this, the resin was fully pre-loaded with acetate instead of an acetate-chloride solution. Figure 5.5 shows that the model presents a trend closer to these experimental data. This states the importance of having a fully pre-loaded resin during desorption, which is comparable to other desorption-reaction techniques.[28]

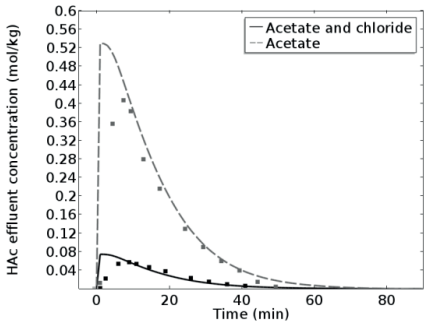


Figure 5.5 Dynamic CO_2-expanded methanol desorption of acetate at 31 bar operation pressure for resin pre-loaded with acetate or with a mixture of acetate and chloride. Markers are experimental data, the model is represented by lines.

The dispersion coefficient of the desorption step was fitted to the fully loaded acetate experiment and was not calculated using empirical correlations. A more detailed study of the dispersion coefficient of desorption with CO_2-expanded methanol is needed.

The equilibrium and the dynamic experiments show that the resulting concentration of acetic acid in CO_2-expanded methanol is limited by the methyl carbonic acid concentration. The actual column system presents an improvement from our previous reported data, from 0.8-2.4 g/L to 20 g/L HAc, and the model can be used to design a simulated moving bed multicolumn system. A multicolumn system can improve the total resin usage and the breakthrough capacity can be increased,[29] but the concentration of HAc remains limited by the methyl carbonic acid concentration (pressure of CO_2) and ratio between acetate and other anions in the resin. It would be useful to extend the proposed model to the desorption of mixtures of organic acids, as they are commonly encountered in fermentation and acidogenic anaerobic digestion.[18]

5.5 Conclusions

This chapter presented an equilibrium-dispersive model to describe and validate the recovery of acetate by anion exchange with a consecutive desorption with CO_2-expanded methanol. The equilibrium parameters were estimated as: $K_{Cl^-}^{Ac^-} = 0.125$, $K_{Cl^-}^{HCO_3^-} = 0.206$ and $K_{OV,HAc} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$ for batch adsorption, and $pK_{MeCO_3^-}^{Ac^-} = 3.71$ for batch desorption. Using these parameters, the maximum equilibrium concentration of acetic acid (after batch desorption) was predicted to be 0.48 mol/kg at 61 bar. The dynamic behavior for all species were described using the equilibrium-dispersive model. For column adsorption, it was concluded that acetic acid also binds to the resin, since there was a higher loading of total acetate at pH 5 in comparison with pH 7, complemented with a lower elution of bicarbonate. Additionally, the higher selectivity of chloride in comparison to acetate caused an overshooting of acetate. For column desorption, it was concluded that the acetic acid concentration in the CO_2-expanded methanol was limited by the methyl carbonic acid concentration and the ratio of acetate to chloride loaded to the resin. The maximum achieved acetic acid concentration was 0.427 mol/kg (20 g/L_{MeOH}) at an operating pressure of 31 bar. The concentrations reported in this chapter are an improvement from previous reported data, and the model can be used to design a multicolumn system.

5.6 Acknowledgements

This research was financed by the Netherlands Organisation for Scientific Research (NWO) domain Applied and Engineering Sciences (TTW) and Paques B.V. partnership: The Volatile Fatty Acid Platform.

5.7 Nomenclature

Symbol	Description	Units
a	Redlich-Kwong parameter	(bar $K^{0.5}$ m^6 mol^{-2})
a_i	Ion size parameter	(nm)
A_c	Column cross sectional area	(m^2)
A	Debye-Hückel parameter for solvent	($kg^{0.5}$ $mol^{-0.5}$)
b	Redlich-Kwong parameter	(kg/mol)
B	Debye-Hückel parameter for solvent	($mol^{-1/2}$ $kg^{-1/2}$ nm^{-1})
D_{app}	Apparent dispersion	(m^2 s^{-1})
f	Fugacity	(bar)
HETP	Height equivalent to a theoretical plate	(m)
I	Ionic Strength	(mol kg^{-1})
k	Reaction rate	(s^{-1})
K_a	Equilibrium constant acetic acid dissociation	(Adimensional)
K_B^A	Equilibrium constant of ion exchange	(Adimensional)
K_{ACA}	Dissociation constant of methyl carbonic acid	(Adimensional)
$K_{CO_2,i}$	Dissociation of carbonic acid or bicarbonate	(Adimensional)
$K_{H_{CO_2}}$	Partition constant of carbon dioxide in water	(Adimensional)
K_m	Dissociation constant in methanol	(Adimensional)
K_{ov}	Adsorption constant of acetic acid	(mol kg^{-1}_{resin})/(mol $kg^{-1}_{solution}$)
K_1	Partition constant of carbon dioxide in methanol	(Adimensional)
L	Packed length of column	(m)
m	Molal concentration	(mol kg^{-1})
P	Pressure	(bar)
q	Molal concentration in resin phase	(mol kg^{-1})
q_{max}	Maximum resin capacity	(mEq g^{-1})
R	Ideal gas constant	(m^3 bar K^{-1} mol^{-1})
t	Time	(s)
t_0	Characteristic time of tracer	(s)
T	Temperature	(K)
u_{int}	Interstitial velocity	(m s^{-1})
v	Molar volume	(mol m^{-3})
$\dot{V}$	Operating flow rate	(m^3 s^{-1})
V_c	Packed volume of column	(m^3)
W	Mass	(g)
z	Valence	(Adimensional)
Greek		
γ	Activity coefficient in liquid phase	(Adimensional)
$\gamma_\pm$	Mean activity coefficient	(Adimensional)
ε	Bed void fraction	m^3_{int}/m^3_{column}
ϵ_r	Dielectric constant	(Adimensional)
ε_t	Total column porosity	(m^3_{pore}+ m^3_{int})/m^3_{column}
ρ	Density	(kg L^{-1})
τ	Residence time of response peak in system with column	(min)
τ_{col}	Residence time of response peak in isolated column	(min)
φ	Fugacity coefficient	(Adimensional)

Subscript	
A	Component A
Ac^-	Acetate ion
B	Component B
eq	At equilibrium
Feed	Feed to the column
H^+	Hydrogen ion
HAc	Acetic Acid
HCl	Hydrochloric acid
i	Component i
in	Inlet conditions
int	Interstitial
j	Component j
MeOH	Methanol
$MeCO_3^-$	Methyl carbonate ion
$MeCO_3H$	Methyl carbonic acid
Res	Resin
solv	Solvent

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A.5. Supporting Information

A.5.1 Parameters for the calculation of the activity coefficient

Table A.5.1 Parameters of different ions for the Truesdell-Jones and Debye-Hückel equation. [12, 30]

Ion	a (nm)	b (kg/mol)
HCO_3^-	0.54	0
CO_3^{2-}	0.54	0
H^+	0.9	0
OH^-	0.35	0
Cl^-	0.35	0.015
Ac^-	0.45	0
Na^+	0.40	0.075

Table A.5.2 Debye-Hückel parameters for solvent at 25 °C and 1 atm.

Solvent	A ($kg^{1/2}\,mol^{-1/2}$)[a]	B ($kg^{1/2}\,mol^{-1/2}\,nm^{-1}$)	Ref.
Water	0.5108	3.28	[15, 31]
Methanol	1.65	-	[15]

a. Calculated by equation 19

A.5.2. Fugacity of carbon dioxide

$$f_{CO_2} = \Phi * P \tag{A.5.1}$$

A.5.3 Fugacity coefficient

The fugacity coefficient is calculated as shown in equation A.5.2: [32]

$$ln\Phi = \frac{Pv_{CO_2}}{RT} - 1 - ln\left(\frac{\left(v_{CO_2} - b_{CO_2}\right)P}{RT}\right) - \frac{a_{CO_2}}{b_{CO_2}RT^{1.5}} ln\left(1 + \frac{b_{CO_2}}{v_{CO_2}}\right) \tag{A.5.2}$$

Where $a_{CO_2} = 6.45 \cdot 10^{-5}$ bar $K^{0.5}$ m^6 mol^{-2}, $b_{CO_2} = 2.97 \cdot 10^{-5}$ m^3 mol^{-1} and $R = 8.314 \cdot 10^{-5}$ m^3 bar K^{-1} mol^{-1}. v_{CO_2} is calculated by equation A.5.3.

A.5.4 Gas Molar volume

The molar gas volume, v_{CO_2}, from equation A.5.2 is calculated with the Redlich-Kwong equation of state as shown in Equation A.5.3:

$$P = \frac{RT}{v_{CO_2} - b_{CO_2}} - \frac{a_{CO_2}}{T^{1/2}v_{CO_2}\left(v_{CO_2} + b_{CO_2}\right)} \tag{A.5.3}$$

A.5.5 Dispersive model

Table A.5.3. Parameters for the equilibrium dispersive model.

Parameter	Units	Adsorption 1	Adsorption 2	Desorption
$\dot{V}$	(mL/min)	2.0	0.3	1.5
pH		5.0	7.6	-
L	(m)	$8.7 \cdot 10^{-2}$	$8.8 \cdot 10^{-2}$	$8.5 \cdot 10^{-2}$
D_{app}	(m^2/s)	$6.6 \cdot 10^{-6}$	$6.6 \cdot 10^{-6}$	$6.6 \cdot 10^{-3}$ [a]
u_{int}	(m/s)	$1.1 \cdot 10^{-3}$	$0.16 \cdot 10^{-3}$	$0.83 \cdot 10^{-3}$
$m_{Ac^-,feed}$	(mmol/kg)	8.91[b]	14.38	-
$m_{HAc,feed}$	(mmol/kg)	5.94[b]	0	-
$m_{Cl^-,feed}$	(mmol/kg)	8.53	8.91	-
q_{max}	(mol/kg)	1.9	1.9	1.9
$m_{HMeCO_3,feed}$	(mol/kg)	-	-	0.5297[c]
K_1 and K_2	(1/s)	1000	1000	1000
$K_{HCO_3^-}^{Ac^-}$		0.607	0.607	-
$K_{HCO_3^-}^{Cl^-}$		4.84	4.85	-
$K_{OV,HA} * (1-\varepsilon)$	(mol/kg_{resin}/ mol/$kg_{solution}$)	0.42	-	-
$\frac{K_{MeCO_3^-}^{Ac^-} K_{ACA}}{K_m \rho_{MeOH}}$		-	-	1.969
ε		0.384	0.384	0.384
Dead volume	mL	1.33	1.33	3.3

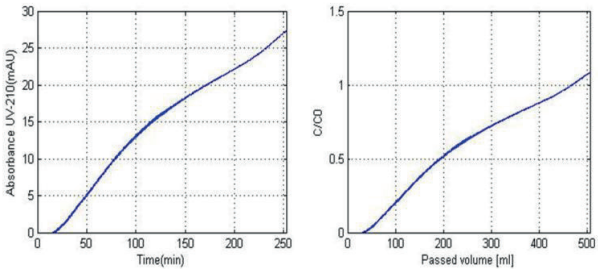
[a.] Calculated by fitting the data.

[b.] Ratio calculated from total acetate concentration and initial pH by using equation 1.

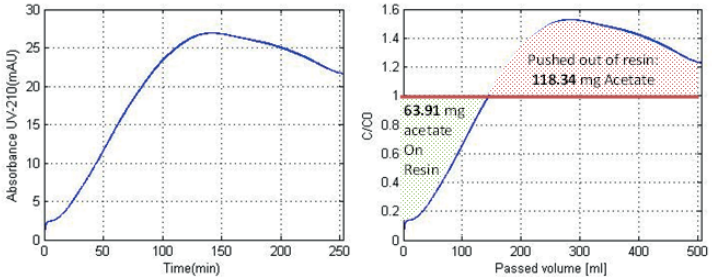
[c.] Value for the resin loaded fully with acetate. For the resin loaded with acetate and chloride the concentration is $m_{HMeCO_3,feed}$*0.14. In which 0.14 is the ratio of g of acetate/g total anions loaded to the resin.

A.5.6. Regeneration of the resin loaded with acetate and chloride with CO_2-expanded methanol

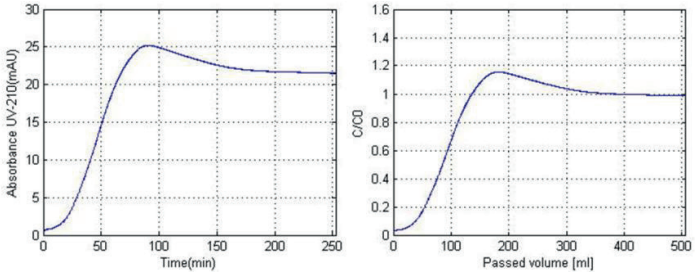
Figure A.1 (a-c) shows a reduction of the loading capacity to a resin loaded with a solution of acetate and chloride for three cycles of adsorption and desorption with CO_2-expanded methanol at 31 bar (operating pressure). This suggests that the CO_2-expanded methanol does not desorbs all the ions such as chloride.



a. Adsorption cycle 1. Fresh loading of the resin



b. Adsorption cycle 2. Resin after regeneration with CO_2-expanded methanol at 31 bar.



c. Cycle 3. Resin after 2nd regeneration with CO_2-expanded methanol at 31 bar.

Figure A.5.1. Adsorption of loading of the resin with a feed of acetate (0.84 g/L) and chloride (0.32 g/L) at pH 5 for 3 cycles after desorption with CO_2-expanded methanol at 31 bar.

Chapter 6

Perspectives for the Application of the Technology

6.1. Carboxylic acids produced from wastewater

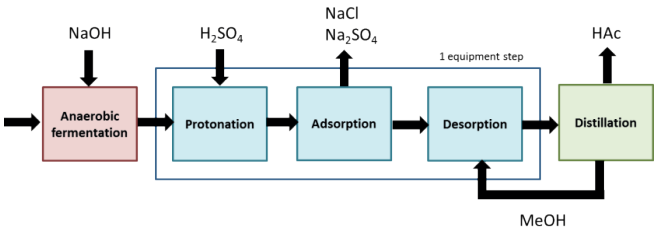
As discussed in previous chapters, several carboxylic acids can be produced from anaerobic wastewater treatment. The most common produced carboxylates are acetate, propionate, butyrate and lactate; additionally, valerate, caproate and caprylate can be produced depending on the type of wastewater and further processing conditions. The concentrations of the produced carboxylic acids in wastewater are in the range of 2 to 30 g/L.[1] In this thesis, a new method for recovery and upgrading of these carboxylates was developed. The method uses anion exchange resins and CO_2-expanded alcohols for the recovery of the carboxylates at a pH above their pK_a without the coproduction of salt byproduct (**Chapter 3**). It was proven to work for carboxylates recovered from real paper mill wastewater (**Chapter 4**), and it facilities the further integration of the downstream process. Furthermore, promising concentrations during desorption of 20 g/L (acetic acid) were obtained (**Chapter 5**). In this chapter, the outcomes of this research are put into perspective for the application of the technology. First, several concentration and purification steps are compared on their feedstock and energy costs. Then, the market of the carboxylic acids and their esters (methyl and butyl) are considered. At the end, final remarks and requirements for application are discussed.

6.2. Concentration and purification of the carboxylic acids

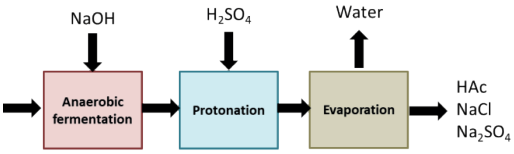
Chapter 1 presented a general sequence for the recovery, purification and upgrading of the carboxylates (Figure 1.1). Our technology focuses on the concentration step and the further integration with the upgrading step. Water is removed in the concentration step. In this section, this concentration technology is compared with other methods reported in literature. The considered technologies are: protonation/adsorption/desorption/distillation; protonation/ evaporation (distillation); electrodialysis/protonation/evaporation; and ion exchange/CO_2-expanded methanol/ distillation, and are shown in figure 6.1. In figure 6.1, the clarification and upgrading steps are not illustrated for simplification. The process steps that are illustrated are fermentation, concentration and purification.

The concentration steps involve a protonation of the carboxylate anion before or after the water removal. This requires the addition of (other) acids and bases. Some of the inorganic acids that are used for the protonation of the carboxylates are sulfuric acid, hydrochloric acid and CO_2. For traditional techniques, sulfuric acid is preferred because of its lower costs per H^+ equivalent.[2] Carbon dioxide has been reported as an interesting option because of its low price and toxicity, and its versatility for recycle and integration, e.g. as co-substrate during

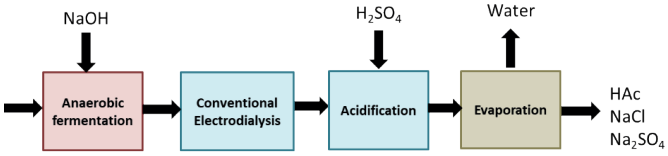
fermentation. However, its low solubility in water and its limited protonation capacity complicate the implementation when using traditional technology. In the current comparison, it is used only as protonating agent in the CO_2-expanded methanol option. The inorganic bases are used to control the pH during fermentation. Calcium hydroxide gives the lowest cost per equivalent OH^-, but it gives some precipitation issues (as discussed in **Chapter 4**). Other bases are sodium hydroxide, potassium hydroxide and sodium bicarbonate. The integrated design of the protonation step would avoid the byproduct salt formation, as it can be reused in the process (as shown in figure 6.1d).



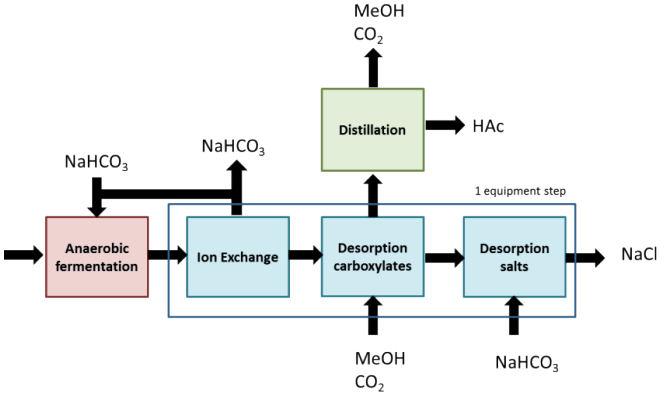
a. Protonation, adsorption, desorption with methanol and distillation. *Adsorption case.*



b. Protonation and evaporation of water in excess. *Evaporation case.*



c. Electrodialysis, protonation and evaporation of water in excess. *Electrodialysis case.*



d. Anion exchange, desorption with CO_2-expanded methanol and distillation. *Anion exchange case.*

Figure 6.1. Concentration of acetate by the different compared technologies.

The carboxylates (or carboxylic acids) are concentrated by adsorption/methanol desorption, electrodialysis or ion exchange/CO_2-expanded methanol desorption. This is

followed by a purification step in which the solvent is removed. The removal of the solvent (water or methanol) is one of the energy intensive steps of the technology. Since water and methanol have a lower boiling point than all the carboxylic acids, this step requires an energy intensive evaporation of the solvent. The enthalpy of evaporation for water and methanol are 2257 and 1107 kJ/kg. From this perspective, methanol is a better option as solvent when the same amount must be removed. Moreover, since the boiling point of methanol is 64.7 °C, low quality energy (achieved by heat integration) can be used for its removal. However, the removal of methanol from acids might be impractical since many equilibrium stages and high reflux ratio are required in cases such as glacial acetic acid. To avoid this high reflux, azeotropic distillation with low molecular weight solvents is recommended (for intermediate concentration of acids from 10-50%).[3] Direct distillation of lactic acid is not acceptable, since the dimer and other polymers of the acid are produced at high temperatures, resulting in poor yields of lactic acid recovered.[2] In this study, the energy required for the removal of the solvent is assumed equal to the enthalpy of vaporization (Table 6.1). This underestimates the energy required for the separation of the solvent, but gives a first estimation of the feedstock and energy costs. All other assumptions are detailed in Table 6.1. The calculated price per kg of product should be taken as estimation to facilitate the comparison between options, but not used directly to calculate process feasibility. A detailed process evaluation must be performed to check for the feasibility of each option.

Table 6.1 Assumptions for the calculation of the feedstock and energy costs.

Process	Assumptions
General for all options	Cost of base added during fermentation not considered. 330 operating days. 30 ton/h wastewater, COD ~19 g/L, inorganic anion (chloride) 5 g/L. 100 % yield in all the steps. Solvent recovered completely. H_2SO_4 required for protonation is used stoichiometrically, and has a price of 0.24 €/kg. Cost of treating (salt) waste produced is not considered. No heat integration considered. Revenue of treated wastewater not considered. Low pressure steam cost of 20 €/ton.
Protonation, adsorption and desorption with methanol and distillation	Washing with water and methanol in between cycle for 2 bed volumes. No product losses between washing steps. Resin removes the protonated form of the carboxylic acid. Resin is reused for 2000 cycles and has a price of 2.65 €/kg.
Protonation and evaporation	Energy required for water removal is calculated from the enthalpy of vaporization, and the heat capacity of pure water (from 20°C to 100°C).
Electrodialysis, protonation and evaporation.	2-fold concentration of carboxylate during electrodialysis. Constant energy required per kg of carboxylate of 0.25 kWh/kg during electrodialysis. No interference with other anions. No dependence on concentration of carboxylate during electrodialysis. Protonation and evaporation: the same as previous option. Electricity cost 0.17 €/kWh.
Anion exchange, desorption with CO_2-expanded methanol and distillation	Washing with water and methanol in between cycle for 2 bed volumes. Resin reused for 2000 cycles, and has a price of 2.65 €/kg Compression from 1 to 20 bar of CO_2 with 4 stages. Sodium bicarbonate required is 3 times the amount of chloride bound to the resin, and has a price of 0.12 €/kg. CO_2 price of 0.07 €/kg

All the technologies were compared in relation to the amount of product loaded to the resin (when applicable), the amount of solvent needed for desorption (when applicable), the concentration of the carboxylic acid and the concentration of chloride as inorganic anion. The results are shown in figure 6.2.

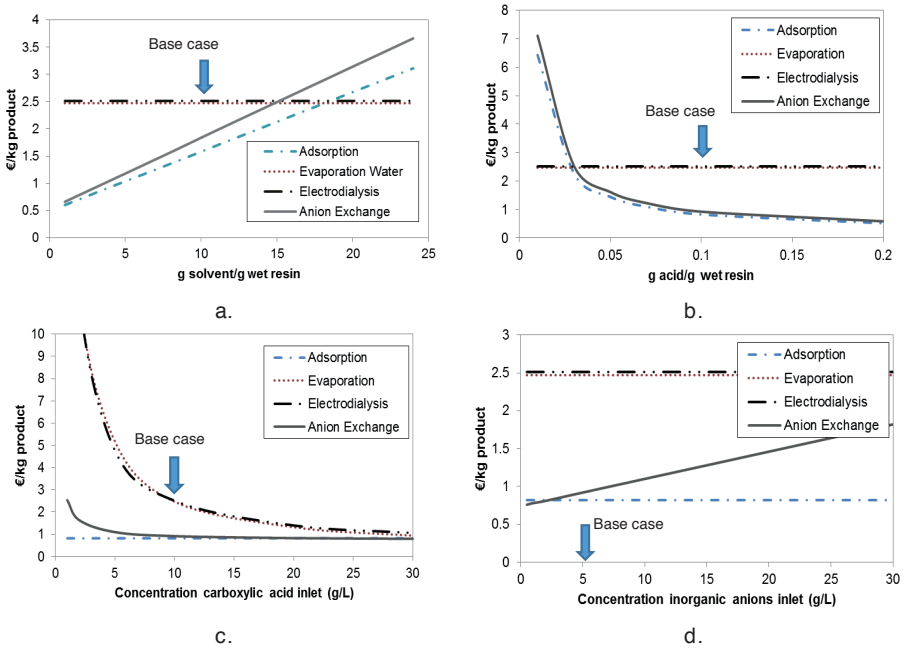


Figure 6.2. Feedstock and energy cost comparison of different concentration technologies. Base case: flow 100 ton/h, carboxylate concentration 10 g/L, loading to resin 0.1 g carboxylate/g resin, inorganic anion concentration (chloride) 5 g/L, methanol and water washing step 2 g methanol/ g resin, amount of desorption solvent 3 g solvent/g resin. **a.** Effect of amount of solvent used for desorption. **b.** Effect of loading to resin. **c.** Effect of carboxylate inlet concentration. **d.** Effect of inorganic anion (chloride) inlet concentration.

The amount of solvent used for desorption is a main parameter that affects the adsorption and anion exchange case (Figure 6.2a). For the anion exchange, we have reported (**Chapter 5**) that the minimum amount of solvent achieved for desorption with CO_2-expanded methanol was 2.5-3 g solvent/g wet resin. It is expected that this can be improved further with a multi-column countercurrent operation. For the adsorption at low pH, the desorption from a cross-linked poly(4-vinylpyridine) resin has been reported to require 2.4 bed volume of methanol.[4] It is required to check if this holds for higher molecular weight carboxylic acids. Higher molecular weight carboxylic acids have stronger hydrophobic interactions (higher log P), which might require more methanol for desorption. Moreover, losses of carboxylic acids during the washing steps should be checked. In the anion exchange process case, the carboxylates remain attached to the resin during the washing cycles with pure water and methanol. In general, the utilization of low amounts of methanol reduce the cost of the recovery to 1 €/kg.

Figure 6.2b shows the variation of the feedstock and energy costs related to the resin loading capacity. The resin must have a capacity higher than 0.05 g/g wet resin to achieve at least a price of 1.5 €/kg (figure 6.2b). Reported values for loading to an adsorption resin (at pH

below the pK_a) and anion exchange resin are above 0.05 g/g for many carboxylic acids and carboxylates.[4, 5] Acetic acid and lactic acid are two carboxylic acids that do not achieve this minimum loading with adsorption at low pH. The low log P of these molecules (Table 1.1, **Chapter 1**) impedes their recovery by hydrophobic interactions or hydrogen bonding. With an increase on pH, the opportunity to recover other carboxylic acids by adsorption (hydrophobic interaction) reduces notably. This is not the case for the anion exchange resin, for which the loading only depends on the charge of the species. However, anion exchange is affected by the competition with other anions. This competition reduces the effective loading to the resin and has a direct impact in the process feasibility.

To achieve low energy cost during the direct evaporation of water, the concentration of carboxylates must exceed 30 g/L (Figure 6.1b). Above this value (30 g/L), evaporating water has similar costs as other technologies (no heat integration considered). For the electrodialysis case, the main costs are the protonation of the carboxylate and evaporation of water (Figure 6.1c). The 2-fold concentration by electrodialysis of the carboxylates is in the same order of magnitude as the evaporation of the same amount of water. Electrodialysis is effective for the in-situ recovery of carboxylates, if an increase of the fermentation productivity is required. An additional variation could be the protonation of the carboxylate using a bipolar membrane. However the produced carboxylic acid is not further concentrated (as reported by others), and the net advantage is the reutilization of the base in fermentation (which was not considered as a cost in this analysis).[6]

Figure 6.2d shows the effect of the inorganic salt concentration. The inorganic salt concentration affects the recovery of the carboxylate, especially in the anion exchange case. Similarly, it should influence the energy requirements during electrodialysis. However, in this analysis the energy requirement of electrodialysis was considered constant. Additionally, it influences the purity in the evaporation and electrodialysis cases, as the salt remains with the carboxylic acid stream. The cost variation for the anion exchange case was calculated by the additional bicarbonate solution needed to regenerate the resin loaded with inorganic anions. A reduction of this cost might be achieved if the bicarbonate solution release during adsorption is used to regenerate the resin loaded with inorganic anions. Other contaminants affect the anion exchange or adsorption process and reduce the loading capacity.

Without heat integration, the feedstock and energy cost for the carboxylates from diluted aqueous streams can be below 1 €/kg. The highest energy cost is the evaporation of the solvent. Heat integration can reduce this cost further. A typical rule of thumb for heat integration is that 50% of energy savings can be reached.

These results show that the CO_2-expanded methanol technology seems to be promising for carboxylates at low concentrations, typically found in wastewater. If the concentration is higher, then other technologies should be considered. The inorganic salt concentration is a main limiting step for the CO_2-expanded methanol technology, from which alternatives for resin regeneration should be considered. Additionally, anion exchange seems to be the only alternative, from the considered options, for the recovery of small molecules such as acetate and lactate at low concentration (below 30 g/L). Adsorption is an interesting option; however, the low hydrophobic interactions of small molecules makes difficult its implementation.

A detailed multicolumn system should be designed, and with this a continuous process working at maximum capacity can be achieved. Furthermore, capital investment and the

assumptions of full yields for adsorption and desorption must be evaluated. The market price of the carboxylic acids and their derivatives are considered in section 6.3.

6.3. Market of carboxylic acids and their esters

The market size and price of different carboxylic acids affects the feasibility of their recovery from dilute aqueous solutions. The carboxylic acid market size is expected to grow in the following years and surpass USD 20 billion by 2024.[7] The global market is expected to rise because of the increase in the polymer industry, cosmetics, personal care market (stearic, butyric and valeric acid) and food products (polyvinyl acetate for food and beverage storage and propionic acid for prevention of salmonella growth).[8]

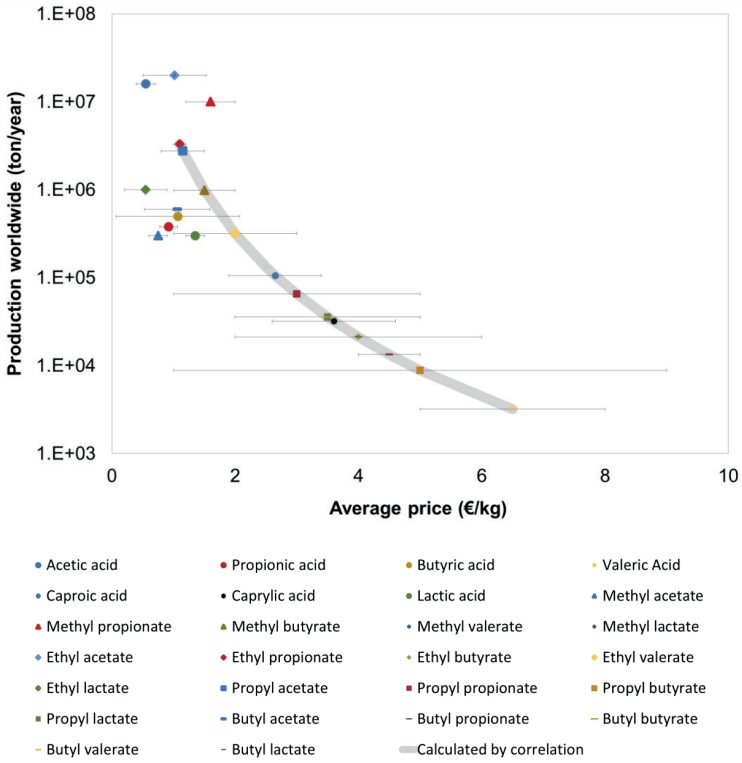


Figure 6.3. Reported market price versus annual production of carboxylic acids and their esters (methyl- to butyl-). Price and market size as reported by different suppliers. The market size of the chemicals in grey are calculated by correlation as suggested by others.[9]

Figure 6.3 shows the market size and average price for different carboxylic acids and esters to which the carboxylic acids can be upgraded. It shows that most derivatives have a price below 2 €/kg. The prices above 2 €/kg have a small market size and varying price that indicates a strong dependence on the specific application. The determination of the right product and derivative is fundamental for the application of this technology. Main variables, such as price and market size, can affect the feasibility of the technology. Additionally, the integration of the concentration step with the upgrading of the chemicals for several wastewater plants should be analyzed. This would identify the application of the technology to different industrial sectors to make the process feasible.

6.4. Other potential applications with different carboxylic acids

As mentioned before, the technology developed in this thesis uses CO_2-expanded alcohols for the desorption and protonation of carboxylates. The CO_2-expanded alcohol produces an alkyl carbonic acid that is used for the protonation of the anions bound to the resin. The main advantage of the technology is the high solubility of CO_2 in the alcohol (**Chapter 3**), which produces a higher amount of alkyl carbonic acid in comparison with the amount of carbonic acid produced in water. This facilitates the protonation at lower CO_2 pressures. In this section, the formation of the alkyl carbonic acid is evaluated for the protonation of different carboxylates.

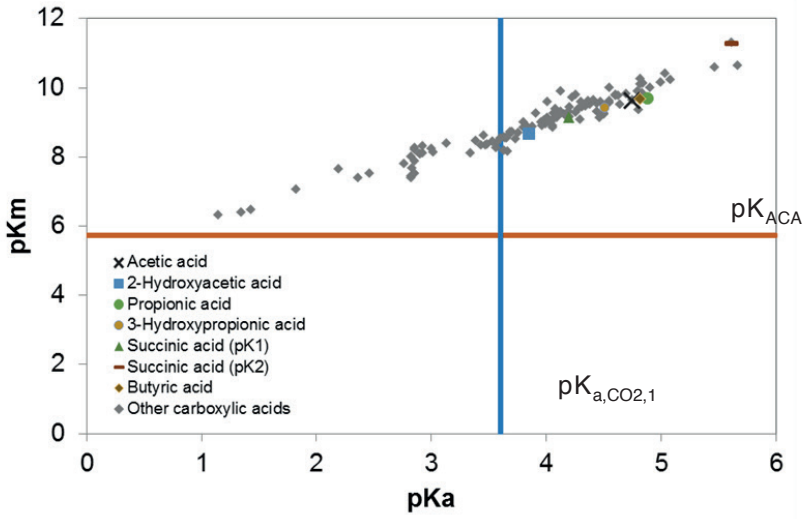


Figure 6.4. Dissociation constants in water and methanol of different carboxylic acids and comparison with the dissociation of methyl carbonic acid (pK_{ACA}) and carbonic acid ($pK_{a,CO2,1}$). Data taken from others [10-12]

Figure 6.4 shows the logarithmic of the dissociation constants (pK_a= -$\log_{10}(K_a)$) of different carboxylic acids in water (pK_a) and methanol (pK_m), and their comparison with those of methyl carbonic acid (pK_{ACA}) and carbonic acid ($pK_{a,CO2,1}$). The pK_m of all the carboxylic acids in the list are higher than the pK_{ACA} of methyl carbonic acid, which means that methyl carbonic acid is a stronger acid than the evaluated carboxylic acids. This facilitates their protonation with methyl carbonic acid. By contrast, this is not the case for carbonic acid as many of the carboxylic acids have a lower pK_a than the $pK_{a,CO2,1}$. This means that carbonic acid is a weak acid which cannot protonate some of these carboxylic acids. As an example, the protonation of acetate with CO_2 has a difference of 1.15 pH units in water and 3.9 pH units in methanol. In other words, a lower pressure of CO_2 must be added to methanol in comparison with water to protonate the same amount of carboxylate. The difference is also observed with other examples like 2-hydroxyacetic acid (0.25 pH and 2.95 pH), which are additionally closer to the $pK_{a,CO2,1}$. The closer the carboxylic acids are to the $pK_{a,CO2,1}$ or the pK_{ACA}, the higher the CO_2 pressure that is needed for its protonation.

It would be interesting to compare the values of the dissociation constant of methyl carbonic acid with other CO_2-expanded alcohol. For example, ethanol is an option for the application of this technology. However, values of ethyl carbonic acid dissociation have not

been reported to the best of our knowledge. Since the solubility (mole basis) of CO_2 in ethanol is higher than in methanol (**Chapter 3**), a larger dissociation constant (smaller pK_{ACA}) might be expected. However, experimental values for a combined pK_{eff} (including dissociation constant of the alkyl carbonic acid and the partitioning of CO_2 between gas and alcohol, $K_{eff} = K_1 \cdot K_{ACA}$) shows a similar value of 10.1 compared to 8.94 in methanol.[12] A detailed analysis for different alcohols and their impact in the further upgrading of the carboxylic acids is needed.

6.5. Use of released bicarbonate

The bicarbonate released upon ion exchange with acetate should be used in the process to avoid salt waste production. Options are to recycle the bicarbonate to the fermentation for pH control, or use it for the desorption of the strongly bound inorganic anions from the resin (**Chapter 5**). For these options, it might be required to concentrate the bicarbonate solution. The concentration of the bicarbonate solution is dependent on its counter ion. Table 6.2 shows the solubility of different carbonate salts at 20 °C.

Table 6.2. Solubility of (bi)carbonate salts at 20 °C [13]

Compound	Solubility (g/100 g water)
Calcium carbonate (calcite)	0.0013
Calcium bicarbonate	16.60
Potassium carbonate	110.5
Potassium bicarbonate	33.2
Sodium carbonate	21.5
Sodium bicarbonate	9.6

As discussed in **Chapter 4**, the presence of calcium causes precipitation problems with an increase of pH in the adsorption column. However, once this limitation is overcome by keeping the CO_2 pressure high during adsorption, calcium carbonate might be easily precipitated by releasing the CO_2 pressure and reused. For sodium and potassium, their precipitation occurs at concentrations above the operating conditions of our method. This means that precipitation does not occur during adsorption, but further water removal is needed to concentrate the solution.

Additionally, further research on the effect of recycling the bicarbonate stream to the fermentation is required to evaluate the impact on the anaerobic open culture fermentation. As mentioned in **Chapter 4**, the reuse of the bicarbonate stream in the fermentation might direct the anaerobic open culture fermentation to specific product formation.

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Summary

The growing human population leads to an increase in resource utilization and waste generation. This is a challenge for society, and the traditional routes for production of energy and chemicals have to be reconsidered. In this regard, alternatives that are not dependent on petroleum sources have to be developed. An alternative is to recover resources from waste streams and upgrade them to chemicals. One example is to recover carboxylates produced by anaerobic open culture fermentation and upgrade them to high-value products such as esters. The recovery of carboxylates is commonly hindered by the high costs of the downstream processing. The complications for their recovery are their low concentration (2-20 g/L), high solubility in aqueous solution, pK_a below operational pH, low partition coefficient (especially for small molecules) and boiling point above the water boiling point (Table 1.1, **Chapter 1**).

In this thesis, a new method for the recovery and upgrading of carboxylates from aqueous (waste) streams was developed. The method consists on the recovery of the carboxylates using an anion exchange resin and its further upgrading to esters. Two different options were considered, namely the alkylation with dimethyl carbonate (**Chapter 2**) and desorption with CO_2-expanded alcohols (**Chapter 3-5**).

Chapter 2 analyzed the opportunities for alkylation of carboxylates recovered from aqueous streams. The aim of this chapter was to reduce the amount of alkylating agent (dimethyl carbonate) per mole of ester produced. This is critical for low value products such as methyl esters of carboxylates present in wastewater (Table 2.1, **Chapter 2**). Several reactions pathways for the formation of methyl acetate were considered (Figure 2.2, **Chapter 2**). Methanol, as byproduct, was produced during the alkylation with dimethyl carbonate because of the hydrolysis of the methyl carbonate anion. A molar yield of methyl acetate on acetate of 0.84 and modest selectivity (0.54─ 0.95 mol methyl acetate/mol methanol) were obtained with an anion exchanger fully in the acetate form. Water and dimethyl carbonate concentrations had a strong effect on the yield and selectivity of the reaction. Model calculations indicated that 1 mol of dimethyl carbonate is consumed for the alkylation of 1 mol of a monocarboxylate salt (such as acetate). As a result, the large-scale feasibility of the alkylation can be comprised by the low yield on dimethyl carbonate.

Since dimethyl carbonate can be produced from methanol and CO_2, we wondered if it might be possible to use these raw materials for the desorption of the carboxylate from the anion exchange resin. A mixture of carbon dioxide and an alcohol below the critical pressure are known as CO_2-expanded alcohols. **Chapter 3** showed for the first time the utilization of CO_2-expanded alcohols for desorption of carboxylates from an anion exchange resin. The CO_2-expanded alcohols form alkyl carbonate anions that are used during desorption and regeneration. The system was coupled with a catalyst to produce esters. Using CO_2-expanded methanol, we achieved a high desorption yield at 10 bar of CO_2 and 20 °C. An ester yield of 1.03 ± 0.07 mol methyl acetate/acetate$_{in}$ was obtained for the combined desorption-esterification at 5 bar of CO_2 and 60 °C. The method was proven to be applicable for the recovery of other carboxylates such as lactate (0.70 mol methyl lactate/mol lactate$_{in}$) and succinate (0.18 mol dimethyl succinate/mol succinate$_{in}$), and with other alcohols such as ethanol (0.67 mol of ethyl acetate/ mol acetate$_{in}$). Different process integration options for desorption and esterification

step were analyzed (Figure 3.1, **Chapter 3**). The method is versatile and can be optimized depending on the specific application.

The next step was to validate the method developed in **Chapter 3** with a real wastewater stream. In **Chapter 4**, wastewater from a paper mill plant was obtained and analyzed. The main carboxylates presented in the wastewater were acetate, propionate, butyrate, valerate and lactate (Table 4.1, **Chapter 4**). These carboxylates were recovered using an anion exchange resin in the bicarbonate form. It was observed, that the wastewater pH and the presence of other inorganic anions (e.g. chloride) have a strong effect on the total loading on the resin. Additionally, cations, such as calcium, can cause precipitation problems at high pH. The resin was regenerated and methyl esters produced using CO_2-expanded methanol at 60 °C. Esters yields ranged from 1.08 ± 0.04 mol methyl acetate/mol of $acetate_{in}$ to 0.57 ± 0.02 mol methyl valerate/mol of $valerate_{in}$. It was demonstrated that the recovery of carboxylates is a possibility for the valorization of paper mill wastewater. However, the methyl esters have to be recovered from the methanol and CO_2 mixture, and high concentrations are required for a feasible process.

In **Chapter 5** we calculated the maximum concentrations for the desorption of acetate with CO_2-expanded methanol. A model was developed to describe the method for batch and column experiments. The model consisted of equilibrium parameters for the adsorption and desorption step. An equilibrium-dispersive model described the recovery of acetate by an anion exchange resin with the consecutive desorption with CO_2-expanded methanol in a column operation. The equilibrium parameters were estimated as: $K_{Cl^-}^{Ac^-} = 0.125$, $K_{Cl^-}^{HCO_3^-} = 0.206$ and $K_{OV,HA} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$ for batch adsorption, and $pK_{MeCO_3^-}^{Ac^-} = 3.71$ for batch desorption. Using these parameters, the maximum equilibrium concentration of acetic acid (after batch desorption) was predicted to be 0.48 mol/kg at 61 bar (Figure 5.3, **Chapter 5**). It was concluded that the acetic acid concentration in the CO_2-expanded methanol was limited by the methyl carbonic acid concentration and the ratio of acetate to chloride pre-loaded to the resin. The maximum acetic acid concentration achieved was 0.427 mol/kg (20 g/L_{MeOH}).

At the end, in **Chapter 6**, we used the knowledge generated during this project to analyze the scenario in which the method might be used. In this chapter, we showed that the method is applicable for recovery and upgrading of carboxylates, especially at low concentration. Anion exchange seems to be the main alternative, from the considered options, for the recovery of small molecules such as acetate and lactate at low concentration (below 30 g/L). To avoid the salt byproduct formation from our method, the released bicarbonate should be reused in the process. Options are to recycle the bicarbonate solution to the fermentation for pH control, or use it for the desorption of the strongly bound inorganic anions from the resin. However, for both options the diluted stream might need to be concentrated. Additionally, further research on the effect of recycling the bicarbonate stream to the fermentation is required to evaluate the impact on the anaerobic open culture fermentation. Finally, the market of the carboxylic acids and ester derivatives were analyzed and discussed (Figure 6.3, **Chapter 6**). In conclusion, we developed a new technology to upgrade carboxylates from wastewater. The method was validated for different scenarios, but a further implementation and direct contact with customers and end-users is critical for its application.

Samenvatting

De groeiende wereldbevolking zorgt voor een toename in grondstoffengebruik en afvalproductie. Om deze uitdagingen voor de samenleving aan te pakken zullen traditionele methodes voor productie van energie en materialen herzien moeten worden en is het noodzakelijk om alternatieven te ontwikkelen die niet afhankelijk zijn van petrochemische grondstoffen. Het omzetten van afvalstromen naar chemische bouwstoffen is één van de alternatieven die een bijdrage levert aan een oplossing voor de toename in zowel afvalproductie als grondstofgebruik. Een voorbeeld is de productie van carboxylaten uit afvalstromen met anaerobe open cultuur fermentaties en de omzetting van deze carboxylaten naar esters, een product met een grotere waarde. De hoge kosten van het terugwinnen van deze carboxylaten hinderen echter de implementatie van deze technologie. De belangrijkste oorzaken van de hoge kosten zijn de lage productconcentraties (2-20 g/L), de hoge oplosbaarheid in water, de proces pH die boven de zuurdissociatie constante ligt, lage verdelingscoëfficienten van de carboxylaten in extractie (in het bijzonder voor de kleine moleculen) en de hogere kookpunten dan water (Tabel 1.1, Hoofdstuk 1).

In dit proefschrift wordt een nieuwe methode gepresenteerd voor het terugwinnen en opwaarderen van carboxylaten uit waterige (afval) stromen. Eerst worden de carboxylaten uit de waterige stroom gehaald met behulp van een anionenwisselaar, waarna de verdere opwaardering tot esters volgt. Twee verschillende opties worden besproken: de alkylering met dimethylcarbonaat (Hoofdstuk 2) en de desorptie met CO_2-geëxpandeerde alcoholen (Hoofdstuk 3-5).

Hoofdstuk 2 bespreekt de alkylering van carboxylaten gewonnen uit waterige stromen met dimethylcarbonaat (DMC), met als belangrijkste doel de hoeveelheid DMC per mol product terug te brengen. Dit is noodzakelijk voor laagwaardige producten zoals methyl esters van carboxylaten uit afvalwater (Tabel 2.1, Hoofdstuk 2). De vorming van methylacetaat is als voorbeeld genomen en meerdere reactieroutes voor de vorming van dit product zijn overwogen (Figuur 2.2, Hoofdstuk 2). Methanol werd gevormd als bijproduct door de hydrolyse van het methylcarbonaat anion. Wanneer een anionenwisselaar geladen met acetaat werd gebruikt had de reactie een opbrengst van 0.84 mol methylacetaat per mol acetaat met een redelijke selectiviteit (tussen 0.54 en 0.95 mol methyl acetaat/mol methanol). De concentraties van water en dimethylcarbonaat hadden een sterk effect op de opbrengst en selectiviteit van de reactie. Modelberekeningen lieten zien dat 1 mol dimethylcarbonaat nodig is voor de alkylering van 1 mol van een monocarboxylaat zout (zoals acetaat). Door deze lage opbrengst zal de toepassing van het proces op grote schaal moeilijk zijn.

Omdat dimethylcarbonaat geproduceerd wordt uit methanol en CO_2, ontstond de vraag of het mogelijk zou zijn om deze grondstoffen te gebruiken voor de desorptie van de carboxylaten van de anionenwisselaars. Wanneer een alcohol met koolstofdioxide op een druk onder de kritische druk gebracht wordt, wordt CO_2-geëxpandeerde alcohol gevormd. In Hoofdstuk 3 wordt voor het eerst het gebruik van deze CO_2-geëxpandeerde alcoholen voor de desorptie van carboxylaten van anionenwisselaars gedemonstreerd. De CO_2-geëxpandeerde alcoholen vormen alkylcarbonaat anionen die worden gebruikt tijdens de desorptie en regeneratie van de ionenwisselaar. Het systeem werd gekoppeld aan een katalysator om esters te produceren. De

toepassing van CO_2-geëxpandeerde alcoholen leidde tot een hoge acetaat desorptie bij 10 bar CO_2 en 20 °C. Bij een verlaagde CO_2 druk (5 bar) en verhoogde temperatuur (60 °C) werd een ester opbrengst van 1.03 ± 0.07 mol methylacetaat per mol acetaat behaald. De methode van desorptie en verestering was ook toepasbaar voor andere carboxylaten, zoals lactaat (0.70 mol methyllactaat/mol $lactaat_{in}$) en succinaat (0.18 mol dimethylsuccinaat/mol $succinaat_{in}$), en met andere alcoholen, zoals ethanol (0.67 mol ethylacetaat/mol $acetaat_{in}$). Verschillende opties voor procesintegratie van de desorptie en verestering zijn geanalyseerd (Figuur 3.1, Hoofdstuk 3) en deze veelzijdige methode kan worden geoptimaliseerd afhankelijk van de toepassing.

De volgende stap was de validatie van de methode ontwikkeld in Hoofdstuk 3 met afvalwater van een papierfabriek. De meest voorkomende carboxylaten in het afvalwater waren acetaat, propionaat, butyraat, valeriaat en lactaat (Tabel 4.1, Hoofdstuk 4). Deze carboxylaten werden uit het afvalwater teruggewonnen met een anionenwisselaar in de bicarbonaat vorm. De pH van het afvalwater en de aanwezigheid van andere anorganische anionen (bijvoorbeeld chloride) had een sterk effect op de carboxylaat-capaciteit van de ionenwisselaar. Verder kunnen aanwezige kationen, zoals calcium, neerslag veroorzaken bij een hogere pH. De met carboxylaten geladen ionenwisselaar kon worden geregenereerd met CO_2-geëxpandeerd methanol bij 60 °C, waarbij de methyl esters gevormd werden. De ester opbrengst varieerde van 1.08 ± 0.04 mol methylacetaat/mol $acetaat_{in}$ tot 0.57 ± 0.02 mol dimethylvaleriaat/mol $valeriaat_{in}$. Hiermee is aangetoond dat het terugwinnen en opwaarderen van carboxylaten een mogelijkheid is voor de valorisatie van afvalwater van een papierfabriek. Voor een daadwerkelijke toepassing van deze methode moeten de methyl esters gescheiden worden van het methanol en CO_2 mengsel. Hiervoor is de uitdaging om hoge ester concentraties te kunnen halen.

In Hoofdstuk 5 zijn de maximale concentraties die behaald kunnen worden bij de desorptie van acetaat met CO_2-geëxpandeerde methanol berekend. Er is een model ontwikkeld waarmee deze methode in batch en kolom experimenten beschreven kan worden. Het model bevat evenwichtsparameters die de adsorptie en desorptie stappen modelleren. De terugwinning van acetaat met een anionenwisselaar kan beschreven worden met een evenwichts-dispersie model, waarbij achtereenvolgens de adsorptie en desorptie met CO_2-geëxpandeerd methanol in een kolom configuratie worden uitgevoerd. De evenwichtsparameters voor het proces zijn bepaald als: $K_{Cl^-}^{Ac^-} = 0.125$, $K_{Cl^-}^{HCO_3^-} = 0.206$ en $K_{OV,HA} = 0.674 \frac{mol/kg_{resin}}{mol/kg_{solution}}$ voor batch adsorptie, en $pK_{MeCO_3^-}^{Ac^-} = 3.71$ voor batch desorptie. Met deze parameters is berekend dat de maximale evenwichtsconcentratie van acetaat (na batch desorptie) 0.48 mol/kg is bij een CO_2 druk van 61 bar (Figuur 5.3, Hoofdstuk 5). Verder is geconcludeerd dat de azijnzuur-concentratie in de CO_2-geëxpandeerde methanol gelimiteerd is door de methylwaterstofcarbonaat-concentratie en de verhouding tussen acetaat en initiële hoeveelheid chloride op de ionenwisselaar. De maximale azijnzuur concentratie die bereikt kan worden is 0.427 mol/kg (20 $g/L_{methanol}$).

Hoofdstuk 6 sluit het proefschrift af met een analyse van de scenario's waarin de ontwikkelde technologie toegepast kan worden. De methode is toepasbaar voor de terugwinning en opwaardering van carboxylaten, in het bijzonder wanneer deze in lage concentraties aanwezig zijn (onder 30 g/L). Van de overwogen opties voor de terugwinning van carboxylaten lijkt het gebruik van anionenwisselaars het belangrijkste alternatief voor de terugwinning van kleine moleculen zoals acetaat en lactaat. Om de vorming van zout als bijproduct te voorkomen is het noodzakelijk om het gevormde bicarbonaat in het proces te hergebruiken. Dit kan bijvoorbeeld gedaan worden door de bicarbonaat oplossing in te zetten voor pH controle bij de

fermentatie of voor de desorptie van sterk aan de ionenwisselaar gebonden anionen. Voor beide opties moet de bicarbonaatstroom wel geconcentreerd worden. Ook is verder onderzoek naar het effect van bicarbonaat recycling naar de fermentatie nodig om te bepalen wat het effect hiervan is op anaerobe open cultuur fermentaties. Verder is inzicht in de markt vereisten en variabiliteit voor de verschillende toepassingen noodzakelijk voor de toepassing van de technologie en hiervoor is de markt voor carbonzuren en ester afgeleiden is geanalyseerd en besproken (Figuur 6.3, Hoofdstuk 6).

De nieuw ontwikkelde technologie voor de opwaardering van carboxylaten uit afvalwater is de kern van dit proefschrift. De methode is gevalideerd voor verschillende scenario's, maar verdere ontwikkeling in samenwerking met eindgebruikers is noodzakelijk voor uiteindelijke toepassing van de technologie.

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Transcript of records

Discipline-related skills

Courses:	Biotechnology Manufacturing-BIOPRO World Talent Campus	Copenhagen, Denmark
	Fundamental of Selection, Synthesis and Design of Thermal Separation Processes	Oldenburg, Germany
	Introduction to COMSOL Multiphysics	Delft, the Netherlands
	Protein Chromatography: Engineering Fundamental and Development for Process Development	Vienna, Austria
	Renewable Engineering Systems Course	Delft & Wageningen, the Netherlands
	Water Purification by Ion Exchange	Chester, United Kingdom

Research-related skills

Oral Presentations:	Bioresource Technology Conference (BIORESTEC)	Sitges, Spain
	National Dutch Chemistry Conference (CHAINS)	Veldhoven, the Netherlands
	Netherlands Biotechnology Conference (NBC)	Wageningen, the Netherlands
Poster Presentations:	Delft Process Technology Institute Conference	Rotterdam, the Netherlands
	European Symposium on Biochemical Engineering Sciences	Lille, France
	Faraday Discussion: Bioresources, Feeding a Sustainable Chemical Industry	London, United Kingdom
Education Assistance:	MSc. Course Numerical Methods, Modeling and Simulation	TU Delft
	BSc. Course Sustainable Entrepreneurship	TU Delft
	Supervision of 4 MSc thesis and 1 MSc internship	TU Delft
	Writing peer-reviewed journal articles	

Transferable skills

Courses/Activities:	Achieving your goals and performing successfully in your PhD	Graduate School TU Delft
	Art of Presenting Science	Graduate School TU Delft
	Lead a Better Academic Life	Graduate School TU Delft
	PhD Startup	Graduate School TU Delft
	Proposal for Imagine Chemistry	AkzoNobel Chemistry startup Challenge
	StartLife Startup Incubation Program	Wageningen University and Research
	Writing a Scientific Article	Graduate School TU Delft
	YesDelft! Startup Discovery Day	YesDelft!

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Carlos Iván

Nadie escoge a su familia, o a su raza, cuando nace,
ni el ser bueno, malo, lindo, feo, inocente o culpable.
Del nacimiento hasta la muerte toda vida es una apuesta:
de nuestra voluntad depende la respuesta.

(Vida, Rubén Blades & Editus)

About the author

Carlos Iván Cabrera Rodríguez was born on the 31st of December 1984 in Puerto Armuelles, Panamá. He finished his Higher Secondary Education in 2002 and started his Diploma Degree (Licenciatura) in Chemical Engineering at the University of Costa Rica (UCR). During his degree, he worked as Research Assistant at the Cellular and Molecular Biology Research Center (Centro de Investigación en Biología Celular y Molecular, CIBCM) at the University of Costa Rica. His research focused in the development of a biopesticide based on *Bacillus thuringiensis* against the coffee berry borer. He graduated in 2008 with his thesis entitled: Agro-industrial waste: Culture media for the production of a biopesticide. After his diploma studies, he continued working at the CIBCM, and additionally started as researcher at the Technology Institute of Costa Rica (ITCR) and lecturer at the National University of Costa Rica (UNA).

In 2009, he received a full fellowship from the Netherlands Fellowship Program (NFP-NUFFIC) to pursue his MSc studies in Biotechnology specialization Process technology at Wageningen University and Research (WUR). His MSc thesis focused on the recovery of medium chain fatty acids produced by chain elongation at the Environmental Technology Department (ETE) from Wageningen University, under de supervision of Dr. ir. Bert Hamelers and Dr. ir. Tim Grootscholten. After his MSc, he worked as Chemical Engineer at Hexion (Rotterdam, NL), and then at the start-up Waste2Chemical as Process Technologist (Wageningen, NL)

In November 2013, he joined the Bioprocess Engineering group at Delft University of Technology (TU Delft) under the supervision of Dr. ir Adrie Straathof and Prof.dr.ir Luuk van der Wielen. During his PhD research, he developed a method for the desorption of carboxylates from strong anion exchange resins with CO_2-expanded alcohols, which is described in this thesis.

In November 2017, he started working as a Postdoctoral researcher at the Biobased Chemistry and Technology group from Wageningen University and Research (WUR) on modeling of carbon dioxide capture. Additionally, he is working on the implementation of the technology described in this thesis to recover carboxylates from waste streams.

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The carboxylate upgrading team

November 2016

Top from left to right: Carlos I. Cabrera-Rodríguez, Adrie J.J. Straathof, Luuk A.M. van der Wielen, Vidhvath Viswanathan. Bottom from left to right: Panagiotis Kagioulis, Carlos M. Cartín-Caballero, Mónica Moreno-González, Florence A. de Weerd and Evgenia Platarou.

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