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# Development and Optimization of Ethyl Lactate Production via Reactive Distillation

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by

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Wien, 13.06.2019

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# Abstract

Ethyl lactate is an environmentally-friendly biobased solvent, which is promising for the substitution of volatile organic compounds. The state of the art production process is a Fischer esterification with a subsequent product separation via distillation. The topic of this work is the development and optimization of ethyl lactate production via reactive distillation in an existing pilot plant.

An initial evaluation showed that the separation operation is the weak point of the process. Water has to be removed with the top product. This separation task however, is contrary to the concept of rectification, because reflux of the top product reduces the separation efficiency. It was necessary to operate the plant without reflux in a reactive stripping operation.

After an optimization in lab scale, the separation of water was successfully implemented in pilot scale - however, with the drawback of very high ethanol consumption and energy demand. At a lactic acid feed rate of 4.3 mol/h a reboiler duty of 2100 W was required to remove a sufficient amount of water from the reactive mixture and a molar feed ratio of  $n_{\text{EtOH}}/n_{\text{Lac}} = 25\text{-}30$  was required to reach an ethanol excess of 3.6-4.2 in the bottom product. The recovery of ethanol from the top product is crucial to the atom efficiency of the overall process. A membrane process (pervaporation) is recommended for this step, in order to avoid the azeotrope ethanol-water.

The evaluation of the residence time distribution of the column suggested that the optimal liquid load was above 8 L/h in the pilot scale setup. The bottom product had to be partially recycled to the lactic acid feed to achieve a sufficient residence time distribution for satisfactory reactant conversion. A mixture of reactants was used as lactic acid feed. The pre-heating of this feed mixture could be studied in future experiments to evaluate the effect of transporting thermal energy from the bottom product to the reactive section of the column.

Reactive distillation was successfully demonstrated in lab scale experiments. It was tried to transform the determined reaction conditions to pilot scale. However, this was not successful. The effective catalyst activity was the limiting factor, even at optimal flow and wetting conditions. The catalyst seemed to be (partially) deactivated. The deactivation of Amberlyst 46 by cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) and the regeneration with hydrochloric acid HCl (5 w% aqueous solution) was tested in lab scale. Both species of cations strongly affected the catalyst activity. The regeneration with HCl (5 w% aqueous solution) was successfully demonstrated.

Considering the results of this work, it is questionable, if the production of ethyl lactate via reactive distillation is reasonable, due to the high energy demand of the separation operation.

# Zusammenfassung

Ethyllactat ist ein umweltfreundliches Lösungsmittel, das aus nachwachsenden Rohstoffen hergestellt werden kann und flüchtige organische Verbindungen (VOCs) ersetzen könnte. Der übliche Herstellungsprozess ist eine Fischer-Veresterung von Milchsäure mit Ethanol mit einer nachfolgenden destillative Aufreinigung. Das Thema dieser Arbeit ist die Prozessoptimierung eines Herstellungsverfahrens für Ethyllactat mittels Reaktivdestillation. Experimente wurden an einer bestehenden Pilotanlage durchgeführt.

Der destillative Trennprozess wurde als Schwachstelle des Verfahrens erkannt. Wasser muss über das Destillat aus der Kolonne entfernt werden, dies widerspricht jedoch dem Konzept einer Rektifikation, weil mit steigendem Rückflussverhältnis die Trennwirkung sinkt. Die Kolonne musste ohne Rückfluss betrieben werden. Durch eine Optimierung im Labormaßstab wurde das Entfernen von Wasser in der Pilotanlage erreicht, jedoch ging dies mit einem hohen Ethanoleinsatz und Energieverbrauch einher. Bei einem Milchsäurefeed von 4.3 mol/h wurde eine Heizleistung von 2100 W benötigt und ein molares Einsatzverhältnis von  $n_{\text{EtOH}}/n_{\text{Lac}} = 25-30$  war nötig, um einen Ethanolüberschuss von 3.6-4.2 im Sumpfprodukt zu erreichen. Die Rückgewinnung von Ethanol aus dem Destillat ist von großer Bedeutung für die Atomökonomie des Gesamtverfahrens. Für diese Trennaufgabe empfiehlt sich ein Membranprozess (Pervaporation) um das binäre Azeotrop Ethanol-Wasser zu umgehen.

Untersuchungen der Verweilzeitverteilung zeigten, dass eine Flüssigkeitsbelastung von mindestens 8 L/h für eine optimale Flüssigkeitsverteilung in der Kolonne nötig ist. Das Sumpfprodukt muss teilweise zum Milchsäure-Feed zurückgeführt werden um eine ausreichende Verweilzeit für die Veresterungsreaktion zu erreichen. Anstatt eines reinen Milchsäure-Feeds wurde ein Gemisch aus Milchsäure und Ethanol verwendet. Eine Feed-Vorwärmung könnte in zukünftigen Experimenten untersucht werden, um festzustellen, welchen Einfluss der Wärmetransports vom Sumpfprodukt in die reaktive Kolonnenzone auf das Betriebsverhalten der Anlage hat. In Laborexperimenten konnte die Reaktivdestillation erfolgreich durchgeführt werden. Es wurde versucht, die ermittelten Betriebsbedingungen in der Pilotanlage nachzustellen, jedoch ohne Erfolg. Die effektive Katalysator-Aktivität war der limitierende Faktor – selbst bei optimalen Strömungsbedingungen in der Kolonne. Der Katalysator dürfte deaktiviert gewesen sein. Die Deaktivierung und Regeneration des verwendeten Amberlyst 46 wurde in Laborexperimenten untersucht. Aufgrund des hohen Energiebedarfs für das Abtrennen von Wasser erscheint es fraglich, ob Ethyllactat sinnvoll mittels Reaktivdestillation hergestellt werden kann.

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# 1 Introduction

## 1.1 Peak Oil and Sustainable Development

Today's global economy is highly dependent on fossil resources as primary material for the production of energy and consumer products. This dependency leads to a major issue of our time because firstly, these fossil resources are limited and secondly, their use results in greenhouse gas emissions that increment the progressing climate change. [1]

In the Rio agreement [2] of 1992 the UN member states committed themselves to transferring their economic activities to a sustainable way, to preserve the world's ecosystem for future generations. The limitation of easily accessible and therefore cheap crude oil, the predominant resource for the chemical industry at the time, already comes in sight. According to various studies the "peak oil" – the moment when petrol production reaches its maximal capacity – will be reached before the year 2050. [3] A broad review of forecasts and reports of oil production stated in 2016 that the production peak for regular conventional oil was already reached in 2005 and the peak for all oil production could be expected for ~2020. [1]

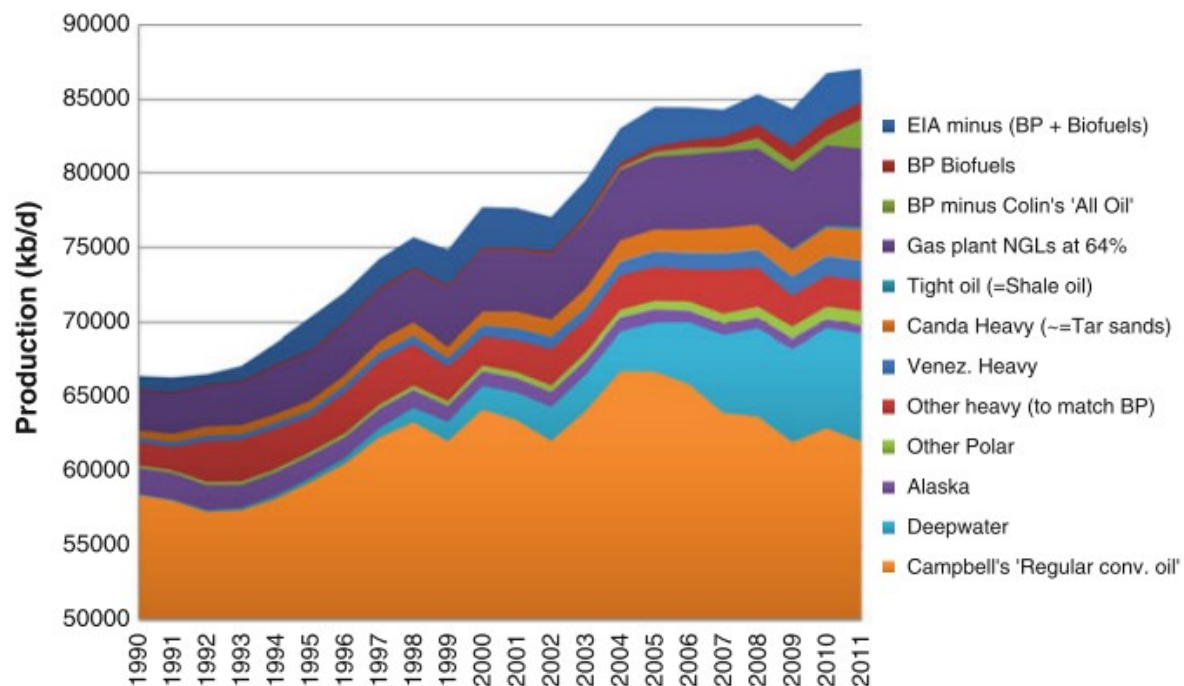


Figure 1: Global oil production, Figure taken from [1]

Regardless of the current and near future supply situation, the utilization of crude oil as fundamental resource for our economy is not sustainable. It causes tremendous amounts of CO<sub>2</sub>-emissions that are contrary to the internationally agreed objectives on global climate

change. The international energy agency IEA proposed a forecast for crude oil production considering two different future development scenarios: [4]

- The New Policies Scenario (NPS) shows the expected development following existing and new policies under the current political attitude.
- The Sustainable Development Scenario (SDS) shows the development that would be necessary to meet the internationally agreed objectives on global climate change, air quality and universal access to modern energy.

It is apparent from Fig. 2 that a huge technology shift towards renewable resources and sustainable processes will be required to achieve the sustainable development scenario.

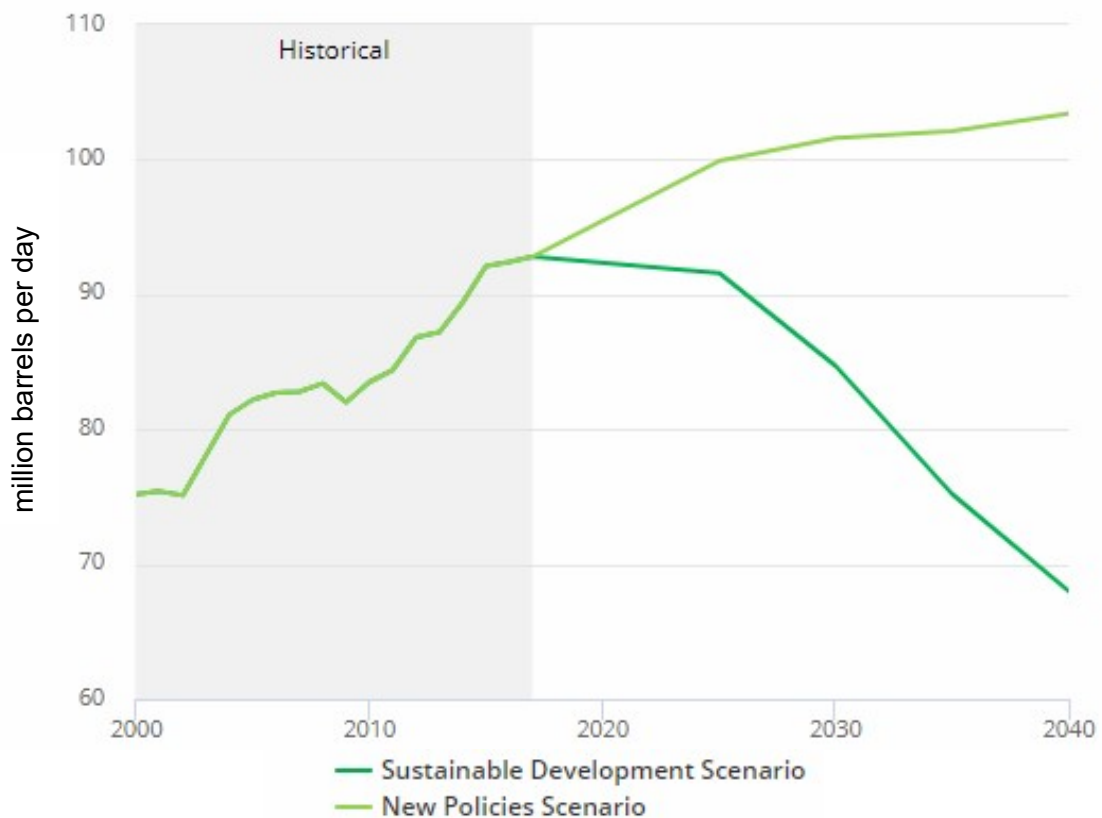


Figure 2: Global oil production scenarios, Figure taken from [4]

## 1.2 Biorefineries

Biorefineries are a means to the long term goal of sustainable production of all products in an economy based on biomass, often referred to as “bioeconomy”. A definition is given by the IEA Bioenergy in Task 42:

*“Biorefining is the sustainable processing of biomass into a spectrum of marketable biobased products and bioenergy.”* (IEA Bioenergy, Task 42, [5])

In the EU, R&D activities in the field of biorefineries are funded by the Horizon 2020 program. Horizon 2020 was issued to meet the EU’s energy and climate changing targets for the year 2020. It is estimated by the European Commission, that the technology shift towards biological resources and biorefinery technology could save up to 2.5 billion tons of CO<sub>2</sub>-equivalent per year by 2030. [6] The bio-based share of all chemical sales in the EU is predicted to rise from 12.3% in 2015 to 22% by 2020, and 30% market share is the target for 2030. [7]

Similar to conventional petrol refineries, biorefineries fractionate raw material in a first step, called the primary refinery. As much as possible of the feedstock is used to avoid waste streams. Some biological structures have natural functionalities that can have the same purpose in final products (e.g. the mechanical strength of cellulose in wood can be used for textile fibres). It is crucial to the process efficiency of biorefineries that these existing functionalities are used in a smart way. Instead of breaking natural macromolecules down to monomers and then, linking these monomers to macromolecules again to adapt the feedstock to existing synthesis processes, the natural macromolecules should rather be extracted and used directly whenever possible. [3] However, at present many biological structures cannot be separated and used this way by economically and environmentally reasonable means. Therefore, the concept of “cascaded use of resources” is applied. Residual biomass is fractionated into basic substances according to the chemical structure and then used in platform technologies to form a large number of final products. Carbohydrates are often processed by fermentation into intermediates, which are used as chemical building blocks in various syntheses. The production processes based on platform chemicals are called the secondary refinery. [8]

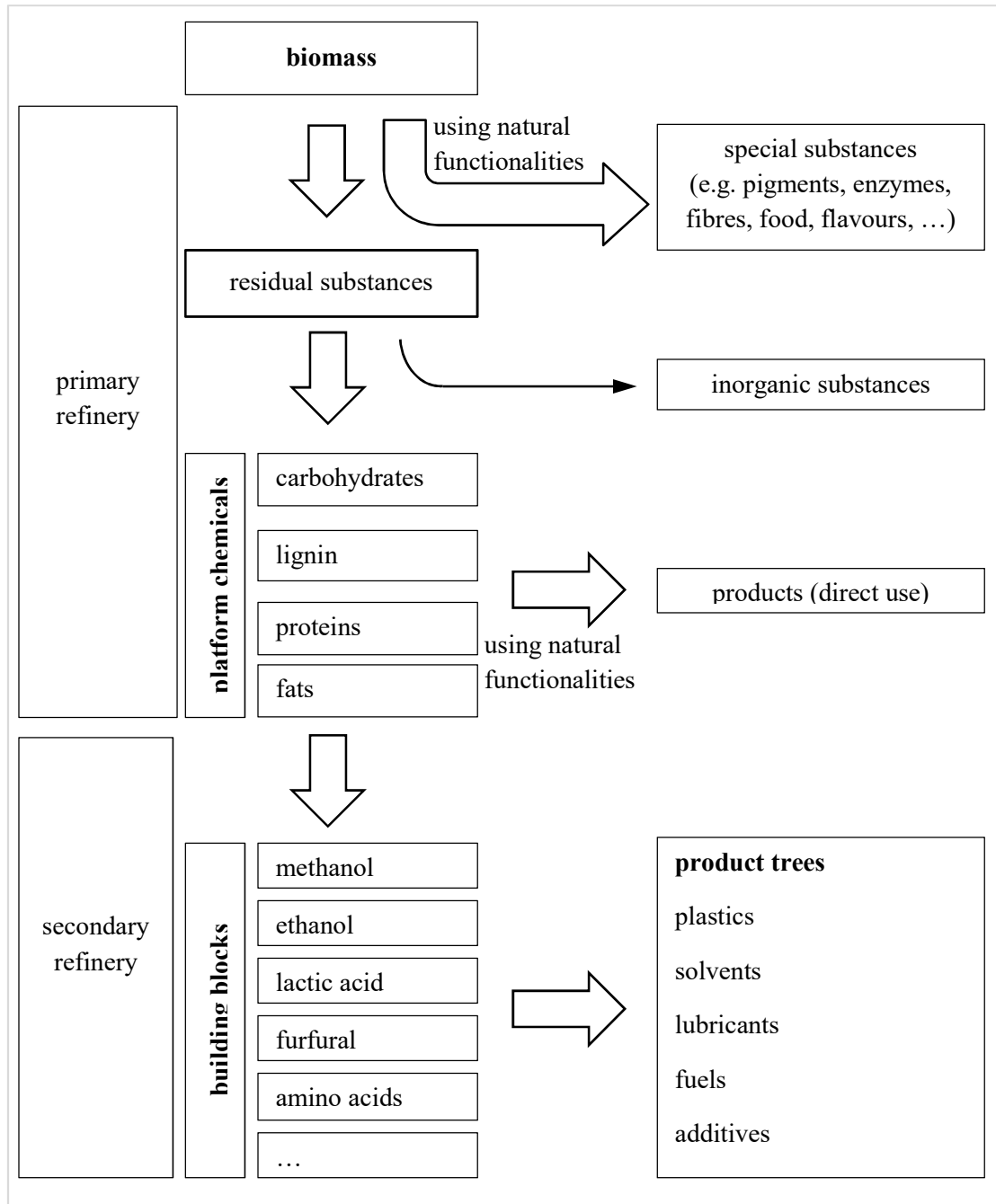


Figure 3: Concept of cascaded use of resources in biorefinery systems, Figure based on [8]

A great challenge on the way to a sustainable bioeconomy will be to ensure the supply of the required biomass without converting natural habitats into new agricultural land. The demand of biomass is expected to grow caused by 3 main drivers: “the increasing world population,” “prosperity growth in combination with higher consumption and profusion per capita” and “political ambitions for the use of biomass as sustainable resource”. Diminishing profusion of food, packaging and consumer goods will play an important role in ensuring supply safety. [9]

Due to the great variations of biomass composition, different biorefinery systems have been developed for the use of specific resources: [8]

- “Whole Crop Biorefineries” use biomass with high starch content (e.g. corn, cereals)
- “Green Biorefineries” use biomass with high water content (e.g. grass, clover)
- “Lignocellulosic Biorefineries” use primal materials that contain cellulose (e.g. wood, straw, pulp waste)

In recent years the R&D activities especially in Europe have shifted from processing edible biomass (like corn, sugarcane or potatoes) in biorefineries to the utilization of residual and waste streams of agriculture and organic municipal solid waste (MSW). These resources are not in competition to food and feed production. [10] According to an estimation of McKinsey in 2003, the residual and waste streams of agriculture could provide the raw material for the production of approx. 40% of all organic bulk chemicals worldwide. [3]

Modern biorefinery concepts, considered as type III biorefineries combine the technology for converting multiple feedstocks by flexible production processes into a large pool of final products. Due to the high flexibility, these biorefineries could shift the production and adapt it to the actual supply situation. A multitude of conversion and synthesis processes and interdisciplinary optimization of biotechnological, chemical, thermal and mechanical unit operations is needed. [8] Flexibility on the product side is achieved by a diversity of processes that start from the same chemical building blocks. As an example, the product tree of lactic acid is explained, which includes ethyl lactate as a product of lactic acid and ethanol. Important products made from lactic acid, which have the potential for a large-volume use and the substitution of petrol based products are: [11]

- Polylactic acid (PLA) and other polymers and copolymers as thermoplastics for fibres and packaging
- Lactate esters as environmentally friendly “green” solvents
- Oxygenated industrial chemicals (propylene glycol, propylene oxide, acrylic acid and acrylic esters and others) as additives and for various synthesis

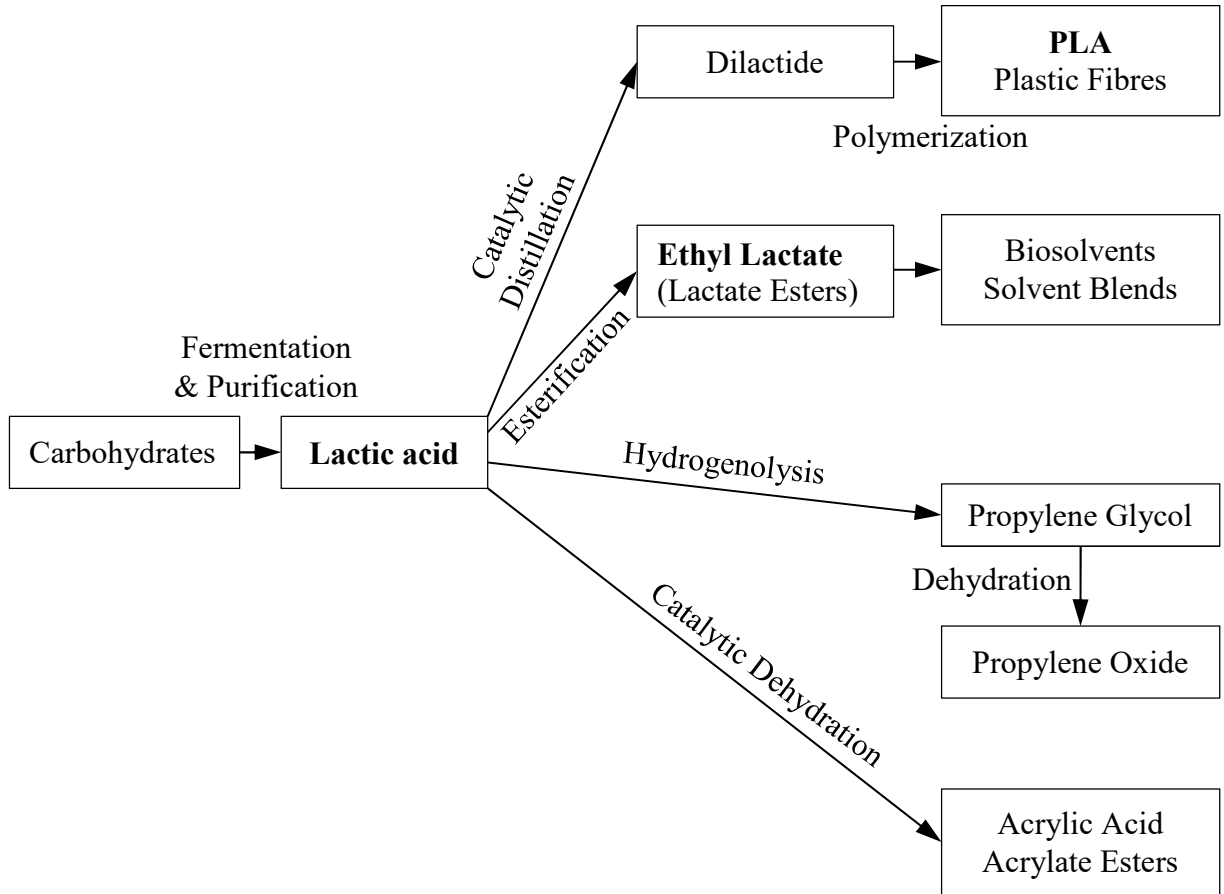


Figure 4: Product tree of lactic acid, Figure adapted from [11]

### 1.3 The Green Safer Solvent Ethyl Lactate

The 12 principles of green chemistry are the fundamental guidelines for the development of sustainable eco-friendly processes in the chemical industry. Principle No. 5 addresses solvents:

*“The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.”*

(Anastas, P. T.; Warner, J. C.: Green Chemistry: Theory and Practice, 1998 [12])

In many processes the vast majority of the accruing waste is caused by solvents. [12] To reduce their environmental impact, researchers and industry are searching for alternatives to toxic and petrol-based VOCs (volatile organic compounds) for many years already. There has been remarkable progress in Europe and the USA, where VOC emissions are constantly going down. Even though, the reduction of VOC emissions (especially in Asia) is still a massive challenge. [13]

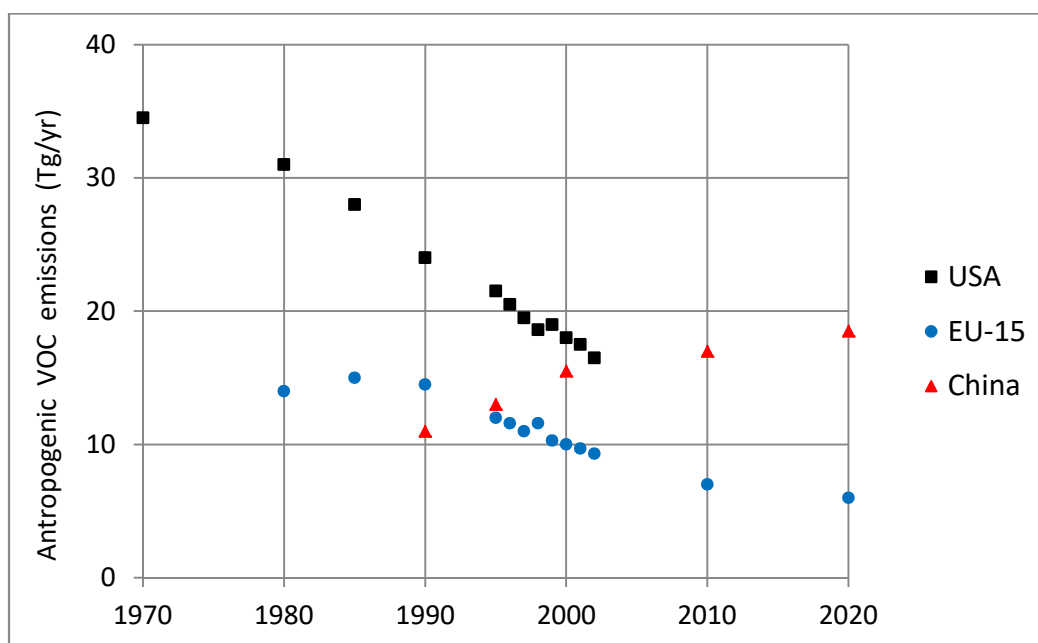


Figure 5: Anthropogenic VOC emission estimates and projections, Figure adapted from [13]

In optimal processes the chemical reactions can be implemented satisfactorily without any solvent at all, as solvents always involves energy demand and environmental impacts in their production and recovery. Water or supercritical CO<sub>2</sub> as solvents also present good alternatives in many cases. However, their use is limited, because many organic chemicals have an unsatisfactorily low solubility in them. Where VOCs are difficult to replace, solvents derived

from platform molecules of biorefineries, such as ethyl lactate, should be considered. A broad range of new solvents is needed to meet the requirements of challenging applications. [14] Gu and Jérôme proposed a list of criteria, that environmentally benign safe solvents should fulfil in order to provide a sustainable alternative to conventional petrol-based solvents. No solvent meets all of these criteria, they are rather meant as guidelines for the product development. [15] In Table 1 an assessment of ethyl lactate regarding these criteria was done.

*Table 1: Assessment of ethyl lactate as green solvent, based on [15]*

<b>criteria [15]</b>	<b>explanation [15]</b>	<b>ethyl lactate</b>
availability	constant and industrial scale production capacity	The resources ethanol and lactic acid are produced in large quantities.
price	stable and competitive to conventional solvents	Approx. 3-4 €/kg, could decrease to 1.66 €/kg and be competitive to many conventional solvents. [16]
recyclability	easy solvent recovery (low energy demand)	easily recyclable [17]
grade	purity needed for the application (technical grade preferred)	can be used at technical grade and in solvent blends. [11]
synthesis	efficient production process	A number of potentially efficient production processes was proposed. The optimization is still an ongoing research topic. [17]
toxicity	negligible to ensure consumer safety and environmental friendliness	negligible toxicity, approved by the FDA as food additive [17]
biodegradability	readily biodegradable to avoid accumulation in the environment	readily biodegradable [17]
performance	properties must meet the requirements of the individual application	depends on the particular application.
stability	thermal and chemical stable	relatively stable unless exposed to water [17]
flammability	not flammable to ensure consumer safety	flammable liquid and vapour [18]
storage	easy and safe to store and transport	easy to store, not a VOC [17]
renewability	derived from renewable resources	produced from biorefinery platform chemicals [17]

Ethyl lactate has very favourable properties regarding environmental, health and safety aspects. Many conventional petrol-based solvents have the drawback of considerable toxicity and their potential to act as greenhouse gases and ozone depleting. Ethyl lactate however has negligible toxicity, is non carcinogenic and is even approved for the use as food additive by the US food and drug administration FDA. It does not act ozone depleting, has a low vapour



pressure at ambient conditions and is therefore not considered a VOC. Moreover, ethyl lactate is readily biodegradable, which means that it passed tests for rapid and complete biodegradation following OECD standards. [17] These benefits make it especially promising for end user applications such as cleaning agents or solvents for printer inks and paints, where the substitution of VOCs is especially important. [14] According to the Canadian National Pollutant Release Inventory, in 2008 general solvent use outside the industrial manufacturing accounted for 21% of VOC emissions, whereas the chemical industry was only responsible for 0.7%. [19]

Ethyl lactate is a polar protic solvent with high solvency power, which dissolves e.g. cellulose acetate, many resins, greases and oils. The main physical properties of ethyl lactate are summarized in Table 2. Due to its high boiling point, low vapour pressure and low surface tension it is also interesting for the coating industry. [17]

*Table 2: Physical properties of ethyl lactate at 293 K [18]*

boiling point $T_b$	(K)	427.15
vapour pressure $p^{\text{sat}}$	(Pa)	210
density $\rho$	( $\text{kg L}^{-1}$ )	1.031
dynamic viscosity $\eta$	( $10^{-3} \text{ Pa s}$ )	3.71
heat capacity $c_p$	( $\text{J mol}^{-1} \text{ K}^{-1}$ )	250 [17]
surface tension $\sigma$	( $10^{-3} \text{ N m}^{-1}$ )	70.5

Ethyl lactate is used for the following applications: [17]

- Industrial cleaning agents for electronics, polyurethane production, metal surfaces
- Household cleaners
- Solvent for paints, coatings and inks
- Solvent for many organic synthesis
- Pharmaceutic and food applications, conserving the function of biological active compounds

Technically ethyl lactate has the potential to substitute at least 14 conventional solvents, which are listed in Fig. 6. An important factor for the actual substitution in applications is the market price. It is about 3-4 €/kg at the time, but could decrease significantly as process technology improves. It is estimated that the price could be as low as 1.66 €/kg. [17] This

decline would allow a direct competition with many of the solvents named in Fig. 6 and could open a large market of approx. 2.27 mio. t/a to ethyl lactate. [16]

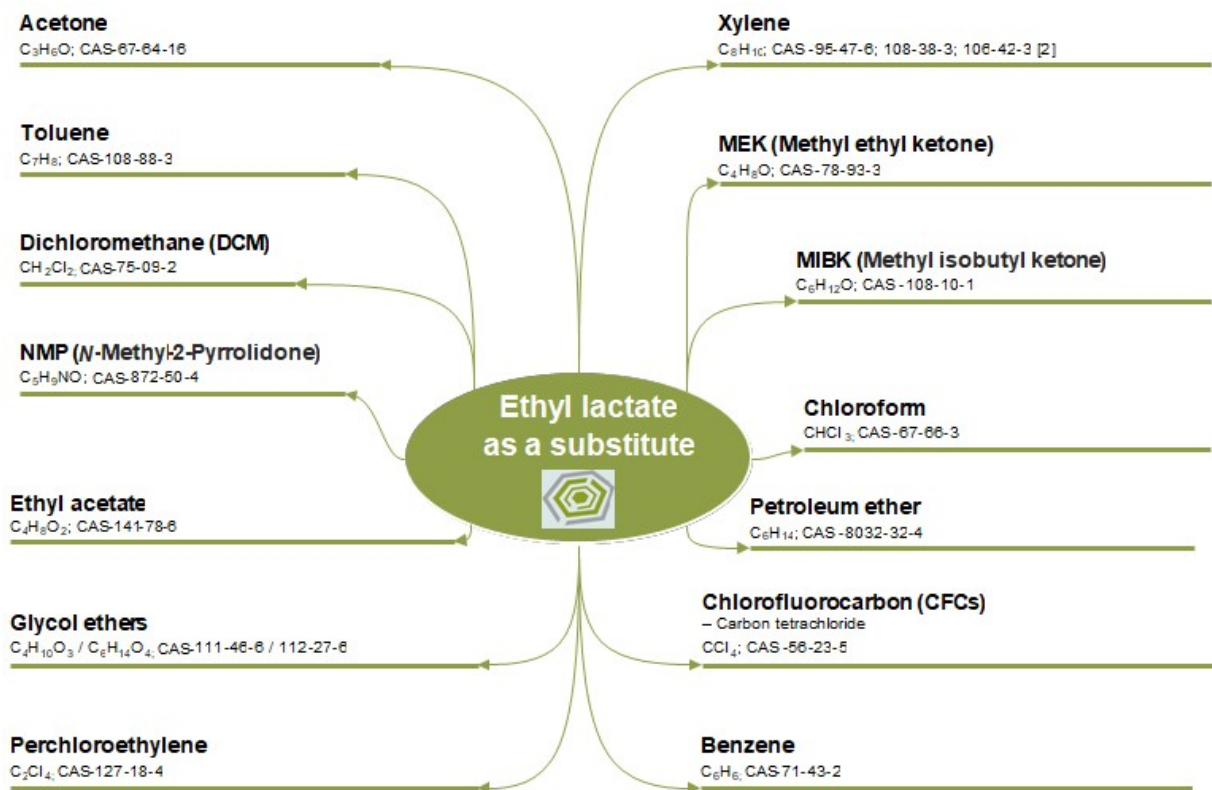


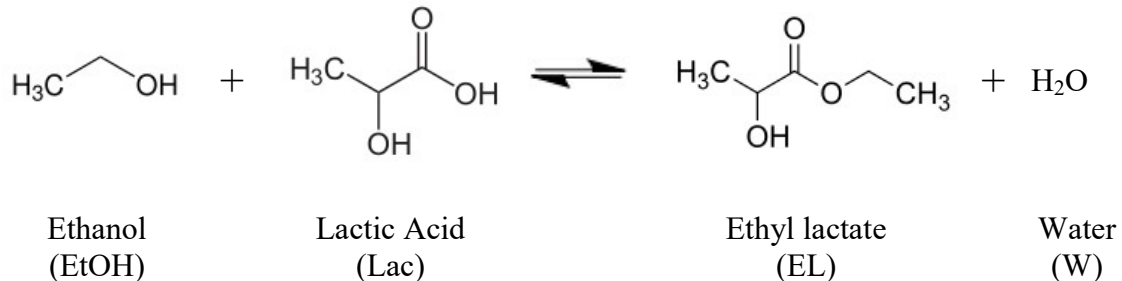
Figure 6: Substitution potential of ethyl lactate, Figure taken from [20]

Ethyl lactate is produced by the esterification of lactic acid with ethanol. Thus it requires only renewable resources and can be considered as the combination of two important building blocks of biorefinery platform technology. In the conventional production process the esterification reaction is carried out until the chemical equilibrium is reached. Then ethyl lactate is separated from the reaction mixture by distillation. An acid catalyst is used to speed up the reaction, the most common being sulfuric acid. [17]

The subsequent separation of ethyl lactate requires a large amount of energy. Therefore more efficient production concepts have been proposed. A promising approach is the concept of process intensification by reactive separation processes. Nearly complete conversion of the raw materials and high product purity can be achieved in a single device. Examples for this approach are membrane supported reactors and reactive distillation devices. [17]

## 1.4 Reaction Fundamentals

An esterification is the reaction of an acid with an alcohol to form an ester as a product and water as a side product. In the case of ethyl lactate formation the following chemical reaction occurs:



An esterification is a reversible reaction, which means that the forward reaction (esterification) and the back reaction (hydrolysis) occur simultaneously.

### 1.4.1 Chemical Equilibrium

At the state of chemical equilibrium the global reaction rate is zero, which means that the forward and back reaction are equally fast. The state of chemical equilibrium of a reactive mixture is characterized as the state of maximum entropy, respectively minimal free Gibbs energy of a closed system. It is described by the equilibrium constant  $K$ . The thermodynamic equilibrium constant is defined in terms of activities according to Eq. 1:

$$K = \exp\left(-\frac{\Delta G^0}{RT}\right) = \prod_i a_i^{\nu_i} \quad (\text{Eq. 1})$$

It is a function of temperature and pressure. The thermodynamic equilibrium constant can be divided into a product of mole fractions  $x_i$  and a product of activity coefficients  $\gamma_i$ . Applying the law of mass action for ethyl lactate formation gives Eq. 2:

$$K = \frac{a_{\text{EL}} a_{\text{W}}}{a_{\text{EtOH}} a_{\text{Lac}}} = \frac{x_{\text{EL}} x_{\text{W}}}{x_{\text{EtOH}} x_{\text{Lac}}} \frac{\gamma_{\text{EL}} \gamma_{\text{W}}}{\gamma_{\text{EtOH}} \gamma_{\text{Lac}}} = K_x K_\gamma \quad (\text{Eq. 2})$$

Pereira et al. found Eq. 3 for the temperature dependency of the equilibrium constant by fitting the experimental data of 14 runs between 323.15 and 362.87 K, using high concentrated lactic acid and an initial molar ratio of  $n_{\text{EtOH}}/n_{\text{Lac}} = 1.1\text{-}2.8$ : [21]

$$\ln K = 2.9625 - \frac{515.13}{T \text{ (in K)}} \quad (\text{Eq. 3})$$

With a standard reaction enthalpy of 4.28 kJ/mol [21], it is a slightly endothermic reaction. The equilibrium composition is almost independent of temperature.

The product of the equilibrium mole fractions  $K_x$  is significantly influenced by the initial molar reactant ratio  $n_{\text{EtOH}}/n_{\text{Lac}}$ . This is because the activity coefficients of the non-ideal quaternary system vary with the composition of the mixture. [22] Delgado, Sanz and Beltrán studied this effect for ethyl lactate production. Fig. 7 shows the obtained values for  $K_x$  over a large range of the initial molar reactant ratio (experimental data at  $T = 347\text{-}373\text{ K}$ ).

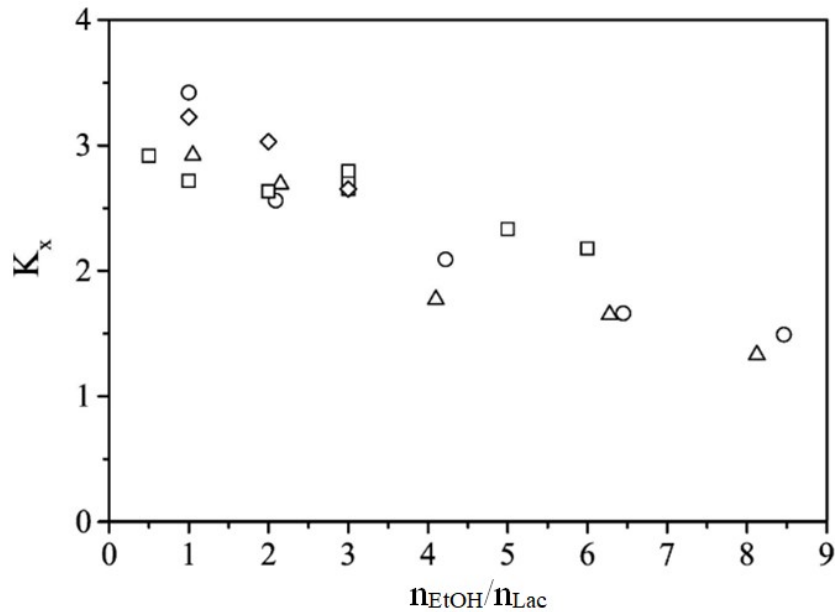


Figure 7: Compilation of experimental data of the equilibrium constant based on mole fractions  $K_x$  as a function of the initial reactant ratio  $n_{\text{EtOH}}/n_{\text{Lac}}$ , Figure taken from [22]

With increased excess of ethanol,  $K_x$  shifts towards lower values, which means that the effect of increased conversion caused by additional excess ethanol is declining.

#### Composition of reactive mixtures

The term “reactant equivalent” is introduced to describe the composition of a reactive mixture independently of the reaction progress. The lactic acid equivalent is defined in Eq. 4.

$$Eq_{\text{Lac}} = n_{\text{Lac}} + n_{\text{EL}} \quad (\text{Eq. 4})$$

The ethanol equivalent is defined in Eq. 5.

$$Eq_{\text{EtOH}} = n_{\text{EtOH}} + n_{\text{EL}} \quad (\text{Eq. 5})$$

For a system with a single reaction, the reactant equivalents in a closed system are constant. Unlike the molar amount of a reactant species, the reactant equivalent does not change as the

esterification proceeds. The conversion of lactic acid and the yield of ethyl lactate were used as success indicators for the esterification reaction. They are defined in Eq. 6 and Eq. 7.

*Conversion of lactic acid:*

$$X_{\text{Lac}} = \frac{n_{\text{Lac},0} - n_{\text{Lac}}}{n_{\text{Lac},0}} \quad (\text{Eq. 6})$$

*Yield of ethyl lactate referred to lactic acid:*

$$Y_{\text{EL,Lac}} = \frac{n_{\text{EL}} - n_{\text{EL},0}}{n_{\text{Lac},0}} \quad (\text{Eq. 7})$$

For the purpose of comparability, all values of lactic acid conversion and ethyl lactate yield in this work refer to the total number of lactic acid equivalents  $\text{Eq}_{\text{Lac}}$  in a mixture. The unreacted state, where  $n_{\text{EL},0} = 0$  was used as reference state. Side reactions are neglected in this work, therefore  $X_{\text{Lac}}$  and  $Y_{\text{EL,Lac}}$  are equivalent.

$$X_{\text{Lac}} = \frac{\text{Eq}_{\text{Lac}} - n_{\text{Lac}}}{\text{Eq}_{\text{Lac}}} = \frac{n_{\text{EL}}}{\text{Eq}_{\text{Lac}}} = Y_{\text{EL,Lac}}$$

### Calculation of the equilibrium composition

The equilibrium composition was calculated from the thermodynamic equilibrium constant  $K$ . The term for the activity coefficients  $K_\gamma$  was estimated considering data from Delgado, Sanz and Beltrán. [22]

The stoichiometric correlations Eq. 8 – Eq. 11 were used. The initial state is denoted with index 0 and the equilibrium state with index \*.

$$K_x = \frac{x_{\text{EL}} x_{\text{H}_2\text{O}}}{x_{\text{EtOH}} x_{\text{Lac}}} \quad (\text{Eq. 8})$$

$$x_{\text{W}}^* = x_{\text{W}}^0 + x_{\text{Lac}}^0 - x_{\text{Lac}}^* \quad (\text{Eq. 9})$$

$$x_{\text{EL}}^* = x_{\text{Lac}}^0 - x_{\text{Lac}}^* \quad (\text{Eq. 10})$$

$$x_{\text{EtOH}}^* = x_{\text{EtOH}}^0 - x_{\text{Lac}}^0 + x_{\text{Lac}}^* \quad (\text{Eq. 11})$$

The mole fractions of water, ethyl lactate and ethanol at the state of equilibrium were eliminated by substitution. A quadratic equation for the equilibrium mole fraction of lactic acid was obtained.

$$0 = (x_{\text{Lac}}^*)^2 + x_{\text{Lac}}^* \cdot p + q \quad (\text{Eq. 12})$$

Where p and q are:

$$p = \frac{1}{1-K_x} (K_x (x_{\text{Lac}}^0 - x_{\text{EtOH}}^0) - x_{\text{W}}^0 - 2x_{\text{Lac}}^0)$$

$$q = \frac{1}{1-K_x} x_{\text{Lac}}^0 (x_{\text{Lac}}^0 + x_{\text{W}}^0)$$

Solving the quadratic equation for  $x_{\text{Lac}}^*$  gives Eq. 13.

$$x_{\text{Lac}}^* = -\frac{p}{2} + \sqrt{\frac{p^2}{4} - q} \quad (\text{Eq. 13})$$

As an example, the equilibrium composition was calculated for a mixture of 80 w% lactic acid and 95 w% ethanol with an initial molar reactant ratio of  $n_{\text{EtOH}}/n_{\text{Lac}} = 3$  at 363 K. The initial composition and the results are given in Table 3.

$$K = \exp\left(2.9625 - \frac{515.13}{363.15 \text{ (in K)}}\right) = 4.68 = K_x K_\gamma$$

The term of activity coefficients  $K_\gamma$  was calculated from literature data. [21] The results were compared to Figure 7 to check plausibility. At an initial molar ratio of  $n_{\text{EtOH}}/n_{\text{Lac}} = 3$  the value of Figure 7 is  $K_x = 2.6-2.7$ . This is in accordance to the value calculated in Eq. 14.

$$K_\gamma = \frac{\gamma_{\text{EL}} \gamma_{\text{W}}}{\gamma_{\text{EtOH}} \gamma_{\text{Lac}}} = \frac{1.2125 \cdot 1.7715}{1.0707 \cdot 1.1511} = 1.74 \rightarrow K_x = 2.69 \quad (\text{Eq. 14})$$

The equilibrium mole fraction of lactic acid was calculated using the quadratic equation. The other mole fractions and the lactic acid conversion were calculated from the obtained value.

*Table 3: Calculation of the equilibrium composition of a particular mixture*

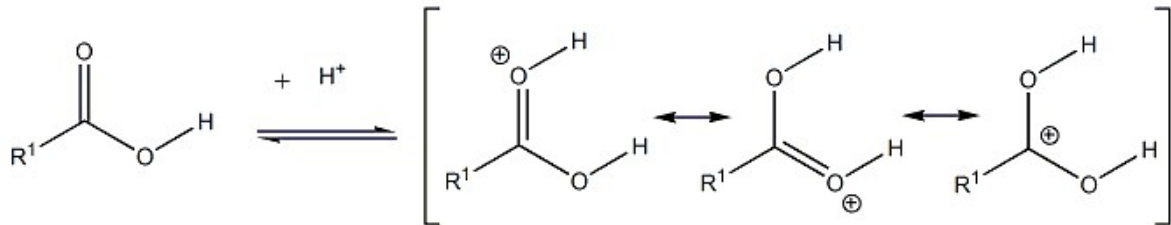
component	ethanol	lactic acid	ethyl lactate	water
initial weight fraction	0.54	0.35	0	0.12
initial mole fraction	0.53	0.18	0	0.29
activity coefficient [21]	1.0707	1.1511	1.2125	1.7715
equilibrium mole fraction (calculated)	0.40	0.05	0.13	0.42
equilibrium mole fraction (experimental, this work)	0.43	0.08	0.10	0.39

The calculated value for the equilibrium conversion of 72% was significantly higher than the experimentally determined value of 56%.

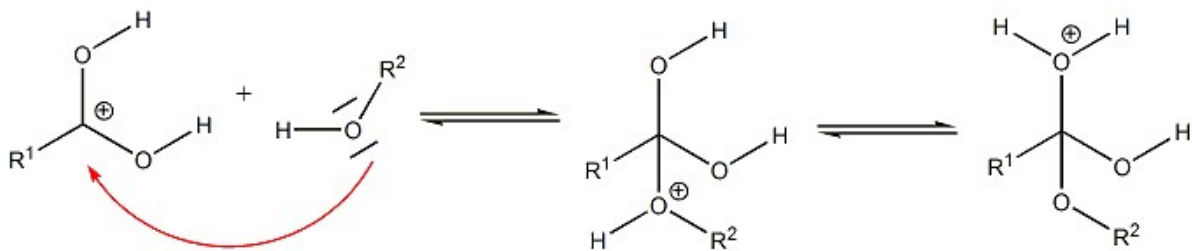
## 1.4.2 Reaction Mechanism

Ethyl lactate formation follows the mechanism of a Fischer esterification, illustrated in Fig 8.

1) Protonation of the acid



2) Nucleophilic addition of the alcohol



3) Elimination of water

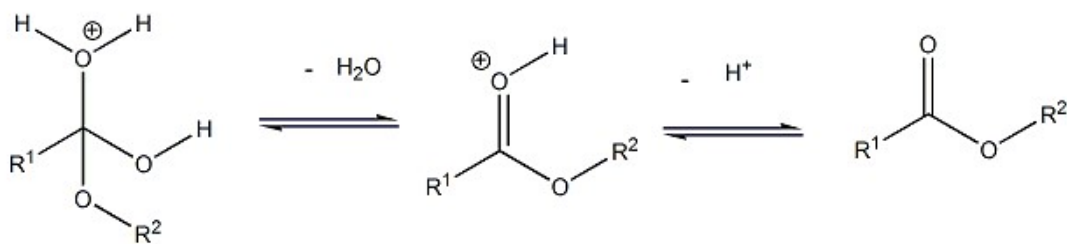


Figure 8: Mechanism of a Fischer esterification, Figure based on [23]

In the first step lactic acid is protonated, forming a resonance-stabilized carbocation. Then, ethanol is added forming a tetrahedral transition state by a nucleophilic attack at the carbocation. The transition state is stabilized by a tautomeric proton transfer from the oxygen atom of ethanol to the OH-group of the acid. In the final step, water is eliminated from the tetrahedral structure, forming ethyl lactate.

A strong acid is needed, not only as catalyst, but also to protonate the acid in order to make the reaction with a nucleophile (the alcohol) possible. The limiting step to the reaction rate is the formation and dissolution of the tetrahedral transition state. This step is catalysed by a strong acid. Water and alcohol are leaving groups of comparable basicity. Therefore an excess of ethanol or the removal of products from the mixture has to be applied to achieve a high conversion of the acid. [23]

### 1.4.3 Catalysis

A catalyst is a substance that increases the reaction rate of a chemical reaction without being consumed by it. Usually only small amounts of a catalyst are required to increase a reaction rate substantially. A catalyst reduces the activation energy of a chemical reaction and therefore, increases the reaction rate of forward and back reaction. The chemical equilibrium is not influenced by it.

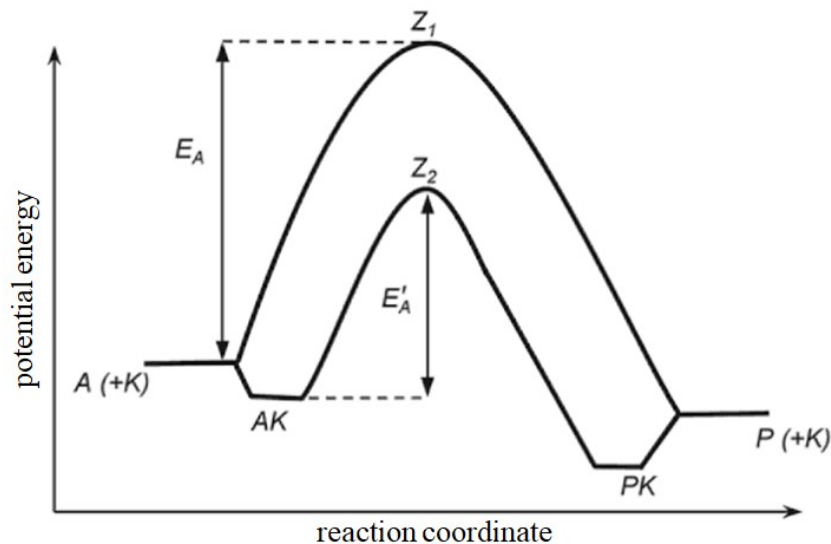


Figure 9: Simplified energy plot of the catalysis of the chemical reaction  $A \leftrightarrow P$  catalysed by  $K$   
Figure based on [24]

A catalyst can be either homogenous or heterogeneous. A homogeneous catalyst is a substance in the same phase as the reactants. It is equally distributed in the reactive phase and the reactivity can be easily adjusted by its concentration.

A heterogeneous catalyst is a different phase. Commonly solid catalysts are used for liquid or gaseous reactants. A heterogeneous catalyst is easily separated from the reactive system and reused. Its effectiveness depends not only on its reactivity, but also on mass transfer phenomena. The overall reaction rate is limited by the slowest step of the whole sequence, which can be either the chemical reaction, or one of the mass transfer steps (adsorption or diffusion). The exact sequence of steps depends on the catalysis mechanism. [24]

In this work a strong acidic cation-exchange resin (Amberlyst 46) was used as a heterogeneous catalyst. The Amberlyst resin is a crosslinked polymer (Poly-styrene-divinylbenzene) with sulfonic acid groups as catalytic active sites. [25]



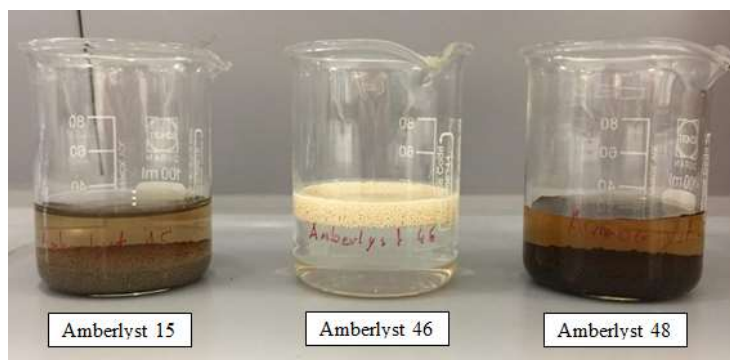
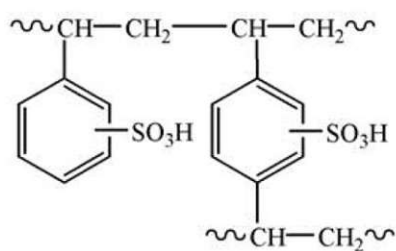


Figure 10: Schematic structure of Amberlyst resins, Figure taken from [25]

Figure 11: Amberlyst particles

#### 1.4.4 Reaction Kinetics

An esterification is a reversible reaction, which means that the forward reaction (esterification) and the back reaction (hydrolysis) occur simultaneously. The overall reaction rate is a function of the composition and temperature of a reactive system. The influence of the composition is characterized by the Langmuir-Hinshelwood (LH) mechanism with the chemical reaction at the catalyst surface as limiting step. In the Langmuir-Hinshelwood (LH) mechanism both reactants are transported from the bulk phase to the catalyst surface and adsorbed by the catalyst. Then, the reaction takes place at a catalytic site. The products are desorbed from the surface and transported into the bulk phase. [26]

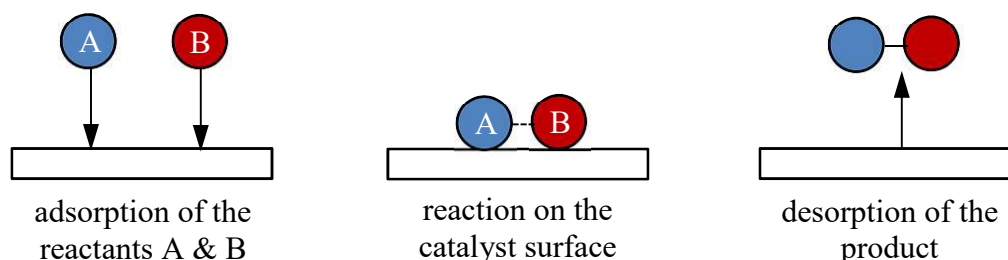


Figure 12: Langmuir-Hinshelwood mechanism, Figure based on [26]

The LH-model describes the catalysis more adequately than a pseudo-homogeneous model, because it considers the selective adsorption of the reactants. The components are adsorbed by the Amberlyst resin in descending order of selectivity: water > ethanol >> lactic acid > ethyl lactate. [22] The adsorption constants  $k_i$  are given in Table 4.

Table 4: Adsorption equilibrium constants of Amberlyst resins [22]

adsorption equilibrium constants $k_i$	
$k_W$	8.2421
$k_{EtOH}$	5.0193
$k_{EL}$	0.1270
$k_{Lac}$	0.5121

The reaction rate is characterized by Eq. 15: [22]

$$r = \frac{1}{m_{\text{cat}}} \frac{1}{v_i} \frac{dn_i}{dt} = \frac{k \left( a_{\text{Lac}} a_{\text{EtOH}} - \left( \frac{a_{\text{EL}} a_{\text{H}_2\text{O}}}{K} \right) \right)}{(1 + \sum_i k_i a_i)^2} \quad (\text{Eq. 15})$$

The temperature dependency of the reaction rate is described by the rate constant  $k$ . It is modelled by the Arrhenius-equation (Eq. 16).

$$k = k^0 \exp\left(-\frac{E_A}{RT}\right) \quad (\text{Eq. 16})$$

The activation energy  $E_A$  and the pre-exponential factor  $k^0$  are reaction-specific properties. The pre-exponential factor  $k^0$  is proportional to the frequency of molecular collisions of reactants. The activation energy  $E_A$  is the minimum amount of energy required of colliding reactant molecules for the reaction to take place. These parameters are evaluated in an Arrhenius plot. The Arrhenius equation is expressed in its linear form (Eq. 17) by applying the logarithm on both sides of Eq. 16.

$$\ln k = \ln k^0 + \left(-\frac{E_A}{R}\right) \frac{1}{T} \quad (\text{Eq. 17})$$

Rate constants are measured at different temperature levels. The logarithm of the rate constant  $\ln(k)$  is plotted over the reciprocal temperature  $1/T$ . The parameters are determined by a simple linear data regression.

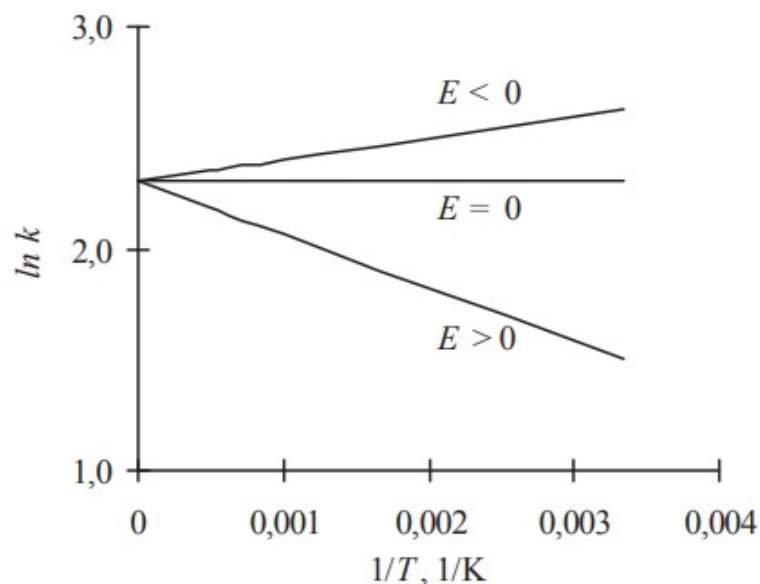


Figure 13: Example of an Arrhenius plot, Figure taken from [27]

In the absence of an external catalyst, the esterification is enhanced by lactic acid. The corresponding Arrhenius plot is shown in Fig. 12. The homogeneous reaction has a high activation energy of  $62.50 \text{ kJ mol}^{-1}$ . [22]

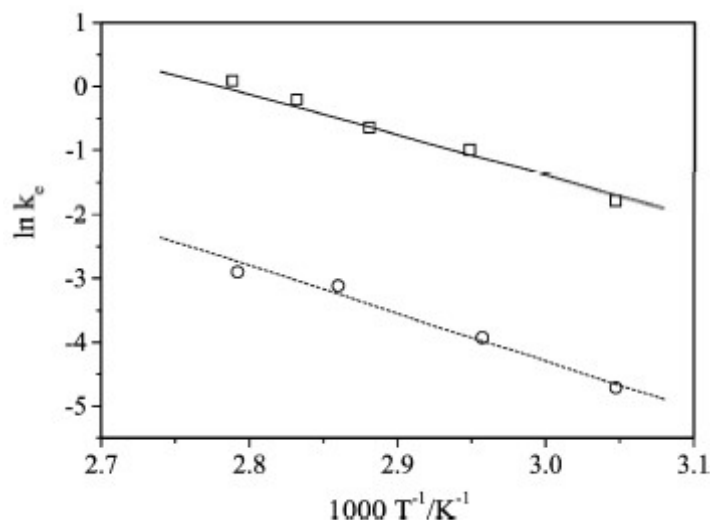


Figure 14: Arrhenius plot of the esterification of lactic acid with ethanol ( $n_{EtOH}/n_{Lac}=3$ ). homogeneous reaction (○), reaction catalysed by 2.5 w% Amberlyst 15 (□); Figure taken from [22]

No data on the reaction kinetics of ethyl lactate formation using Amberlyst 46 was found in literature. The kinetics was therefore evaluated experimentally in lab scale (see 2.3 Characterization of the Pilot Plant).

The esterification of lactic acid is very selective for ethyl lactate formation. Only small amounts of side products are formed, they are neglected in this work. Oligomerization can occur because of the bifunctional structure of lactic acid. [21] The intermolecular self-esterification of two lactic acid monomers is given in Figure 13 as an example of the many oligomerization reactions.

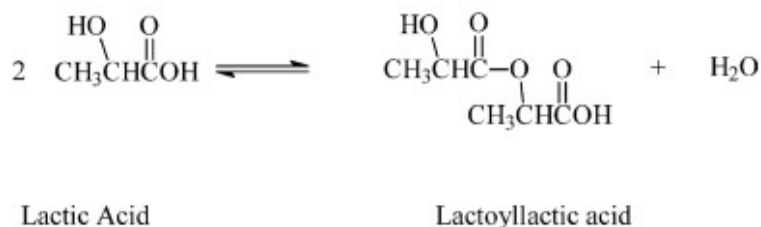


Figure 15: Intermolecular self-esterification of lactic acid monomers, Figure taken from [28]

The oligomer distribution of aqueous lactic acid solutions was studied over the full composition range by Vu et al. [28]. The molar composition of 80 w% lactic acid was calculated from this data: 58.3% water, 35.6% lactic acid monomers, 5.8% lactic acid dimers, 0.2% lactic acid trimers.

## 1.5 Vapour-Liquid-Equilibrium (VLE)

For a thermal separation operation the knowledge of the VLE is essential. The separation by distillation is based on the fact, that the composition of the vapour phase of a mixture is (in general) different than the corresponding liquid phase composition. Requirements for a vapour-liquid-equilibrium are the equilibrium conditions: equal temperature, pressure and fugacity of each component in both phases.

The criterion of equal fugacity for the general case of non-ideal vapour and liquid phase is modelled by Eq. 18.

$$f_{i,V} = \phi_i y_i p = f_{i,L} = \gamma_i x_i p_i^{\text{sat}} \phi_i^{\text{sat}} \quad (\text{Eq. 18})$$

The VLE of the quaternary system ethanol-lactic acid- water-ethyl lactate was studied by Delgado, Sanz and Beltrán. The Virial equation truncated after the second term was used to calculate the behaviour of the vapour phase (fugacity coefficients  $\phi_i$ ). The saturated vapour pressure of the pure components ( $p_i^{\text{sat}}$ ) was calculated by the Antoine equation. For the estimation of the activity coefficients ( $\gamma_i$ ) the UNIQUAC method was applied. [29]

The virial equation (Eq. 19) is an equation of state (EOS) for non-ideal gas phases. The first term is equivalent to the EOS for ideal gas, the other terms consider the deviation from ideal behaviour.

$$\frac{p}{RT} = \frac{1}{V_m} + \frac{B_{2V}(T)}{V_m^2} + \frac{B_{3V}(T)}{V_m^3} + \dots \quad (\text{Eq. 19})$$

The Antoine equation (Eq. 20) is used to calculate the vapour pressure of pure components as a function of temperature ( $\vartheta$  in °C).

$$\log_{10}(p_i^{\text{sat}}) = A - \frac{B}{\vartheta + C} \quad (\text{Eq. 20})$$

The UNIQUAC (universal quasi-chemical theory) method is an estimation method for activity coefficients. It consists of a combinatory part  $\gamma_C$ , which is a component specific value and a rest part  $\gamma_R$  which considers the molecular interaction forces. The rest part is obtained by fitting experimental data of binary mixtures. For a quaternary mixture 6 sets of binary interaction parameters are required. [30]

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (\text{Eq. 21})$$

Delgado, Sanz and Beltrán used the above model to evaluate the binary system water - ethyl lactate. They found a maximum pressure azeotrope at a low ethyl lactate mole fraction (about 6.5 mol% ethyl lactate). [29]

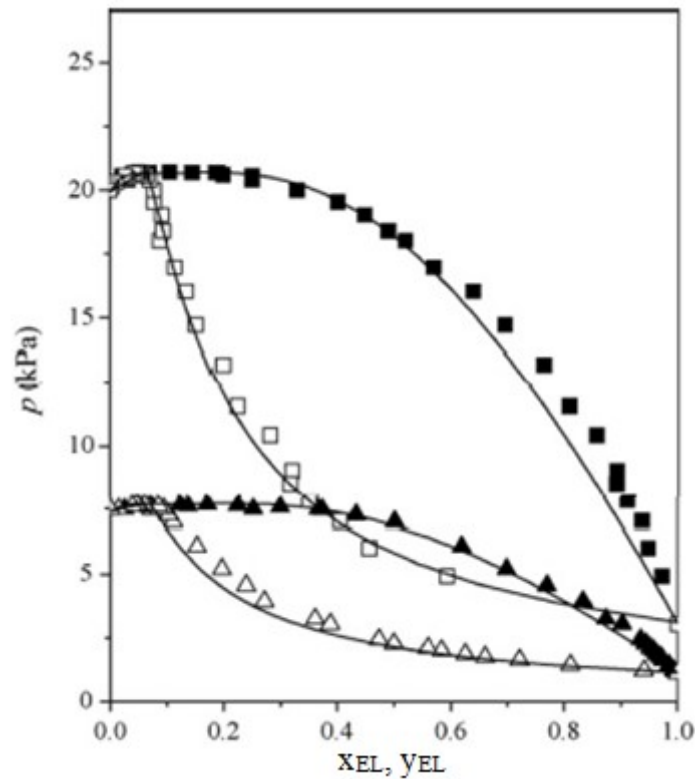


Figure 16: VLE of the binary system water - ethyl lactate, points: experimental data of [31] at 313 K (▲, △) and 333 K (■, □), lines: calculation of [29], Figure taken from [29]

The quaternary reactive mixture ethanol - lactic acid - ethyl lactate - water is a non-ideal system with 2 azeotropes. The boiling points of the pure components are listed in Tab 5, the azeotropes are characterized in Table 6.

Table 5: Boiling points and molar mass of the pure components [29]

	Ethanol	Lactic Acid	Ethyl Lactate	Water
boiling point $T_b$ (K)	351.44	490	427.65	373.15
molar mass $M$ ( $\text{g mol}^{-1}$ )	46	90	118	18

Table 6: Azeotropes of the quaternary system ethanol - lactic acid - ethyl lactate - water [31]

binary azeotropes	composition	temperature (K)
minimum boiling azeotrope	96 mol% ethanol, 4 mol% water	351.35
minimum boiling azeotrope	93.5 mol% water, 6.5 mol% ethyl lactate	not found

### 1.5.1 Phase Diagrams

Phase diagrams are a useful tool to evaluating separation operations. For binary systems a McCabe-Thiele diagram is used. For the graphical representation of quaternary reactive systems Barbosa and Doherty developed a concept of reactive phase diagrams. [32]

Rectification is the continuous counter-current distillation in a column. Most commonly a single feed stream is separated into a bottom and a top product. The conditions of the separation operation are adjusted to meet the predefined purity levels. The separation operation in a binary system is illustrated in a McCabe-Thiele diagram. The mole fraction of the lower boiling component in the vapour phase  $y$  is plotted over the mole fraction of the same component in the liquid phase  $x$ . For the equilibrium line VLE data is plotted. The operation lines are calculated from mass balances according to Eq. 22 and Eq. 23.

*Operation line of the enriching section:*

$$y = \frac{v}{1+v} x + \frac{1}{1+v} x_E \quad (\text{Eq. 22})$$

Where  $v$  is the reflux ratio of distillate and  $x_E$  is the mole fraction of the lower boiling component in the top product.

*Operation line of the intersection line (from the mass balance around the feed point):*

$$y = \frac{f}{f-1} x - \frac{1}{f-1} x_F \quad (\text{Eq. 23})$$

with the thermal factor  $f = 1 + \frac{\bar{H}_L - H_F}{\Delta h_v}$

$\bar{H}_L$  is the enthalpy of the liquid with feed composition at the boiling point,  $H_F$  is the enthalpy of the feed,  $\Delta h_v$  is the heat of vaporization and  $x_F$  is the mole fraction of the lower boiling component in the feed. The thermal factor  $f$  is used to consider the thermal state of the feed flux. For a liquid feed below the boiling temperature ( $f > 1$ ) the intersection line has a positive inclination.

*Operation line of the stripping section:*

The operating line for the stripping section is determined by the bottom product composition (characterized by  $x_S$ ) and the point of intersection of the other two lines.

The number of separation stages is determined by drawing the stages between the operating line and equilibrium line. The inclination of the line of the enriching section depends on the reflux ratio. The separation is intensified by increasing the reflux ratio. At total reflux the maximal separation capacity of a column is applied, which is represented in a McCabe-Thiele diagram as the maximal possible number of separation stages for a given device.

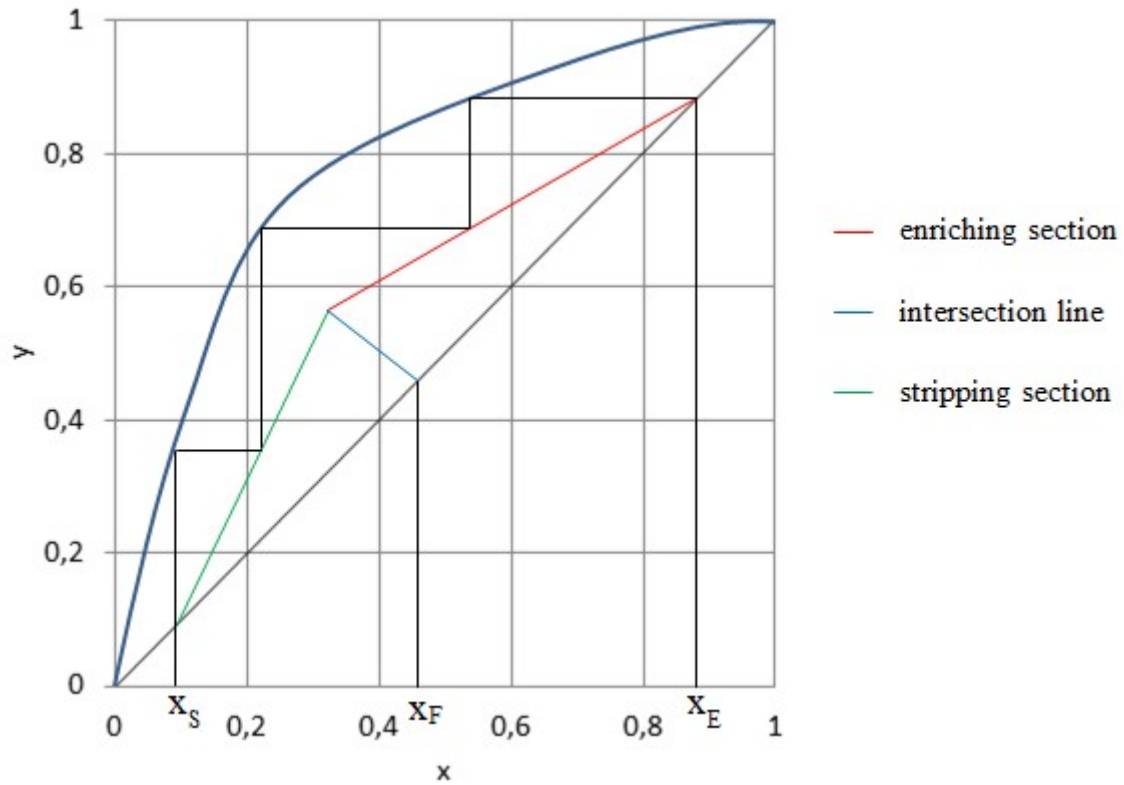


Figure 17: Example of a McCabe-Thiele diagram of a single-feed rectification, Figure based on [33]

Barbosa and Doherty developed a concept of reactive phase diagrams for the graphical representation of quaternary reactive systems. [32] A set of composition variables is defined by Eq. 24 and Eq. 25. One component  $k$  is used as a reference component.

$$X_i = \frac{\frac{x_i}{v_i} - \frac{x_k}{v_k}}{v_k - x_k \left( \sum_{j=1}^c v_j \right)} \quad \begin{array}{l} i = 1, \dots, c \\ i \neq k \end{array} \quad (\text{Eq. 24})$$

$$Y_i = \frac{\frac{y_i}{v_i} - \frac{y_k}{v_k}}{v_k - y_k \left( \sum_{j=1}^c v_j \right)} \quad (\text{Eq. 25})$$

The composition of a mixture is defined by a pair of these parameters. Each state of thermodynamic equilibrium is represented by a point on the liquid surface of the diagram, which fulfils the chemical equilibrium and the corresponding point on the vapour surface, which is in VLE with it. An example of a reactive phase diagram is shown in Fig 16. The vertical axis represents the temperature. For each temperature there is a horizontal composition plane in the diagram. Non-reactive mixtures are located at the outer sides.



Corners represent pure components and the outer planes represent non-reactive binary systems.

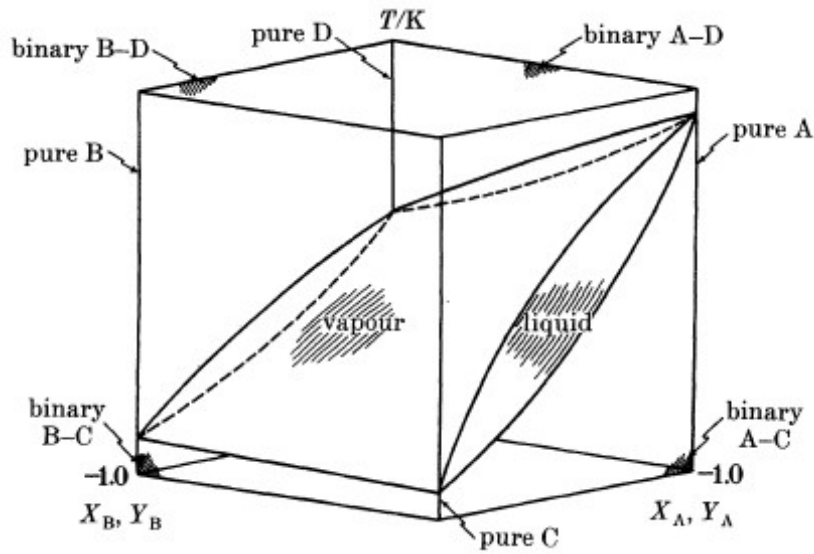


Figure 18: Example of the reactive phase diagram of an ideal quaternary system, Figure taken from [32]

The criterion for reactive azeotropes and pure components is given in Eq. 26.

$$X_i = Y_i \quad (\text{Eq. 26})$$

At the point for a reactive azeotrope the vapour and liquid plane meet tangentially.

The concept of Barbosa and Doherty was applied to the quaternary system ethanol - lactic acid - ethyl lactate - water by Delgado, Sanz and Beltrán. Ethanol was used as the reference component in Eq. 24 and Eq. 25. The used indices are listed in Table 7.

Table 7: Explanation of the used indices

species index	component
k, 1	ethanol
2	water
3	ethyl lactate
4	lactic acid

$$X_2 = -x_2 - x_1$$

$$X_3 = -x_3 - x_1$$

$$X_4 = x_4 - x_1$$

$$Y_2 = -y_2 - y_1$$

$$Y_3 = -y_3 - y_1$$

$$Y_4 = y_4 - y_1$$



The obtained reactive phase diagram is shown in Fig. 17. No reactive azeotrope occurs in this system. [29]

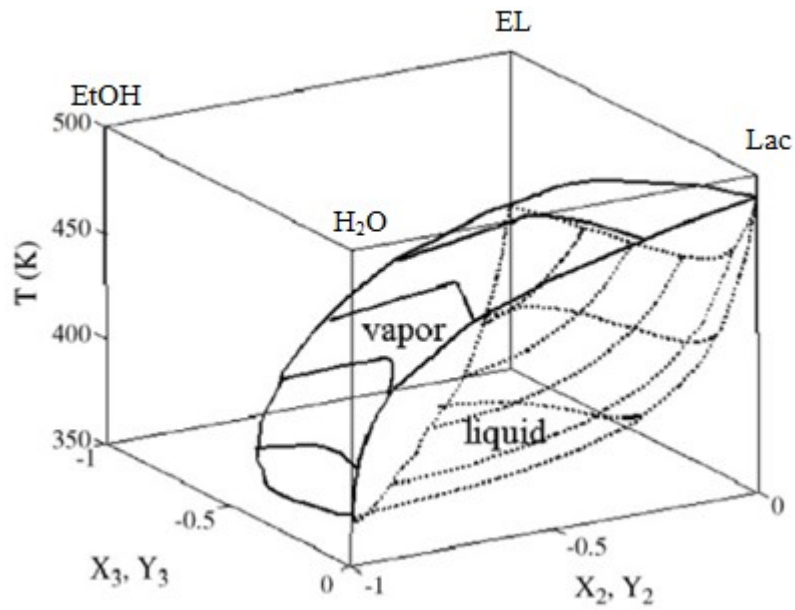


Figure 19: Reactive-phase diagram for the quaternary system ethanol - lactic acid - ethyl lactate - water at 101.325 kPa, Figure taken from [29]

## 1.6 Reactive Distillation (RD)

Reactive distillation is a process that combines a chemical reaction with the simultaneous separation of components by rectification in a single device. It is therefore a highly integrated process, which offers significant advantages for reactive systems with beneficial parameters, but also causes difficulties in the design and operation of reactive distillation plants due to their high complexity.

The mayor benefit of reactive distillation for equilibrium limited chemical reaction systems is the effect of process intensification. By constantly removing a side product, the equilibrium limitation of batch reactors can be overcome, because the chemical equilibrium gets re-established following the law of mass action. The products are continuously transported out of the reactive zone to ensure high reactant concentrations. By this, the driving force for the chemical reaction is retained at a high level. Raised reactant conversion can be reached with close to stoichiometric input streams, whereas conventional batch operations often require a large excess of one of the reactants. In some cases even 100% conversion can be achieved by reactive distillation.

RD-devices are very compact and therefore the investment costs can be lower, compared to conventional reactors with subsequent separation operations. [34] However, the feasibility of reactive distillation is limited to relatively few applications, because chemical reaction and separation by rectification have to be effective at the same operation conditions. The chemical reaction has to be fast enough to reach sufficient reactant conversion at a temperature level that is suitable for the distillation operation. Appropriate volatilities of the components are necessary for the separation via rectification. The complex interactions of mass and heat transfer, the chemical reaction and fluid dynamics make process simulation and scale up procedures complicated. In many cases the experimental approach is reasonable to verify accurate modelling assumptions and determine optimal operation conditions.

To reach sufficient reactant conversion within the column, the residence time distribution in the catalytic zone has to be taken into account for the design and operation of RD plants. If heterogeneous catalysis is used, the content of the catalyst in the RD column is limited, so an effective catalyst with a high density of reactive sites is required. The accessibility of the catalytic sites for the reactants has to be ensured by convenient flow conditions. Therefore, the liquid load in the column packings is important.

For heterogeneously catalysed RD devices special column packings are used. One of the most common packings, Katapak-SP was used in this work. It consists of Mellapak separation packings and catalytic layers, that contain the catalyst in metal wire pockets.

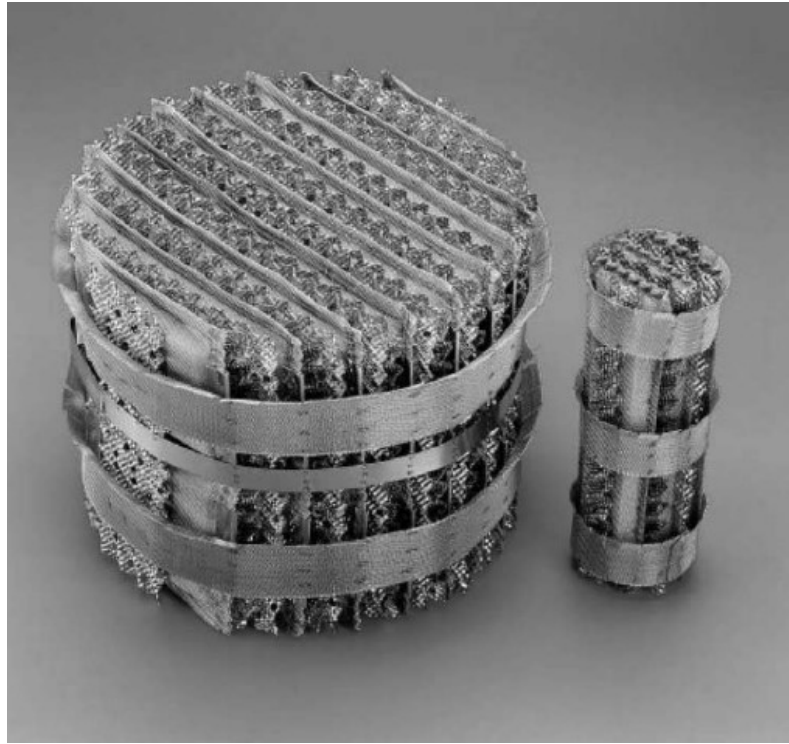


Figure 20: Industrial and lab scale Katapak-SP 12 packing, Figure taken from [35]

### 1.6.1 Liquid Phase Residence Time Distribution (RTD)

For chemical reactors the residence time distribution (RTD) of the reactants is an important factor. By measuring the RTD of a reactor, it is evaluated how much time is available for the chemical reaction to proceed. The residence time distribution RTD (also “exit age distribution”)  $E(t)$  is the distribution of the time needed by fluid particles to pass a chemical reactor. A variation of residence times occurs, because the particles take different paths through the reactor.  $E(t)$  is normalized and of the dimension  $\text{time}^{-1}$ . [36]

$$\int_0^{\infty} E \, dt = 1 \quad (\text{Eq. 27})$$

$E(t)$  is determined by applying the tracer pulse method. A non-reactive substance, which can be measured quantitatively, is issued as a pulse at the entrance section of the reactor. The

concentration of tracer is continuously measured as a response function at the exit section. Eq. 28 is used to normalize the measured concentration: [36]

$$E = \frac{c_{\text{exit}}}{m_{\text{tracer}}/\dot{V}_L} \quad (\text{Eq. 28})$$

$c_{\text{exit}}$  is the concentration of tracer measured at the exit section,  $m_{\text{tracer}}$  is the total amount of issued tracer and  $\dot{V}_L$  is the flow rate through the reactor. The mean residence time  $\tau$  is calculated from  $E(t)$  by Eq. 29. [36]

$$\tau = \int_0^{\infty} t E(t) dt \quad (\text{Eq. 29})$$

In the case of ethyl lactate production, lactic acid is the time limiting component. It does not get evaporated in the experimental setup, so it flows through the column in the liquid phase. In Katapak-SP packings the vapour loading has almost no influence on the liquid phase RTD, as long as it is below the flooding point. The dominating influence parameter is the liquid load. Three flow regimes can be distinguished (as shown in Fig. 19): [37]

1) liquid load below the catalytic load point:

The catalyst pockets are not entirely filled with liquid. The RTD is wide, shows pronounced tailing and a high mean residence time  $t_m$ . This is because of stagnant zones within the column.

2) Liquid load about the catalytic load point:

The pockets are completely filled with flowing liquid. The RTD has minimal variance and tailing is significantly reduced.

3) Liquid load above the catalytic load point:

The RTD is broad because of by-passing liquid that flows outside of the catalyst filled pockets.

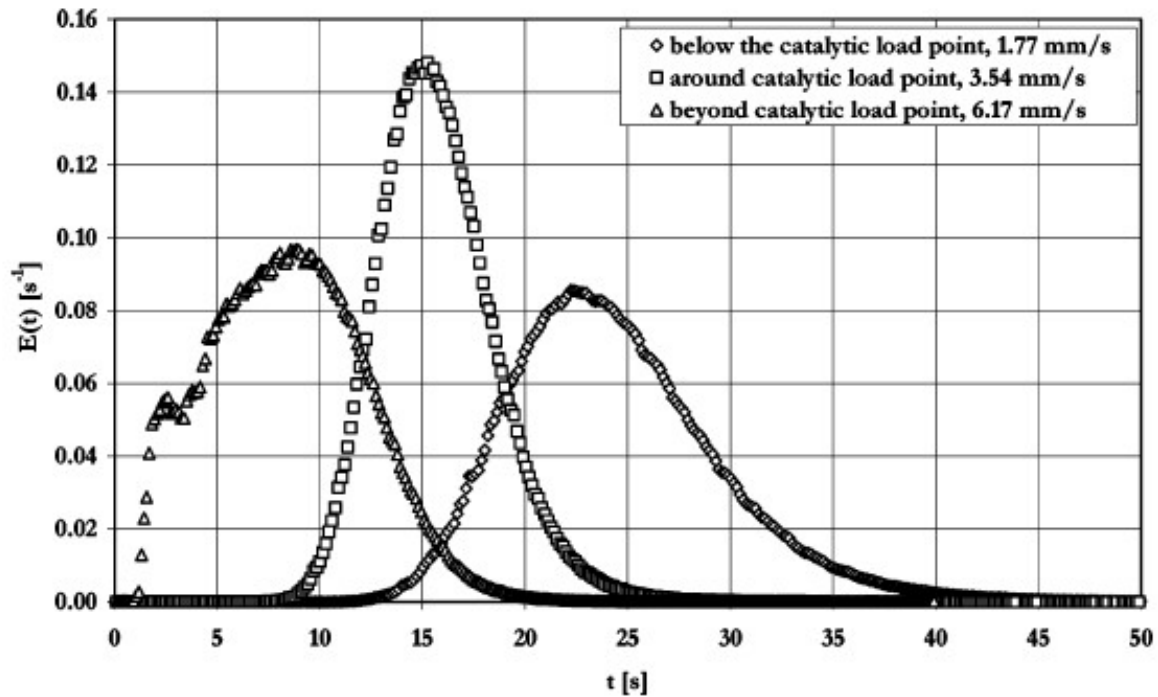


Figure 21: RTD of Katapak-SP 12 at different liquid loads, Figure taken from [38]

The liquid load point of the used pilot plant column was estimated by transferring the experimental results of [35] to the column diameter DN 50 mm. Götze found, that for a Katapak-SP 12 packing with DN 250 mm the liquid load point was about  $10 \text{ m}^3/\text{m}^2\text{h}$ . For the column used in this work this equals a liquid volume flow rate of:

$$\dot{V}_L = 10 \frac{\text{m}^3}{\text{m}^2\text{h}} \cdot (0.05 \text{ m})^2 \cdot \frac{\pi}{4} = 19.6 \frac{\text{L}}{\text{h}}$$

The optimal operation performance of a Katapak-SP packing is expected at a liquid load just above the liquid load point, so the catalyst is used optimally and no liquid back-mixing or flooding occurs. [38]

### 1.6.2 Degree of Freedom Analysis

A degree of freedom analysis was done for the reactive distillation plant. The degree of freedom is the number of independent variables that have to be set to obtain a well-defined operation point of a system. It is calculated from the number of independent stream variables  $V$ , the number of independent chemical reaction  $R$  and the number of constrains  $C$ .

$$\text{DOF} = V + R - S \tag{Eq. 30}$$

Stream variables are values that define input and output streams (flow rate, composition, energy variables). Constrains are either correlations between the stream variables (balances, stoichiometric relations, etc.), or process parameters that are defined by the operator.[39]

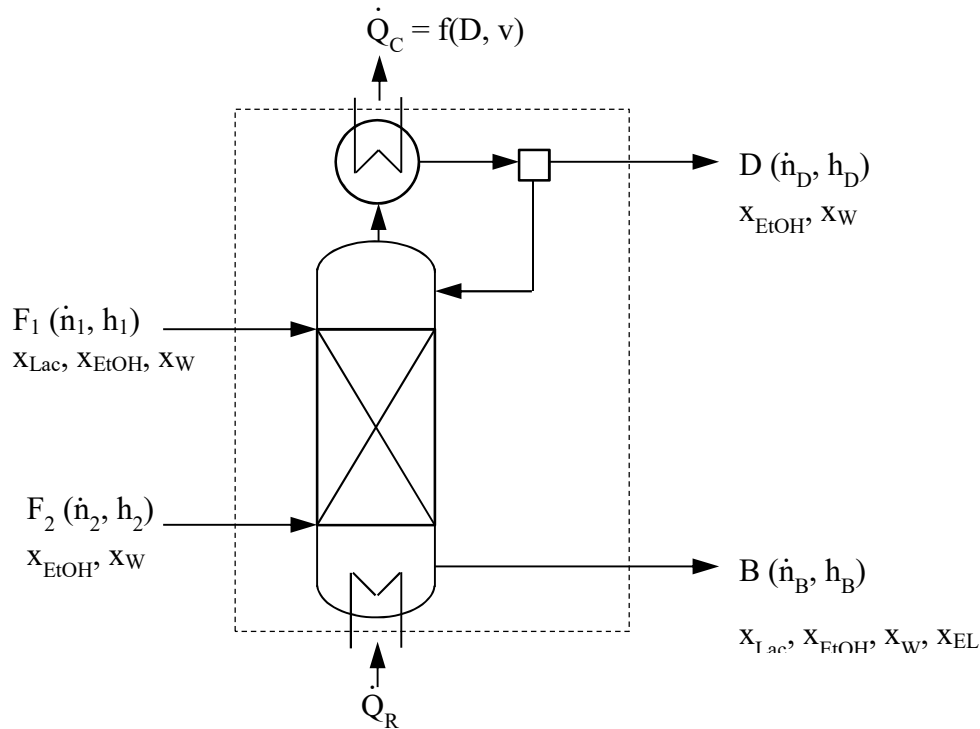


Figure 22: Simplified flow chart of the reactive distillation device

The following 17 independent variables exist in the system:

- 4 material fluxes ( $F_1$ ,  $F_2$ ,  $D$ ,  $B$ )
- 7 independent mole fractions
- 5 energy variables (4 enthalpies of fluxes, reboiler duty  $Q_R$ )
- 1 system variable (reflux ratio  $v$ )

One reaction is considered (the esterification reaction).

The following 9 equations describe the system:

- 4 material balances
- 1 energy balance
- 1 correlation for the temperature of the top product
- 1 stoichiometric correlation
- 2 correlations characterising the separation behaviour (splitting of the total output fluxes, separation of the components)

There are 4 additional constrains:

- 2 feed temperatures are pre-defined
- 2 constrains of feed compositions (The ethanol feed purity and the water content in feed mixture F1 is a result of the used input chemicals.)

The degrees of freedom were calculated using Eq. 30:

$$\text{DOF} = V + R - S = 17 + 1 - 13 = 5$$

Five parameters have to be determined to define an operation point:

- the molar ratio of ethanol and lactic acid ( $n_{\text{EtOH}}/n_{\text{Lac}}$ ) in the feed F1
- the two feed rates
- the reflux ratio and the reboiler duty

The ethanol feed rate was adjusted in such a way, that a constant molar ratio of ethanol and lactic acid ( $n_{\text{EtOH}}/n_{\text{Lac}}$ ) in the bottom product was ensured.

### 1.6.3 Material Balances

In a reactive distillation device the composition of the outlet fluxes is not only a result of mass and heat transfer, but also of the chemical reactions. Therefore, the material balances are formed on a molar base. The overall mass balance is the same as for a conventional rectification with two feed streams:

$$F_1 + F_2 - D - B = 0 \quad (\text{Eq. 31})$$

The component balance for component i is:

$$x_{i,F1} \cdot F_1 + x_{i,F2} \cdot F_2 - x_{i,D} \cdot D - x_{i,B} \cdot B = \Delta n_{i,r} \quad (\text{Eq. 32})$$

$$\text{with } x_{\text{EL},F2} = x_{\text{Lac},F2} = x_{\text{EL},D} = x_{\text{Lac},D} = 0$$

Neither lactic acid, nor ethyl lactate are vaporized in the plant. A balance for the lactic acid equivalents (sum of lactic acid and ethyl lactate molar fluxes) considers all components that only occur in the liquid phase.

$$Eq_{\text{Lac},F1} - Eq_{\text{Lac},B} = 0 \quad (\text{Eq. 33})$$

A mismatch of the lactic acid equivalents would lead to the accumulation or depletion of lactic acid in the reboiler vessel. Therefore, the lactic acid equivalents in the feed F1 and the bottom product have to be balanced for a steady state operation of the column.

### 1.6.4 Comparison of the Production of Ethyl Lactate and Methyl Acetate

One of the most successful examples of reactive distillation processes is the Eastman-Kodak process for the production of methyl acetate. A synthesis that needed eight distillation columns in the conventional process is now done in a single reactive distillation column, consuming five times less energy and having five times lower investment costs. [34]

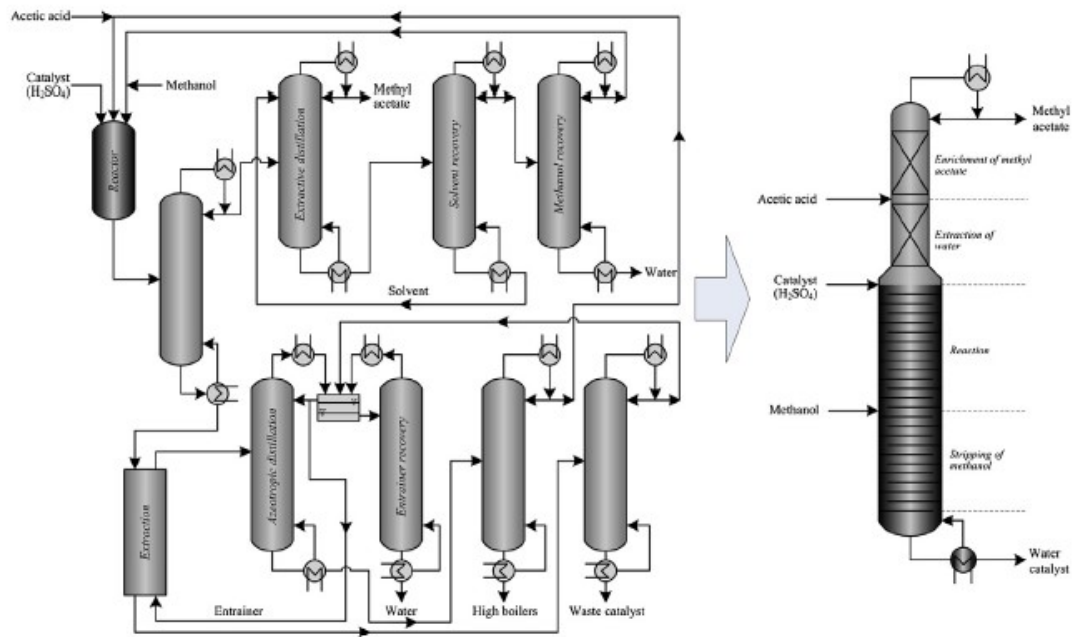


Figure 23: Conventional process (left) and intensified process using reactive distillation (right) for methyl acetate production, Figure taken from [34]

Compared to this system, the ethyl lactate production shows some important restrictions:

- Ethyl lactate has a higher boiling point than water and therefore, is obtained in the bottom product. In contrast, methyl acetate has a lower boiling point than water, so it is gained as top product.
- The Eastman-Kodak process uses sulfuric acid as homogenous catalyst, so the catalytic activity can be tuned and adjusted to ensure high reaction rates and high conversion in the reactive zone. Ethyl lactate production was performed using a heterogeneous catalyst in order to avoid an additional separation task from ethyl lactate in the bottom product. The heterogeneous catalysis is less flexible concerning the catalyst activity and requires a certain liquid load in the column to ensure the contact of the reactants to the catalytic surface.



- Methyl acetate can be enriched by adjusting the reflux ratio. A higher reflux ratio leads to enhanced product purity. In the ethyl lactate production process water has to be stripped to the top product by ethanol. The reflux of top product into the column would lead to the enrichment of ethanol and thus, reduces the separation efficiency. However an operation without reflux requires a high feed rate of ethanol and lead to high amounts of top product, which have to be treated in an additional separation operation to recover ethanol.
- In both reactive systems two azeotropes occur, that influence the operation procedure.

In the Eastman-Kodak process these are:

- methyl acetate/water: this azeotrope can be overcome by the extraction of water with acetic acid
- methyl acetate/methanol: the azeotrope mixture can be avoided by full conversion of methanol in the reactive zone

For the production of ethyl lactate these are:

- water/ethanol: irrelevant for the esterification process because water contents should be much higher, however, it complicates the recovery of ethanol from the top product
- ethyl lactate/water: leads to losses of ethyl lactate to the top product

## 2 Experimental Setup

The experimental setup used in this work is the pilot scale reactive distillation plant illustrated in Fig. 22. The main part is a double-walled column with DN 50, which consists of three sections: non-reactive structured packings (Mellapak from Sulzer) for separation at the top and the lower part of the column, and a catalytic packing in the middle part of the column. The packing in the reactive zone is a Katapak-SP<sup>TM</sup> 12 packing that combines catalyst filled pockets with Mellapak<sup>TM</sup> segments for separation. Amberlyst 46 cation-exchange resin is used as a heterogeneous catalyst for the esterification reaction.

The higher-boiling reactant lactic acid is fed above the catalytic column section (F1), whereas the lower-boiling reactant ethanol is fed just below the catalytic zone (F2). The esterification reaction occurs at the catalysts surface forming ethyl lactate as a product and water as a side product. The rectification process should separate ethyl lactate in the bottom product (B) from excess ethanol and water, which are supposed to be removed at the top of the column (D).

Membrane pumps (ProMinent gamma/L with pressure retention valve, maximum pumping capacity: 16.9 L/h) are used to feed the reactants into the column. For the bottom product a gear pump (Ismatec REGLO-Z, maximal capacity: 12.5 L/h) is used. The top and bottom product are cooled in helical coil coolers and then, flow into round bottom collecting flasks with a volume of 4 L each. Two electrical heaters with a maximal total heat duty of 3 kW are located in the reboiler vessel. The plant is equipped with additional heaters for pre-heating of the feed streams (maximal heating power: 250 W each). The reflux ratio of the column is set by a reflux separator. A water cooling system supplies cooling water for the condenser and the product coolers.

The following experimental parameters were used for the process optimization:

- reflux ratio
- reboiler duty
- lactic acid feed rate
- ethanol feed rate
- pre-heating of feed F2 (ethanol)
- feed composition

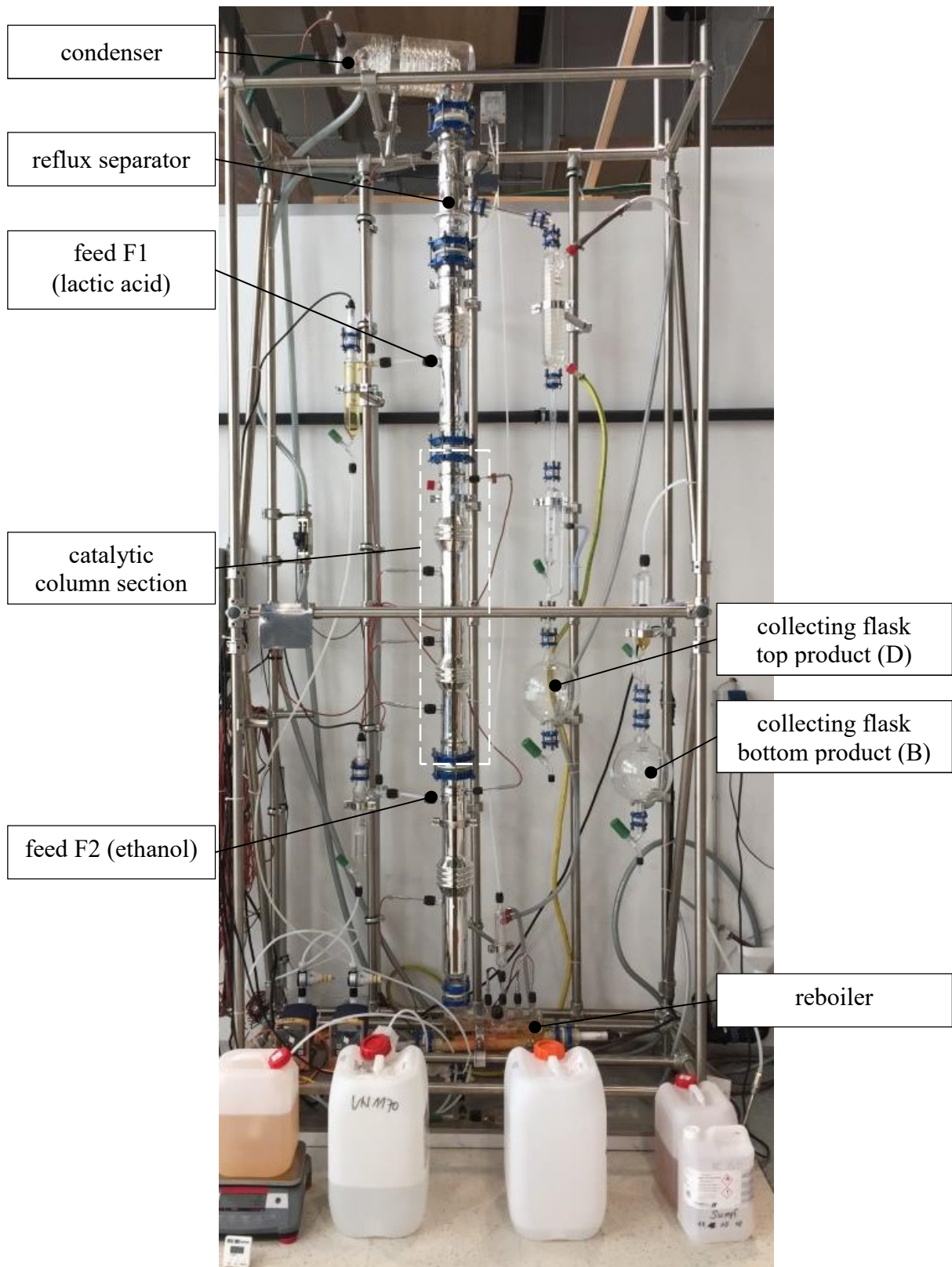


Figure 24: Experimental setup: reactive distillation plant

The plant is controlled by a central operating system that runs on LabView on a PC. The settings for the pumps, the pre-heater, the reflux ratio and the reboiler duty are set using the operating system. The pressure drop and the temperature profile of the column are displayed



## 2.1 Analytics

Samples of reactive mixtures were cooled to room temperature immediately when they were taken, collected for each experiment and stored in a fridge at approx. 300 K until the analysis was started. The composition of bottom product samples was analysed offline by the project partner “Kompetenzzentrum Holz GmbH”, using HPLC-methods. Lactic acid and ethyl lactate were detected by an UV-sensor, ethanol was measured by an RID-sensor (refractive index). The content of oligomers was considered negligible. The water content could not be measured.

The top product was considered a binary mixture of ethanol and water. The composition of these samples was determined by density measurements, using a table from literature[40]. All density measurements were done at-line with an oscillating u-tube density-meter (DMA 35 from Anton Paar GmbH), illustrated in Fig. 26. For some samples, a HPLC-analysis was done to measure the ethyl lactate content. While it was less than 1 w%, the density method was applied and the resulting error was considered tolerable.

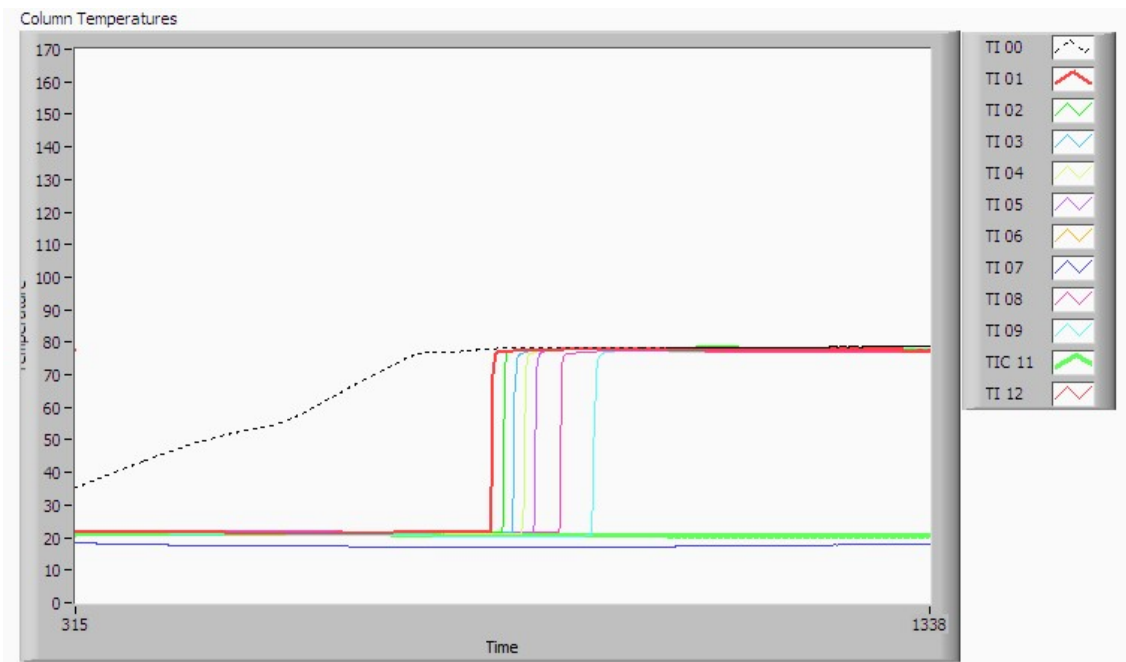


Figure 26: Handheld oscillating u-tube density meter (DMA 35 from Anton Paar GmbH)

## 2.2 Starting procedure

Before an operation point of the plant could be set, the starting procedure had to be done in every experiment. Firstly, the reboiler has to be filled with the starting mixture to a level between the minimum and maximum. The water circuit for all coolers is activated and the electrical switches are turned on before activating the operating system on the PC. The heating-up has to be executed slowly, to ensure an even heating of the glass parts. The reflux ratio is set to total reflux until the temperature profile is fully developed, which can be observed on-line at the operating system. Seven PT100-temperature sensors are distributed over the height of the column. As soon as the rising vapour reaches a sensor, this is indicated by a marked step of the corresponding temperature.





*Figure 27: Development of the temperature profile when heating up the column*

When approaching an operation point of the column, special attention has to be given to the overall mass balance, which is a requirement for a steady state operation. This was done by adjusting the flow rate of the bottom product. When the overall mass balance was closed, a continuous steady state operation point was reached after about 0.5-4 hours, depending on the composition of the starting mixture and the liquid throughput.

At the start of this work no accurate relation between the pump settings and mass fluxes was known. The determination of such a correlation for the membrane feed pumps was difficult, because these pumps are guaranteed to work reproducible at 30-100% of the total pump capacity. However, most of the experiments required lower feed fluxes, which led to less reliable data prediction (especially when using 80 w% lactic acid). Although data from all experiments was collected and evaluated after each run, the correlation taken from linear data regression only offered a rough estimation for the feed fluxes. It was important to purge the feed lines thoroughly, because bubbles in the line reduced the attained flux significantly. The pump settings were adjusted during starting up each experiment, to ensure accurate values. This problem did not arise for the bottom product pump, because the gear pump operated reproducible over the whole capacity range.

## 2.3 Characterization of the Pilot Plant

A characterization of the experimental setup was done to individually examine its behaviour concerning:

- 1) the separation behaviour of the packed column
- 2) The fluid dynamics and liquid RTD in the column
- 3) the catalysis of the esterification reaction

### 2.3.1 Separation Behaviour

It is crucial to the reactive distillation operation, that the side product water is separated from the product ethyl lactate and that both products are transported out of the reactive zone of the column. As discussed before, ethyl lactate (the higher boiling product) is not expected to be vaporized at the temperature level within the column and is therefore separated with the bottom product. For a successful reactive distillation operation, water (the lower boiling product) has to be removed with the top product.

A restriction to this separation task is that the reactant ethanol is the lowest boiling component in the quaternary system. Increased the reflux ratio would lead to an enhanced concentration of ethanol in the top product, retaining water within the column. Therefore, the separation behaviour of the packed column was evaluated to determine the maximal feasible reflux ratio  $v$ , at which the removal of water from the reactive zone is still achieved. Experiments were carried out with the non-reactive binary system water-ethanol.

#### Preliminary Experiment 1:

In this experiment the column was used as a conventional non-reactive rectification column. A binary mixture of 33.5 w% ethanol and 66.5 w% water was used as starting mixture in the reboiler and the single feed at position F2 had the same composition. The reboiler duty was 900 W, all other settings and results are listed in Tab. 8.

The overall mass balance was closed satisfactorily for most of the set-points. The component balances showed high errors, because the experiment did not last long enough to reach the stationary composition profile of the column. The ethanol content of the bottom product decreased during the whole experiment, so ethanol was transported out of the column in a transient process. However, the composition of the top product showed only little variation over time. The data indicates that a reflux ratio below 0.3 would be required to potentially implement the water removal, which is needed for the RD operation.

Table 8: Experimental results for the separation behaviour, Preliminary Experiment 1

reflux ratio $v$ (-)	total	3	1	0.3	0.2	0
feed rate (kg/h)	-	2.2	2.2	2.7	2.7	2.7
distillate rate (kg/h)	-	0.2	0.6	1.2	1.5	1.5
bottom rate (kg/h)	-	1.9	1.5	0.8	0.8	0.9
total (kg/h) and relative (%) error of the overall mass balance	-	0.06 (3%)	0.15 (7%)	0.66 (24%)	0.43 (16%)	0.27 (10%)
ethanol weight fraction top product	0.915	0.935	0.915	0.920	0.840	0.800
ethanol weight fraction bottom product	-	0.325	0.305	0.285	0.165	0.100
total (kg/h) and relative (%) error of the ethanol balance	-	0.09 (12%)	0.24 (33%)	0.45 (50%)	0.45 (50%)	0.39 (43%)

#### Preliminary Experiment 2:

In this preliminary experiment it was tested, if the rising vapour phase was able to absorb additional water in the catalytic zone. The experiment was set up as a rectification with two feed streams. Ethanol (95 w%) was added at the lower feed position (F2). Water of the lactic acid feed stream and the esterification reaction was simulated by adding a constant stream of demineralized water at the upper feed position (F1). Reference values for the input streams were taken from runs of a previous project. [20] The amount of water that has to be removed from the column was calculated as follows:

- water of the lactic acid input stream:

$$\dot{m}_{W,F1} = \dot{m}_{F1} \cdot w_{W,F1} = 1.1 \text{ kg/h} \cdot 20 \text{ w\%} = 0.220 \text{ kg/h}$$

- Maximal possibly amount of water produced in the chemical reaction (calculated for 100% lactic acid conversion):

$$\Delta \dot{m}_{W,r} = \dot{m}_{F1} \cdot w_{Lac,F1} \cdot \frac{M_W}{M_{Lac}} = 1.1 \text{ kg/h} \cdot 80 \text{ w\%} \cdot \frac{18 \text{ g/mol}}{90 \text{ g/mol}} = 0.176 \text{ kg/h}$$

Total mass flux of water that has to be stripped by ethanol:

$$\Delta \dot{m}_W = \dot{m}_{W,F1} + \Delta \dot{m}_{W,r} = 0.416 \text{ kg/h}$$



This obtained value was considered a minimal amount for the experiment. To apply a liquid load and RTD similar to that of earlier experiments at the plant, a mass flux of 1.056 kg/h water was used.

*Table 9: Experimental results for the separation behaviour, Preliminary Experiment 2*

reflux ratio $v$ (-)	0	0.2
water feed rate $F_1$ (kg/h)	1.056	1.056
ethanol feed rate $F_2$ (kg/h)	5	5
distillate rate (kg/h)	1.25	1.25
bottom rate (kg/h)	6.7	6.4
total (kg/h) and relative (%) error of the overall mass balance	2.1 (37%)	1.8 (31%)
ethanol weight fraction top product	0.71	0.75
ethanol weight fraction bottom product	0.45	0.60

For this experiment the same settings as before were applied for the ethanol feed pump, but about double of the intended value (2.3 kg/h) was pumped. This led to a high error in the overall mass balance, so component balances could not be successfully evaluated. The measured composition of the top product indicates that a sufficient amount of water could be removed from the column, if a low reflux ratio  $v$  is applied.

### Preliminary Experiment 3:

Part of the preliminary experiment 1 was repeated until the steady state composition was reached. The set-point without reflux was evaluated, operating the plant in a continuous distillation. A single feed of 35 w% ethanol was used. The reboiler duty was 900 W.

Table 10: Experimental results for the separation behaviour, Preliminary Experiment 3

reflux ratio $v$ (-)	0
feed rate (kg/h)	1.644
distillate rate (kg/h)	0.803
bottom rate (kg/h)	0.873
total (kg/h) and relative (%) error of the overall mass balance	0.032 (2%)
ethanol weight fraction top product	0.65
ethanol weight fraction bottom product	0.015
total (kg/h) and relative (%) error of the ethanol balance	0.032 (6%)

In this experiment the overall mass balance and the component mass balances were closed with a small error <10%. The operation point was evaluated in a McCabe-Thiele plot in Fig. 28. The line of the enriching section is horizontal, because no reflux is applied. To determine the equation of the intersection line, the caloric factor of the feed  $f$  was calculated using material properties from Table 11.

Table 11: Material properties of ethanol and water, data from NIST Chemical WebBook[41]

component	heat capacity $c_p$ (kJ/kgK)	enthalpy of evaporation $\Delta h_v$ (kJ/kg)
ethanol	2.4	997
water	4.2	2280

$$f = 1 + \frac{c_p \Delta T}{\Delta h_v} = 1 + \frac{(35\% \cdot 2.4 + 65\% \cdot 4.2) \frac{\text{kJ}}{\text{kg K}} (80 - 20)\text{K}}{(35\% \cdot 997 + 65\% \cdot 2280) \frac{\text{kJ}}{\text{kg}}} = 1.1$$

Using the caloric factor  $f$ , the equation for the intersection line is:

$$y = \frac{f}{1-f} x - \frac{1}{1-f} x_F = 9.6 x - 1.5$$

In the enrichment zone no separation of the mixture occurs, whereas in the stripping section a counter-current flow occurs and separation takes place. Three theoretical separation steps are expected in this zone. The enrichment of ethanol in this zone is not expected to be a problem for reactive distillation operation, because water is neither transported to the catalytic zone, nor retained there by this effect.

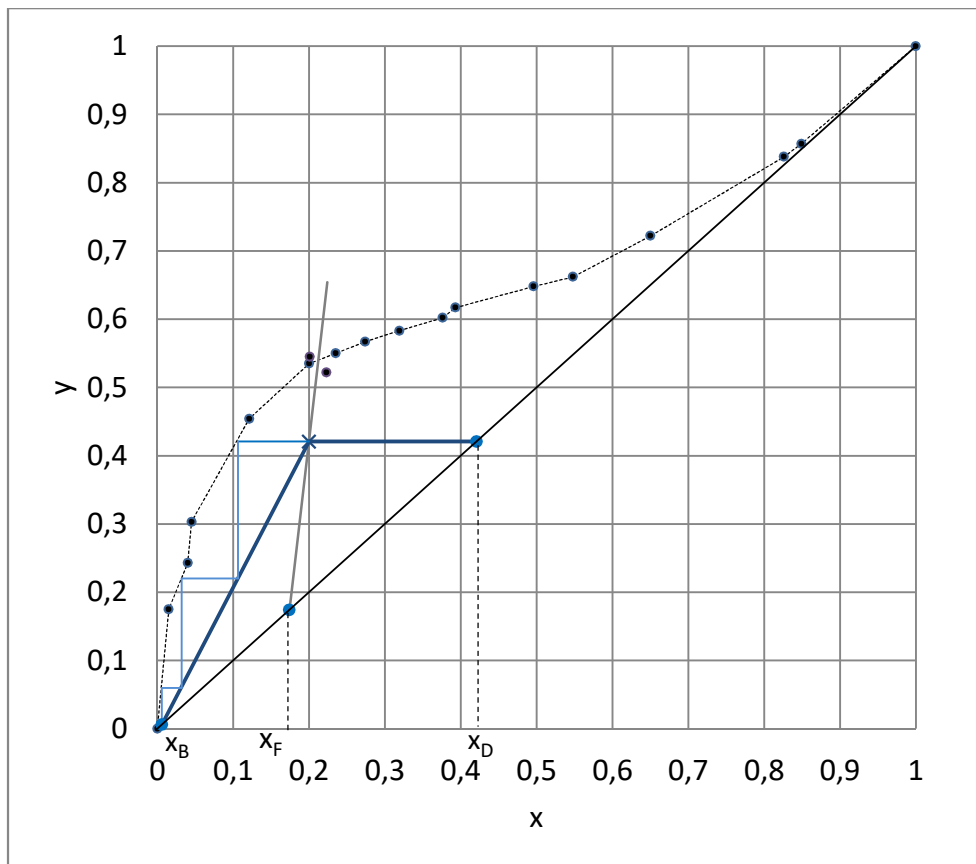


Figure 28: McCabe-Thiele plot of an operation point without reflux

Concerning the separation behaviour, the reactive distillation operation seems to be possible in the pilot plant. Yet, it is at the limit of the operation window. It should be stressed, that the separation operation needed for the process is contrary to the principle of rectification. The separation operation can be considered a stripping process with ethanol as stripping agent for water, rather than a rectification (counter-current distillation). This is in accordance to results of Asthana et al. [42].

### 2.3.2 Liquid Phase Residence Time Distribution (RTD) of the Column

To reach sufficient reactant conversion in the column, the RTD in the catalytic zone has to be taken into account and the accessibility of the catalytic sites for the reactants has to be ensured by convenient flow conditions. As discussed in the fundamentals, the liquid load is the dominating influence parameter on the RTD and flow behaviour in Katapak-SP packings. For the column used in this work, a liquid load point of 19.6 L/h was calculated in the fundamentals section (1.6.1 Liquid phase RTD).

The tracer method was used to evaluate the RTD behaviour of the column. Experiments at three different liquid loads were accomplished - all of them were below the liquid load point of the column, because the experimental setup is limited to a maximum pumping capacity of 12.5 L/h (64% of the calculated value for the liquid load point). All experiments were done at ambient temperature with no external gas phase flow, using lactic acid (80 w% aqueous solution) as a tracer in water as continuous liquid phase. The tracer concentration was measured by a handheld conductivity meter (HI-8033 Handheld EC Meter from Hanna Instruments GmbH). The non-linear correlation between lactic acid concentration and conductivity was determined from solutions with certain tracer concentration. The calibration curve is given in Appendix.

Before and after each run, the column was rinsed with demineralised water until the measured conductivity descended below 25  $\mu\text{S}$ . In a first attempt to detect the tracer, the sensor was held directly into the reboiler vessel. However, this method failed because short circuiting occurred. Liquid coming from the column passed through the reboiler vessel directly into the line of the bottom product. Therefore, discrete samples were taken from the bottom product collecting flask. The liquid in the reboiler was filled to a very low level of about 200 mL in order to reinforce the effect of short circuiting, and thereby diminishing the error by changing the sampling point. Demineralised water was pumped continuously through the column at certain liquid loads. The tracer was injected as a short pulse from a syringe just above the catalytic section of the packed column (as shown in Fig. 29). Samples of about 50 mL were taken from the bottom product in certain intervals and collected for conductivity measurements.



*Figure 29: Setup of the pulse experiments for RTD measurements*

The exit age distribution  $E(t)$  was calculated from the measured concentration by Eq. 28:

$$E = \frac{c_{\text{exit}}}{m_{\text{tracer}} \dot{V}_L}$$

where  $c_{\text{pulse}}$  is the measured tracer concentration,  $m_{\text{tracer}}$  is the total amount of injected tracer and  $\dot{V}_L$  is the liquid load. The results are shown in Fig 30.

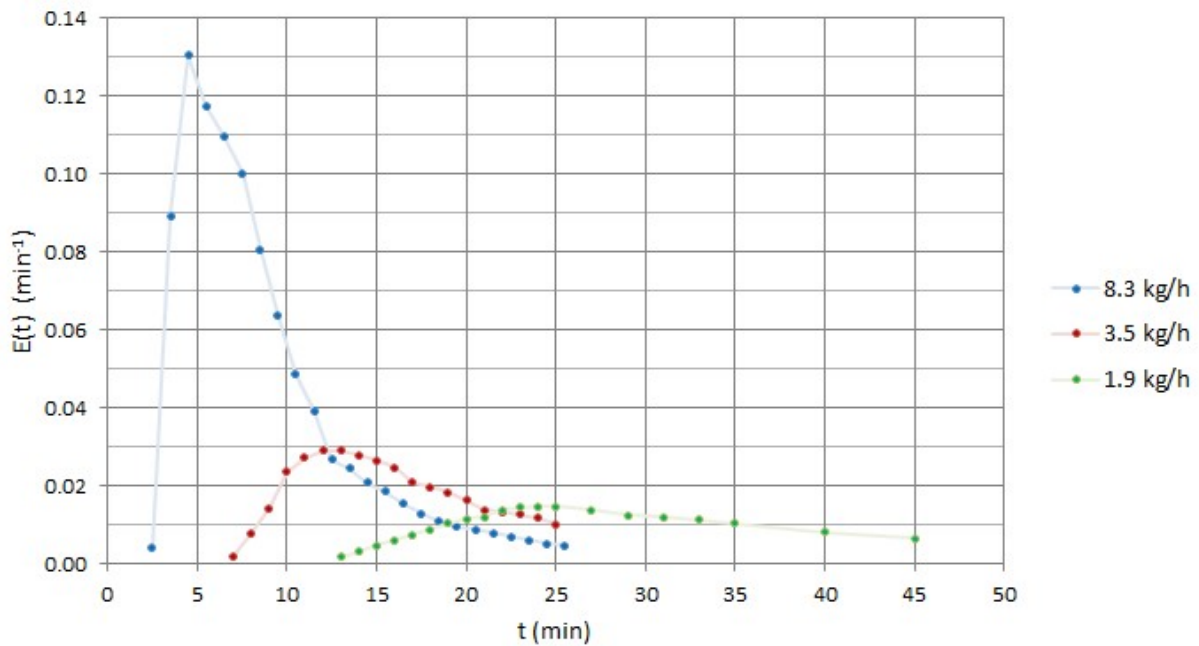


Figure 30: Exit age distribution  $E(t)$  of the Katapak-SP 12 column at different liquid loads

At 8.3 kg/h a relatively sharp distribution was determined. This set-point could be close to the catalytic load point, although below it. The RTD at 3.5 kg/h and 1.9 kg/h show a very broad distribution. The calculated tracer recovery for these set-points was below 50% (Table 12). This indicates that a large share of the tracer gets into stagnant zones. More than half of the tracer has a larger residence time than the experiment lasted. It is expected to exit the column in a slow decline of concentration. The calculation of the mean residence time was only reasonable for the set-point of 8.3 kg/h liquid load, due to the tracer recovery.

Table 12: Tracer recovery and mean residence time  $\tau$  of the pulse experiment

liquid load (kg/h)	tracer recovery	mean residence time $\tau$ (min)
8.3	96%	8.3
3.5	35%	not stated
1.9	32%	not stated

At low liquid loads not all catalyst is used. Zones in the catalytic pockets exist, where the catalyst particles are not wetted. Also, stagnant zones with little mass transfer exist. The optimal operation performance in the experimental setup is expected at high liquid loads above 8L/h.

### 2.3.3 Catalysis, Reaction Kinetics and Chemical Equilibrium

The reaction kinetics of the esterification reaction was evaluated in laboratory experiments, using strong acidic Amberlyst cation-exchange resins as heterogeneous catalysts. The

experiments were done in a batch reactor to study the chemical reaction individually, independent of fluid dynamics and separation effects.

The experimental setup for the catalyst tests is shown in Fig. 31. Ethanol and lactic acid were mixed thoroughly at an initial molar ratio  $n_{\text{EtOH}}/n_{\text{Lac}} = 3$  (starting composition: 53 mol% ethanol, 18 mol% lactic acid, 29 mol% water) in a 250 mL round bottom flask with a reflux condenser. The mixture was heated up by a thermal oil heater. As soon as the target temperature was reached, a reference sample was taken and then, a certain amount of catalyst was added. The homogeneous esterification had already progressed to some extent before the target temperature was reached. Samples of 2 mL were taken every 20 min for 7 hours and another sample after 23 hours to determine the equilibrium composition.

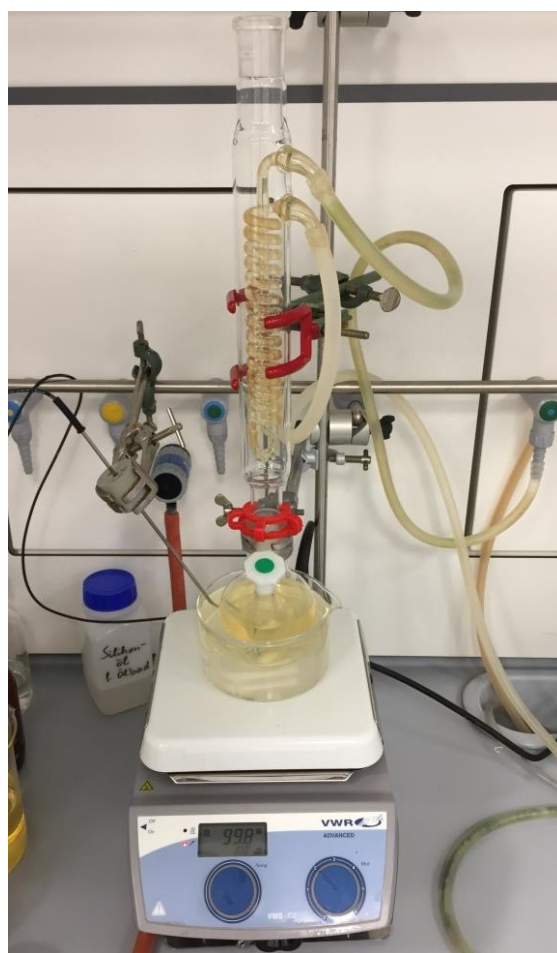


Figure 31: Experimental setup for catalyst tests in lab scale

The temperature dependency of the reaction kinetics was studied using 2.5 w% Amberlyst 46 as catalyst. The results are shown in Fig. 32. The medium temperature (363 K) showed the best results. While at 353 K the catalyst activity is expected to be lower, at 373 K altered adsorption selectivities could be the reason for the reduced activity. The results at 373 K are unexpected and could also be the result of experimental or measurement errors. This



experiment should be repeated to check the reliability of the data. Anyhow, the reaction temperature in the reactive distillation plant did not reach more than 363 K in the experiments of this work. The equilibrium conversion is almost independent of the reaction temperature, which is in accordance to literature. [21]

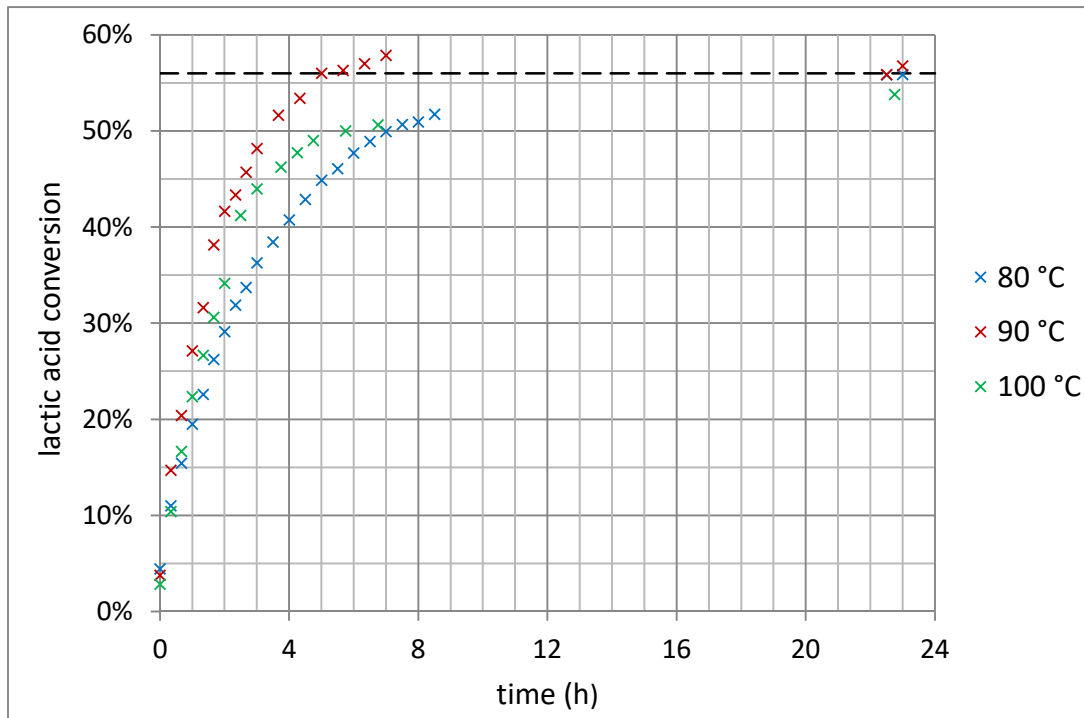


Figure 32: Temperature dependency of the reaction kinetics of ethyl lactate formation using 2.5 w% Amberlyst 46 as catalyst (initial molar ratio  $n_{EtOH}/n_{Lac} = 3$ )

Additionally, two alternative cation-exchange resins were tested, which were recommended by a catalyst fabricator. Amberlyst 48 and Amberlyst 15 have the same type of active sites (sulfonic acid groups) as Amberlyst 46 and are characterized by a higher value of equivalents per particle mass (see Table 13).

Table 13: Density of active sites of different Amberlyst resins (data from product datasheets)

catalyst	Amberlyst 46	Amberlyst 48	Amberlyst 15
density of active sites (eq/kg)	0.8-1.3	$\geq 2.2$	$\geq 2.3$
catalyst bulk density (kg/L)	0.600	0.820	0.780

As expected, the type of catalyst did not influence the equilibrium conversion. The alternative catalysts did not have an increased effectiveness compared to Amberlyst 46. According to the fabricant, the active sites of Amberlyst 46 are solely on the surface of the resin particles and therefore more easily accessible. Part of the active sites of Amberlyst 15 and Amberlyst 48 is



less accessible for the reactive mixture. The higher concentration of active sites did not show a higher catalytic effectiveness.

The density of active sites of strong acidic cation-exchange resins cannot be directly related to the catalytic exchange capacity of the resin. The pore structure and the swelling behaviour of the resin are also important factors. [25]

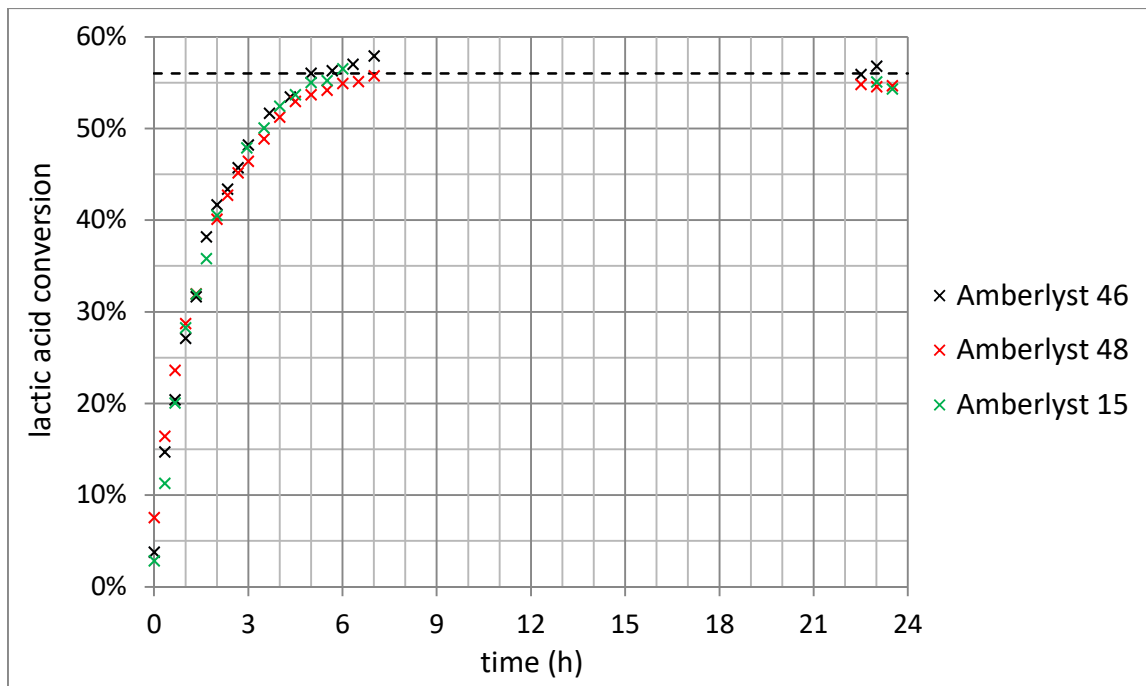


Figure 33: Effectiveness of different Amberlyst resins compared for the catalysis of ethyl lactate formation (2.5 w% catalyst, initial molar ratio  $n_{EtOH}/n_{Lac} = 3$ , temperature = 363 K)

Fig. 34 compares the molar composition of the reactive mixture to the weight fractions of the components over time. The water content was calculated from the lactic acid conversion using reaction stoichiometry. It is evident that (on a molar base) water is the dominant product in the mixture, although it accounts for just 12.9 w% of the initial mixture and 15.6 w% in the state of equilibrium. Thus, not a high mass of water has to be removed to increase the driving force for the reaction significantly.

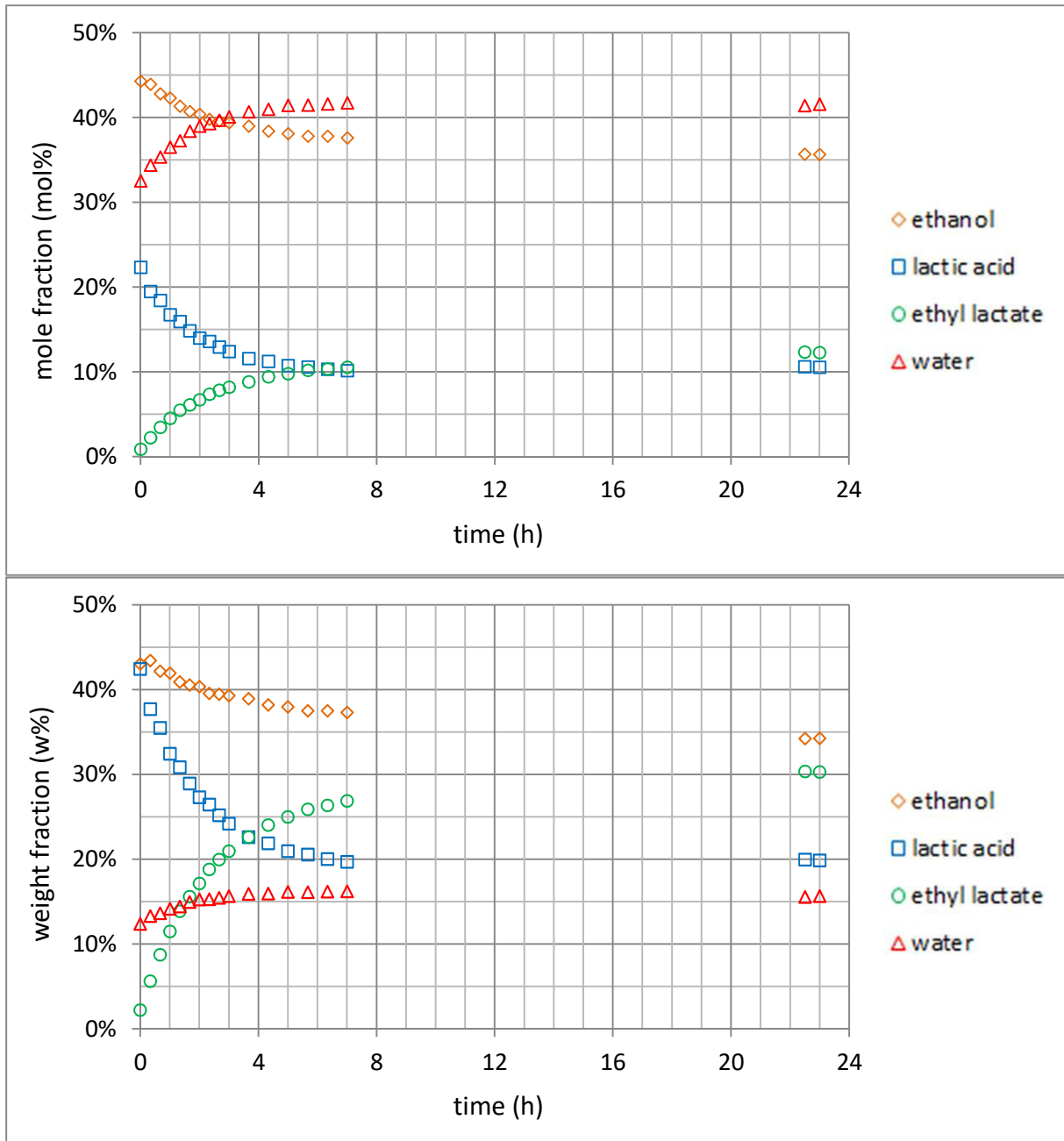


Figure 34: Composition of a reactive mixture ethanol – lactic acid – ethyl lactate - water over time in a batch reactor (ethyl lactate formation with 2.5 w% Amberlyst 46 at 363 K, initial molar ratio  $n_{EtOH}/n_{Lac} = 3$ )

It should be stressed that the amount of catalyst used in these experiments (2.5 w% of the mixture) is much lower than the fraction of catalyst in the pilot scale column. The effectively used fraction of the catalytic packing much depends on fluid dynamics. An estimative calculation was done to determine a reference value. The total catalyst content of the column was calculated from manufacturer specifications. In Katapak-SP 12 packings approx. 30% of the total volume are catalyst filled pockets. [35]

$$V_{\text{pockets}} = V_{\text{packing}} \cdot 30\% = \frac{(0.05\text{m})^2 \pi}{4} \cdot 0.88 \text{ m} \cdot 30\% = 0.518 \text{ L}$$

The utilized Amberlyst 46 particles have a bulk density of  $\rho_b = 0.600 \text{ kg/L}$ . [43] The total mass of catalyst in the column was calculated:

$$m_{\text{Cat}} = V_{\text{pockets}} \cdot \rho_b = 0.311 \text{ kg}$$

The liquid holdup of the column was calculated from the mean residence time at 8.3 L/h liquid load (2.3.2 Liquid Phase RTD of the column).

$$H_L = \tau \cdot \dot{V}_L = 8.3 \cdot 60 \text{ s} \cdot \frac{8.3 \text{ L}}{3600 \text{ s}} = 1.15 \text{ L}$$

This value equals 66% of the total column volume. The density of the reactive mixture is about  $\rho_L = 0.960 \text{ kg/L}$ . Using these values, the catalyst loading in the column at a liquid load of 8.3 L/h is estimated:

$$w_{\text{Cat, est}} = \frac{m_{\text{Cat}}}{H_L \cdot \rho_L} = \frac{0.311 \text{ kg}}{1.15 \text{ L} \cdot 0.960 \text{ kg/L}} = 0.28$$

# 3 Experimental Results and Discussion

The pilot plant used in this work was designed for this process in a previous project. [20] Earlier experiments did not prove to reach reactive distillation conditions in the column. The experiment with the highest documented ethyl lactate yield reached 21%, which is below the batch equilibrium. A process optimization of the ethyl lactate production via reactive distillation should be done in this work. The associated research questions are:

- A) At which setting is the reactive distillation plant operated optimally regarding the ethyl lactate yield?
- B) Which setup is proposed for an overall process for ethyl lactate production with the pilot plant (including the recovery of chemicals and a downstream processing for the product)?

The experimental part is divided into the following stages:

- Implementing a continuous steady state operation of the plant
- Evaluation of operation points from literature, finding limitations
- Scale down approach to lab scale experiments to study the separation of water
- Transferring the results to pilot scale, optimization of the overall process

### 3.1 Implementing a Steady State Operation of the Pilot Plant

In the first esterification experiment of this work an operation point of a previous project [20] was repeated to evaluate the function of the plant. Similar results were obtained (see Table 14). For this operation point the stationary composition was not reached. Lactic acid accumulated in the reboiler over time (see Fig. 35).

Table 14: Settings and results of the first esterification experiment of this work

settings	previous experiment	this work
feed rate of F1 (kg/h) (80 w% Lac)	1.203	1.161
feed rate of F2 (kg/h) (95 w% EtOH)	1.301	1.360
bottom rate (kg/h)	0.770	1.127
reflux ratio	2	2
reboiler duty (W)	2100	2100
pre-heater of feed F2 (W)	105	105
<b>results</b>		
reboiler temperature (K)	383	373
distillate rate (kg/h)	1.734	1.365
distillate composition (w%)	ethanol: 74 % water: 24 % ethyl lactate: 2 %	ethanol: 90 % water: 10 %
bottom product composition (w%)	ethanol: 4 % lactic acid: 54 % ethyl lactate: 19 % water: 23 %	not a steady state
molar feed ratio $n_{\text{EtOH}}/n_{\text{Lac}}$	2.5	2.7
molar excess of ethanol in the bottom product	0.33	Not a steady state
batch-equilibrium conversion	calc.: 68 %, exp.: 50 % (est.)	
lactic acid conversion	21%	20%

A stationary operation with these settings is not possible, because the bottom rate is lower than the lactic acid feed flux. Lactic acid will accumulate over time. The component mass balance for lactic acid can only be stabilized by an accurate bottom rate, because lactic acid does not get into the distillate.

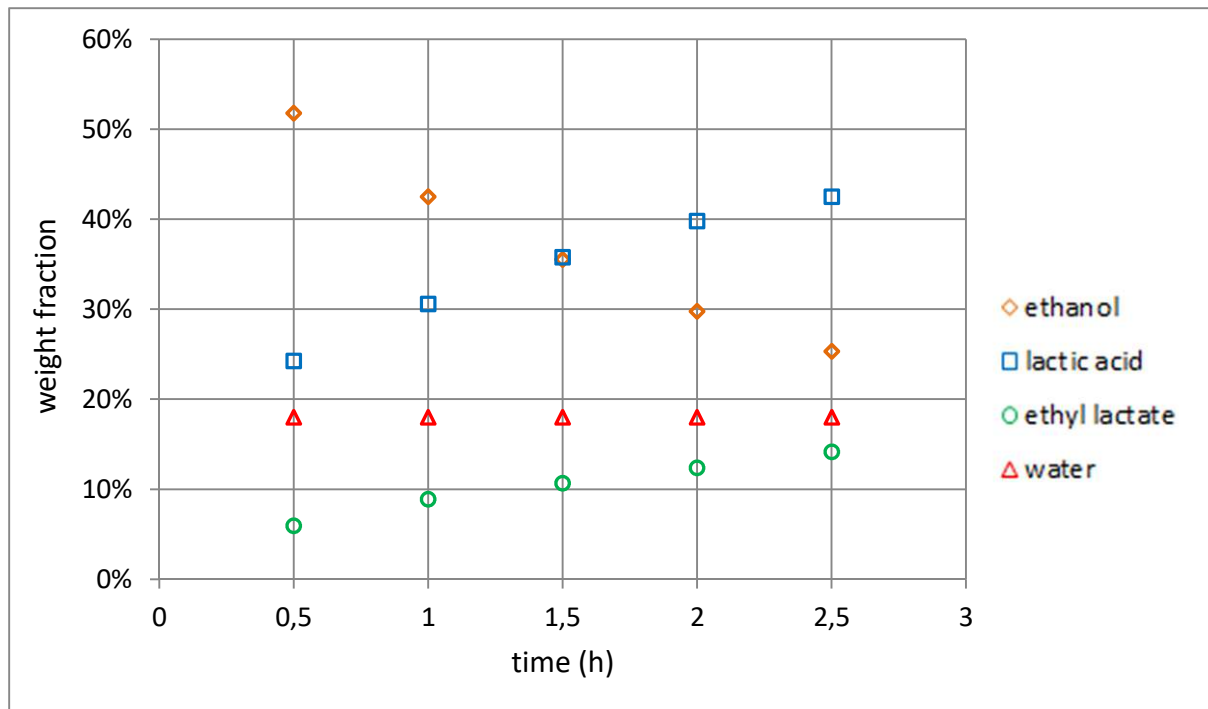


Figure 35: Development of bottom product composition over time in the first esterification experiment of this work (the fraction of water was estimated)

It was documented in the previous experiment, that the lactic acid feed flux would have to be reduced in order to reach higher conversion, but the delivery rate of the pump could not be decreased. To overcome this limitation, a mixture of lactic acid and ethanol was evaluated for the use as feed F1. It did not show any segregation over time. The mixture had a significantly lower viscosity than 80 w% lactic acid, this facilitated the dosage. The operation window for the lactic acid feed flux was widened. An experiment with the minimal feasible lactic acid delivery rate was done. In this experiment, a very high ethanol excess was used to reach a liquid load similar to that applied in earlier experiments. The settings and experimental results are shown in Table 15. The overall mass balance was successfully closed (with a relative error of 3%). The stationary composition was not reached within the duration of the experiment. The component balances for lactic acid and ethyl lactate are subject to high relative errors, due of the low lactic acid feed rate.

Table 15: Settings and results of an experiment with minimal lactic acid feed

<b>settings</b>	
feed rate of F1 (kg/h)	0.156
feed composition of F1 (w%)	ethanol: 47.5 w% lactic acid: 40 w% water: 12.5 w%
feed rate of F2 (kg/h) (95 w% ethanol)	1.247
bottom rate (kg/h)	0.110
reflux ratio	2
reboiler duty (W)	1800
pre-heater for feed F2 (W)	100
<b>results</b>	
reboiler temperature (K)	364
distillate rate (kg/h)	1.340
distillate composition (w%)	ethanol: 91 % water: 9 %
bottom product composition (w%)	ethanol: 44% lactic acid: 34% ethyl lactate: 12% water: 10 % (estimated)
molar feed ratio $n_{\text{EtOH}}/n_{\text{Lac}}$	39.5
molar excess of ethanol in the bottom product	2.0
batch equilibrium conversion	97% (calc.)
lactic acid conversion	22%

A requirement for a steady state operation is that the lactic acid equivalents  $Eq_{\text{Lac}}$  of feed F1 and bottom product are balanced. A simple way to meet this requirement is to maintain the same molar ratio  $n_{\text{EtOH}}/n_{\text{Lac}}$  from the feed F1 to the bottom product. If a constant excess of ethanol is applied in the column, the feed F1 and the bottom product can be balanced independently of the ethanol-feed rate and the distillate rate. This was done in all later experiments of this work.

### 3.2 Evaluation of Operation Points from Literature, Finding Limitations

It was tried to replicate a successful reactive distillation operation point from literature [42], where 66% ethyl lactate yield was reached. A continuous steady state operation at the pilot plant was reached with similar settings (see Fig. 36).

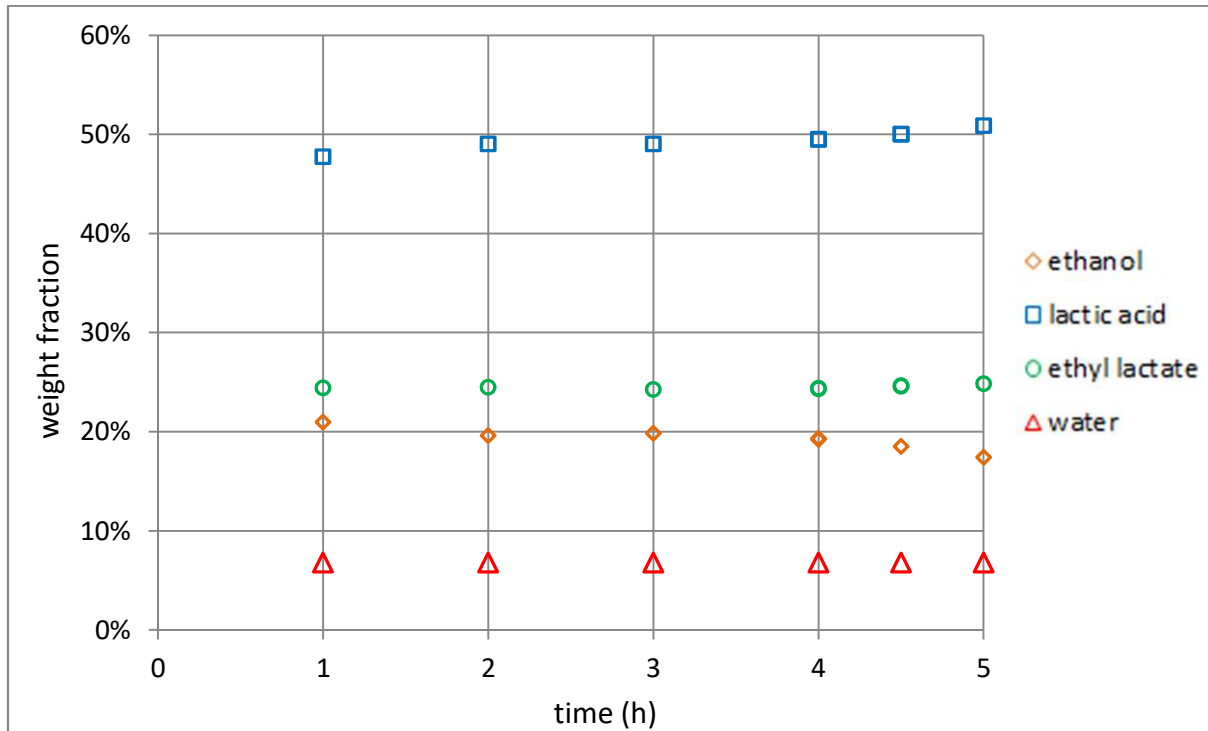


Figure 36: Development of the bottom product composition over time in the first run

The experiment did not reach the target result, an ethyl lactate yield of only 27.4% was obtained. It was unclear at that point, what the limiting phenomenon was. To get an indication if the chemical reaction was limited by the reaction conditions, or if the residence time in the catalytic zone was too low, an experiment with increased residence time was implemented. The collected bottom product of the first run was used as feed F1 in a second run. The reaction conditions (temperature, fluid dynamics, excess of ethanol) were the same as before (in the first run). The only altered parameter was the residence time, which was doubled by recycling the bottom product to the column for a second pass. Table 16 compares the settings and results of the two runs and the reference experiment from literature.



Table 16: Settings and results of an experiment from literature [42] compared to the operation of the pilot plant at similar settings

settings	E10 of Asthana et al.	first run	second run
feed rate of F1 (kg/h)	0.580	1.263	0.874
composition of F1 (w%)	lactic acid: 88% water: 12%	ethanol: 47.5% lactic acid: 40% water: 12.5%	ethanol: 22 % lactic acid: 39 % ethyl lactate: 31 % water: 8 % (est.)
feed rate of F2 (kg/h) (95 w% ethanol)	0.988	0.495	0.689
molar feed rate of lactic acid (mol/h)	5.67	5.61	3.79 (6.1 equivalents)
molar feed rate of ethanol (mol/h)	20.4	23.26	18.4 (20.7 equivalents)
bottom rate (kg/h)	1.036	0.801	0.676
reflux ratio	0	0	0
reboiler duty (W)	750	750	750
pre-heater for F2 (W)	0	0	0
<b>results</b>			
reboiler temperature (K)	363	373	373
distillate rate (kg/h)	0.563	0.916	0.895
distillate composition (w%)	ethanol: 64 % water: 34 % ethyl lactate: 2 %	ethanol: 83% water: 17 %	ethanol: 78% water: 22%
bottom product composition (w%)	ethanol: 37 % lactic acid: 5 % ethyl lactate: 43 % water: 4 % oligomers: 12 %	ethanol: 20 % lactic acid: 49 % ethyl lactate: 24 % water: 7 % (est.)	ethanol: 12 % lactic acid: 44 % ethyl lactate: 38 % water: 7 % (est.)
molar feed ratio $n_{\text{EtOH}}/n_{\text{Lac}}$	3.6	4.1	4.9 (3.4 equivalents)
Molar Excess of ethanol in the bottom product	2.5	0.85	0.71
batch equilibrium conversion	exp.: 62% (est.) calc.: 75%	exp.: 64% (est.) calc.: 77%	exp.: 60% (est.) calc.: 74%
ethyl lactate yield	66%	27.4%	39.6%

In the time span between the two experimental runs the esterification proceeded from 27.4% to 38.1% lactic acid conversion in a container at ambient temperature. In the second run, the lactic acid conversion was only marginally increased. It rose from 38.1% to 39.6%. This indicated that the reaction conditions were the limiting factor for further conversion, rather than the residence time of lactic acid. The stripping capacity for the separation of water was calculated from the measured top product flux and composition as follows:

$$\Delta \dot{m}_W = \dot{m}_D (x_{W,D} - x_{W,F2}) = 0.916 \text{ kg/h} (17\% - 5\%) = 0.110 \text{ kg/h}$$

The maximal required amount of water that has to be removed was calculated from reaction stoichiometry (for total conversion  $X_{Lac} = 1$ ):

$$\Delta \dot{m}_{W,req} = \dot{m}_{F1} \cdot \left( x_{W,F1} + X_{Lac,F1} \cdot \frac{M_W}{M_{Lac}} \right) = 1.263 \text{ kg/h} \cdot \left( 12.5\% + 40\% \cdot \frac{18}{90} \right) = 0.259 \text{ kg/h}$$

Removing water seemed to be limiting the reactive distillation operation.

### 3.3 Scale-down Approach to Optimize the Separation of Water

The next experiments were done following a scale down approach to the problem. The necessary conditions for an optimized separation of water were investigated in lab scale. The experiments were done with a reactive mixture with an initial molar ratio  $n_{EtOH}/n_{Lac} = 3$  (initial composition: 51 mol% ethanol, 17 mol% lactic acid, 32 mol% water). In a first step, the mixture was equilibrated in a batch reactor (250 mL round bottom flask with reflux condenser) at 383 K using 5 w% Amberlyst 46 as catalyst. The measured batch equilibrium was used as a bench mark for the subsequent operation.

In the second step, the same mixture was processed by reactive distillation. The experimental setup is shown in Fig 37. The reactive mixture and the catalyst particles stayed in the reboiler flask throughout the whole experiment. A target temperature was set by a thermal oil heater. Distillate was constantly removed using a distillation bridge. In periodic intervals ethanol (95 w%) was added manually to maintain the molar excess of ethanol in the mixture constant.



Figure 37: Experimental setup for reactive distillation in lab scale

Samples of the mixture were taken periodically to evaluate the progressing conversion over time. The distillate flow rate and composition was measured. The reactive distillation in the lab scale setup was realized following a periodical work routine (shown in Fig. 38), which included sampling, distillate measurements and ethanol addition.

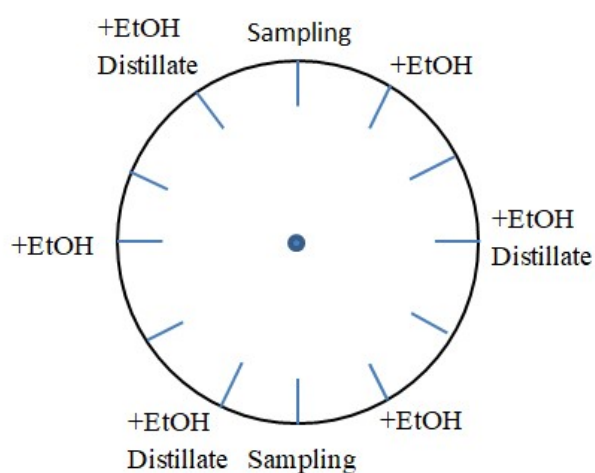


Figure 38: Work routine for reactive distillation in lab scale

The influence of the set temperature was evaluated. The mass flux of separated water was calculated by a mass balance. At a thermal oil temperature of 363 K hardly any distillate was collected, at 373 K a relatively low distillate rate occurred, whereas at 383 K the distillate rate increased substantially.

Table 17: Separation of water in lab scale

set temperature (K)	distillate rate (g/h)	initial weight fraction of water in the distillate	mass flux of separated water (g/h)
363	<1	n.s.	n.s.
373	10	12 %	0.7
383	70-80	18 %	9.1-10.4

At a set temperature of 383 K, water was successfully removed from the mixture. By this, additional chemical driving force for the reaction was created and the chemical equilibrium was relocated towards a higher lactic acid conversion. (see Fig. 39). The reaction proceeded relatively slow (20% additional conversion within 4 hours). A distillate sample was analysed by HPLC methods. A low amount of ethyl lactate (1.5 w%) was detected. It was considered acceptable, whereas further increasing the reboiler duty would probably lead to significant losses of ethyl lactate. At these operation conditions the concept of reactive distillation was successfully implemented in lab scale.

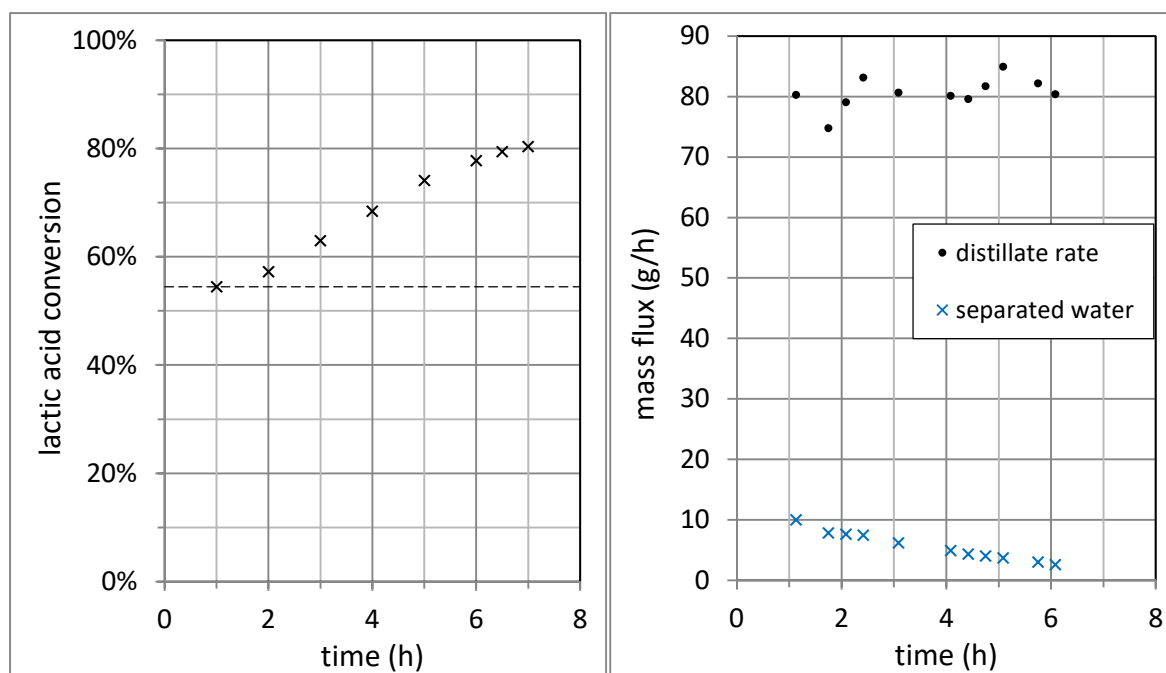


Figure 39: Results of lab scale reactive distillation, left: progress of lactic acid conversion, right: distillate rate, dashed line: batch equilibrium

### 3.4 Transferring the Operation Conditions to Pilot Scale

It was tried to transfer the determined operation parameters to pilot scale. The reboiler temperature was found as the limiting condition for the separation of water. An improvement of the pilot scale operation is expected by increasing the reboiler duty. The following parameters and conditions were considered in the transformation of the reaction conditions:

- Reboiler duty:

A reboiler duty of 2100 W (70% of the maximal heat duty) was applied. The measured reboiler temperature did not reach the set temperature of the lab scale experiment (383 K). However, a very intensive vaporization was achieved. Small amounts of ethyl lactate were found in the top product. Therefore, a higher reboiler temperature would not have been reasonable. Fig. 40 shows the reboiler at this operation state.

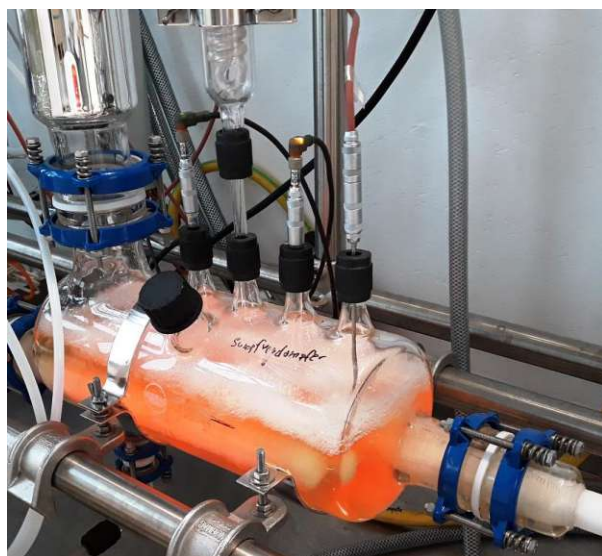


Figure 40: Reboiler during the operation

- Excess of ethanol in the reactive mixture:

A ratio of reactant equivalents of  $Eq_{EtOH}/Eq_{Lac} = 3.5-4.2$  was applied in feed F1 and the same ratio was achieved in the bottom product. The ethanol feed F2 was adjusted to compensate for the fraction of ethanol that went into the distillate.

- Ethanol as stripping agent:

The ethanol feed F2 can be considered as stripping agent (similar to the lab scale setup), because the excess of ethanol equivalents  $Eq_{EtOH}$  in the product stream is not increased by it and its purpose is to remove water from the reactive mixture.

Some important differences between the lab scale and the pilot scale setup had to be considered:

- Reaction temperature: In lab scale the catalyst was located within the reboiler flask, so the reaction took place at reboiler temperature ( $>373$  K). However, in the pilot plant the reaction should occur in the catalytic section of the column. The reaction temperature cannot be set manually. It was lower than in lab scale (360 K) as a result of the vapour temperature.
- Catalyst loading: In lab scale the catalyst loading was defined by the setup (2.5 w% catalyst was used). In lab scale the effective amount of catalyst used depends on the liquid hold-up and fluid dynamics (flow and wetting conditions) in the column. It cannot be set manually and is difficult to determine. In this work it could only be estimated by geometric considerations. A catalyst loading of approx. 28 w% of the liquid hold-up at 8.3 L/h liquid load was determined (see 2.3.3 Catalysis, reaction kinetics and Chemical Equilibrium).
- Separation behaviour: In the lab scale setup the separation is done in a single distillation step without reflux. For the pilot scale setup a minimum number of 3 separation steps is expected in the stripping section. (2.3.1 Separation Behaviour)
- Residence time distribution: The lab scale experiment can be considered a batch operation for lactic acid equivalents, because they remain in the flask during the whole experiment. The pilot scale operation is a continuous process with a certain RTD of the liquid phase. It was adjusted by the recycling of bottom product.

Due to the differences in the setup, it had to be inspected if a successful reactive distillation operation was feasible in the pilot plant at the lab scale conditions. The experiment was organized in three runs. In each run, the bottom product of the steady state operation was collected and used as feed F1 for the next run.

Initially ethanol with a purity of 95 w% was used as feed F2. In the first run the distillate was constantly recycled to the ethanol-feed container. The mass fraction of water in the distillate constantly rose from initially 8 w% to 11 w% at the end of this experiment. An ethyl lactate yield of 27% was reached, which is below the batch equilibrium yield for this mixture (approx. 60%). During the time between the first and second run the esterification proceeded at ambient temperature in a container. The ethyl lactate yield rose from 27% to 38% (within 2 weeks).

In the second run a feed F2 with an initial purity of >90 w% ethanol was used. Due to the high ethanol consumption, the distillate had to be recycled to the feed container until the saturation of ethanol as stripping agent was reached. At the end of this experiment a water content of 13 w% was measured in the distillate and the ethanol-feed. In this experiment the ethyl lactate yield was increased from 38% to 44%.

The collected bottom product of the second run was again reused as feed F1 in a third run, applying the same settings. In this run, a saturated ethanol-feed F2 was used. No more water was removed in the column. The conversion of lactic acid still proceeded at these conditions from 44% to 47%. The separation of water was therefore not limiting the esterification reaction in this run.

The maximal stripping capacity for the separation of water was calculated from the measured top product flux and the composition of the saturated stripping agent (ethanol with 13 w% water):

$$\Delta \dot{m}_{W,\max} = \dot{m}_D (x_{W,D,\max} - x_{W,F2,\min}) = 4.839 \text{ kg/h} (13\% - 5\%) = 0.387 \text{ kg/h}$$

The maximal required amount of water that has to be removed was calculated from reaction stoichiometry (for total conversion  $X_{Lac} = 1$ ):

$$\Delta \dot{m}_{W,\text{req}} = \dot{m}_{F1} \cdot \left( x_{W,F1} + x_{Lac,F1} \cdot \frac{M_W}{M_{Lac}} \right) = 1.115 \text{ kg/h} \cdot \left( 12\% + 35\% \cdot \frac{18}{90} \right) = 0.212 \text{ kg/h}$$

The required stripping capacity for the separation of water with ethanol was successfully implemented. However, the ethanol consumption of this separation operation was very high. A molar feed ratio  $n_{EtOH}/n_{Lac}$  of 25 - 30 was required to reach an ethanol excess of 3.6 - 4.2 in the bottom product.



Table 18: Settings and results of the transformed reaction conditions in lab scale

settings	first run	second run	third run
feed rate of F1 (kg/h)	1.115	1.130	1.130
composition of F1 (w%)	ethanol: 54 % lactic acid: 35 % water: 12 %	ethanol: 54 % lactic acid: 21 % ethyl lactate: 17 % water: 8 % (est.)	ethanol: 58 % lactic acid: 17 % ethyl lactate: 17 % water: 8 % (est.)
state of lactic acid conversion in the feed F1	0%	38%	44%
feed rate of F2 (kg/h)	5.100	4.615	4.615
molar feed rate of lactic acid (mol/h)	4.33	2.64 (4.27 equivalents)	2.14 (3.76 equivalents)
molar feed rate of ethanol (mol/h)	118.4	108.6 (110.2 equivalents)	109.6 (111.2 equivalents)
bottom rate (kg/h)	1.077	1.062	1.062
reflux ratio	0	0	0
reboiler duty (W)	2100	2100	2100
ethanol-feed pre-heater (W)	0	0	0
<b>results</b>			
reboiler temperature (K)	360	360	360
distillate rate (kg/h)	4.839	4.695	4.695
distillate composition (w%)	ethanol: 89 % water: 11 % ethyl lactate: 0.3 %	ethanol: 86.7 % water: 13 % ethyl lactate: 0.3 %	ethanol: 86.7 % water: 13 % ethyl lactate: 0.3 %
bottom product composition (w%)	ethanol: 56 % lactic acid: 24 % ethyl lactate: 12 % water: 8 % (est.)	ethanol: 58 % lactic acid: 17 % ethyl lactate: 17 % water: 8 % (est.)	ethanol: 55 % lactic acid: 17 % ethyl lactate: 20 % water: 8 % (est.)
molar feed ratio $n_{\text{EtOH}}/n_{\text{Lac}}$	27.3	41.1 (25.8 equivalents)	51.2 (29.6 equivalents)
molar excess of ethanol in B ( $\text{Eq}_{\text{EtOH}}/\text{Eq}_{\text{Lac}}$ )	3.6	4.2	3.8
batch equilibrium conversion of the input and the mixture B	calc.: 92% (mixture B: 60%)	calc.: 92% (mixture B: 64%)	calc.: 92% (mixture B: 62%)
total lactic acid conversion	27%	44%	47%



The chemical reaction was not fast enough to reach the chemical equilibrium within 3 passes through the column. The effective catalyst activity seemed to be the limiting factor. In these experiments a liquid load of approx. 1.5-2.5 L/h was applied, which is below the optimal liquid load of >8 L/h. Part of the catalyst particles may not have been wetted and stagnant zones may have occurred in the catalytic packing.

To overcome this limitation, a liquid load of approx. 8-8.5 L/h was applied in the next experiment. At these conditions a mean residence time of the liquid phase of 8 min was expected (as evaluated in 2.3.2 Liquid Phase RTD of the Column). A lower excess of ethanol in the feed F1 and the bottom product was used ( $Eq_{EtOH}/Eq_{Lac} = 1.6-1.9$ ) to reduce the ethanol consumption compared to the previous experiment. For the feed F1, a partially pre-esterified mixture was used and constantly recycled from the bottom product (total mass in the cycle: 17 kg). The plant was operated at two different steady state points of the column for 2.5 hours and 2 hours, respectively. For the first 2.5 hours ethanol with an initial purity of 87.5 w% was used as feed F2. It was recycled until the water content reached 15 w%. Then, the top product was collected in a separate container. For the second operation point 95 w% ethanol was used. The capacity for the separation of water was evaluated for both operation points.

#### Steady state 1:

$$\Delta \dot{m}_{W,1} = \dot{m}_{Dest,1} (x_{W, Dest,1} - x_{W, F2,1}) = 2.977 \text{ kg/h} (26\% - 15\%) = 0.327 \text{ kg/h}$$

#### Steady state 2:

$$\Delta \dot{m}_{W,2} = \dot{m}_{Dest,2} (x_{W, Dest,2} - x_{W, F2,2}) = 3.151 \text{ kg/h} (21.5\% - 5\%) = 0.520 \text{ kg/h}$$

When the stripping agent was changed from 85 w% ethanol to 95 w% ethanol, the temperature marginally decreased from 93 °C to 92 °C. The amount of separated water was strongly increased. Therefore the liquid level of the reboiler vessel sank until the new steady state was reached.

Table 19: Settings and results of a reactive distillation experiment with a high liquid load (approx. 8 L/h)

<b>settings</b>	
feed rate of F1 (kg/h)	8.182
composition of F1	$Eq_{Lac} = 6.82 \text{ mol/kg}$ $Eq_{EtOH} = 11.55 \text{ mol/kg}$
feed rate of F2 (kg/h)	2.975
molar feed rate of lactic acid (mol/h)	52 equivalents
molar feed rate of ethanol (mol/h)	150 equivalents
bottom rate (kg/h)	8.022
reflux ratio	0
reboiler duty (W)	2100
ethanol-feed pre-heater (W)	0
<b>results</b>	
reboiler temperature (K)	365-366
distillate rate (kg/h)	3.151
distillate composition (w%)	ethanol: 78 % water: 20 % ethyl lactate: 2 %
molar feed ratio $Eq_{EtOH}/Eq_{Lac}$	2.88
molar excess of ethanol in the bottom product ( $Eq_{EtOH}/Eq_{Lac}$ )	1.6-1.9
batch equilibrium conversion of the input and the mixture B	exp.: 58% (mixture B: 52-54%) (est.) calc.: 71% (mixture B: 57-62%)
lactic acid conversion	31-34%

During the whole experiment the lactic acid conversion of the mixture rose from 31% to 34%. The batch equilibrium conversion (approx. 52-54%) was not reached. The effective catalyst activity still seemed to be limiting the operation. In this experiment fluid dynamics are not expected to be limiting. It is presumed that the catalyst is (partially) deactivated.

### 3.5 Catalyst Regeneration

The deactivation of Amberlyst 46 by cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) and the regeneration with hydrochloric acid HCl (5 w% aqueous solution) was tested in lab scale. First, a batch-esterification with unused Amberlyst 46 was done. 170 g of a mixture with initial molar composition: 46% ethanol, 38% water, 15% lactic acid and 8.94 g Amberlyst 46 (additional 5 w% of the mixture) as catalyst were used in each batch. The experiments were done in 250 mL round bottom flasks with reflux condensers at 363 K. The results were used as a reference for the deactivation and regeneration experiments.

Then, the catalyst was filtrated, washed and exposed to a salt solution to check the deactivation. Two species of cations were evaluated individually:  $\text{Na}^+$  (100 mL 5 w% NaCl solution) and  $\text{Ca}^{2+}$  (100 mL 10 w%  $\text{CaCl}_2$  solution). The mixture was stirred for 45 minutes. Then the catalyst was washed with DI-Water until the conductivity of the wash water was below 15  $\mu\text{S}$ . The extend of deactivation was evaluated by a batch-esterification experiment with the same catalyst, using a mixture with the same initial molar composition as the reference batch.

Finally, the regeneration of the deactivated catalyst with HCl was tested. The catalyst was stirred in 150 mL of 5 w% HCl for 15 minutes. Then, it was washed with DI-Water until the conductivity of the wash water fell below 15  $\mu\text{S}$ . It was evaluated in a batch-esterification at the same conditions as before, if the regeneration was successful. The ethyl lactate yield in the reference experiment, after deactivation and after regeneration is compared in Fig 41.

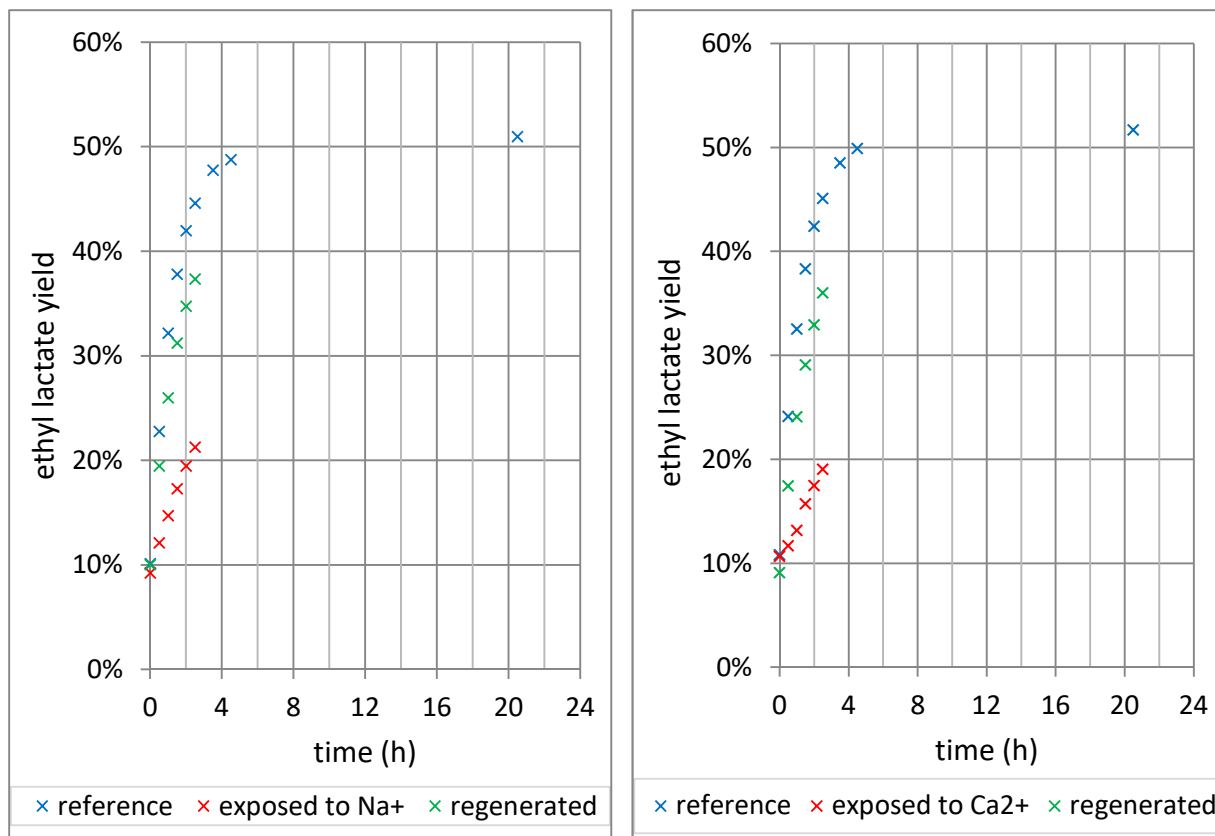


Figure 41: Deactivation and regeneration of Amberlyst 46 compared to a reference batch esterification

It is apparent, that the catalyst activity is strongly affected by the cations. The regeneration with HCl was effective. Most of the initial catalyst activity could be recovered.

## 4 Conclusion and Outlook

The topic of this work is the development and optimization of a process for ethyl lactate production via reactive distillation. The optimal operation conditions should be determined using an existing pilot plant and a reasonable setup for the overall process should be proposed (including the recovery of chemicals and a downstream processing for the product). The associated research questions were:

### **A) At which setting is the reactive distillation plant operated optimally regarding the ethyl lactate yield?**

To successfully implement a reactive distillation operation, two requirements have to be met: Firstly, the separation operation has to function properly to ensure the effect of process intensification. In the production of ethyl lactate this means, that water as side product of the esterification reaction has to be removed from the reactive zone to the top product to a sufficient extend. Secondly, the esterification reaction has to be fast enough at the operation conditions to reach a satisfactory lactic acid conversion within the mean residence time of the column. In the first part of this work, a characterization of the pilot plant was done. The separation behaviour, the residence time distribution and the catalysis were evaluated individually. The catalyst Amberlyst 46 was evaluated in batch experiments in lab scale. It showed similar reactivity as the industrial catalysts Amberlyst 48 and Amberlyst 15.

The following limitations were found for the operation of the pilot plant:

- **Separation:** The required separation operation is contrary to the concept of rectification. Ethanol is a reactant in ethyl lactate formation. Additionally, it is used as a “stripping agent” for the by-product water. Ethanol is more volatile than water, therefore a high excess of ethanol is needed to remove water with the distillate and at the same time, ensure the supply of ethanol for the esterification reaction.

After an optimization in lab scale, the separation of water was successfully implemented in pilot scale - however, with the drawback of very high ethanol consumption. (A molar feed ratio of  $n_{\text{EtOH}}/n_{\text{Lac}} = 25 - 30$  was required to reach an ethanol excess of 3.6 - 4.2 in the bottom product. The separation of water via stripping is not efficient.

- Fluid dynamics: The liquid load of the column has to be close to the upper limit of operation (above 8 L/h) in order to avoid stagnant zones and ensure the wetting of the catalyst particles.
- Liquid phase RTD: The mean residence time of a single pass through the column is too low to reach a satisfactory lactic acid conversion.
- Temperature level: The reaction temperature could not be directly adjusted. It was a result of the vapour temperature. The reboiler temperature was limited by the vaporization of ethyl lactate. Traces of ethyl lactate were found in the distillate in some experiments. Increasing the reboiler duty further, would lead to significant losses of ethyl lactate. A small amount of losses is caused by the binary maximum pressure azeotrope of water-ethyl lactate. [42]
- Purity of the feed substances: Low water contents of the feed substances are favourable for the operation, as the separation of water is a major issue of the process. The purity of ethanol is limited by the recovery process. If a membrane process (pervaporation) is applied to recover ethanol from the distillate, the limitation of the azeotrope ethanol-water can be avoided. The purity of lactic acid is limited by intermolecular self-esterification reactions of lactic acid monomers. Lactic acid of high purity shows high oligomer contents.
- Feed F1: Using a mixture of reactants as feed F1 (instead of 80 w% lactic acid) was favourable for the dosing of lactic acid. A balanced flux of lactic acid equivalents from the feed F1 to the bottom product is a requirement for a steady state.

The following settings were determined for an optimal performance of the plant:

- The operation at zero reflux with a high reboiler duty and high ethanol feed purity are required for the separation of water.
- At a reboiler temperature  $> 90$  °C traces of ethyl lactate were found in the distillate. The separation capacity increases with the reboiler temperature. To find an optimum, the acceptable amount of ethyl lactate losses has to be defined.
- Operating the plant at high liquid loads (above 8 L/h) is favourable for the fluid dynamics and catalyst wetting in the catalytic section of the column.
- The bottom product has to be partially recycled to the feed F1 to achieve a satisfactory RTD.

- For the molar feed ratio  $n_{\text{EtOH}}/n_{\text{Lac}}$  a compromise between ethanol consumption (for the stripping of water) and lactic acid conversion (enhanced by excess ethanol) has to be found.
- The pre-heating of the ethanol feed F2 acts equivalent to additional reboiler duty. [42]
- Pre-heating of the feed F1 was not studied in this work, because it was not implemented in the control system of the plant. Pre-heating of high concentrated lactic acid would lead to enhanced oligomerization. [42] Pre-heating of reactant mixtures seems promising and could be studied in future experiments.

Reactive distillation was demonstrated in lab scale experiments. It was tried to transform the determined reaction conditions to pilot scale. The separation of water was successfully implemented. However, reactive distillation could not be successfully demonstrated in pilot scale. The effective catalyst activity was the limiting factor, even at optimal flow and wetting conditions. The cation-exchange resin seemed to be (partially) deactivated by impurities of the lactic acid feed. The deactivation of Amberlyst 46 by cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) and the regeneration with HCl (5 w% aqueous solution) was tested in lab scale. Both species of cations strongly affected the catalyst activity. The regeneration with HCl (5 w% aqueous solution) was successfully demonstrated. The catalyst in the column should be regenerated or replaced for future experiments at the plant.

**B) Which setup is proposed for an overall process for ethyl lactate production with the pilot plant (including the recovery of chemicals and downstream processing of the product)?**

The recovery of ethanol from the top product is crucial to the atom efficiency of the overall process. A membrane process (pervaporation) is recommended for this step, in order to avoid the azeotrope ethanol-water (at 96 mol% ethanol) and efficiently obtain ethanol of high purity.

The bottom product is a quaternary mixture. Therefore, a down-stream processing (DSP) is needed. The separation can be done by means of distillation. A vacuum distillation could be used to separate ethyl lactate from lactic acid, in order to reduce the effect of oligomerization. Recovered ethanol and lactic acid should be recycled for to achieve high atom efficiency.

The experiments showed that the bottom product has to be partially recycled to the feed F1 to achieve a satisfactory RTD at the plant. In this work, this was done after cooling it down to

ambient temperature. Recycling the bottom product at a higher temperature could have a positive impact on the operation performance. Thermal energy would be transported into the catalytic zone of the column. This could enhance the vaporization of water and a higher reaction rate would be expected (according to the Arrhenius-equation). The influence of the feed temperature could be studied by using the existing pre-heater of the pilot plant. Such experiments should be done under the consideration of safety aspects.

A pre-esterification of the feed mixture could be done in a plug-flow tubular reactor (PFTR), even at a lower temperature level. The batch equilibrium can be reached in this step and then, the reactive distillation column could be used for shifting the equilibrium towards higher conversion. By using a pre-esterification reactor, the recycle ratio of the bottom product could be reduced and a higher overall throughput of the plant could be reached. If the recycled bottom product has to be cooled, a heat integration for the pre-esterification reactor should be considered.

Finally, it should be stressed that the requirement for a reasonable process is not only to overcome the batch equilibrium composition of a mixture by any means. Environmental and economic aspects also have to be considered. In this system, the separation of water by means of distillation does not seem to be energy-efficient.



# Abbreviations

B	bottom product of the column
D	top product of the column
DOF	degree of freedom
EC	electrical conductivity
EL	ethyl lactate
EOS	equation of state
EtOH	ethanol
F1	feed above the catalytic section of the column
F2	feed below the catalytic section of the column
FDA	US-American food and drug administration
HPLC	high-performance liquid chromatography
Lac	lactic acid
LH	Langmuir-Hinshelwood mechanism
MSW	municipal solid waste
NPS	new policies scenario
PLA	polylactic acid
RD	reactive distillation
RID	refractive index
RTD	residence time distribution
SDS	sustainable development scenario
UV	ultraviolet radiation
VLE	vapour liquid equilibrium
VOC	volatile organic compound
W	water

# Symbols

A, B, C	(-)	coefficients of the Antoine equation
$a_i$	(-)	activity of substance i
$B_{iV}(T)$		viral coefficients
$c_p$	(J mol <sup>-1</sup> K <sup>-1</sup> )	isobaric heat capacity
$c_{pulse}$	(kg m <sup>-3</sup> )	measured tracer concentration
$\Delta G^0$	(J mol <sup>-1</sup> )	Gibbs free energy change per mole of reactant
$E(t)$	(s <sup>-1</sup> )	exit age distribution
$E_A$	(J mol <sup>-1</sup> )	activation energy
$Eq_{EtOH}$	(mol)	reactant equivalents of ethanol
$Eq_{Lac}$	(mol)	reactant equivalent of lactic acid
f	(-)	thermal factor of the feed
$f_i$	(-)	fugacity of component i
h	(J mol <sup>-1</sup> K <sup>-1</sup> )	specific enthalpy
$\Delta h_v$	(J kg <sup>-1</sup> )	specific heat of vaporization
$H_L$	(m <sup>3</sup> )	liquid holdup
$\bar{H}_L$	(J kg <sup>-1</sup> )	specific enthalpy of liquid at the boiling point
$H_F$	(J kg <sup>-1</sup> )	specific enthalpy of the feed
k	(mol s <sup>-1</sup> kg(cat) <sup>-1</sup> )	rate constant
$k^0$	(mol s <sup>-1</sup> kg(cat) <sup>-1</sup> )	pre-exponential factor
$k_i$	(-)	adsorption coefficient
K	(-)	thermodynamic equilibrium constant
$K_x$	(-)	term of mole fractions of the equilibrium constant
$K_\gamma$	(-)	term of activity coefficients of the equilibrium constant
M	(kg mol <sup>-1</sup> )	molar mass
$m_{tracer}$	(kg)	total mass of tracer
$\dot{m}$	(kg s <sup>-1</sup> )	mass flux
m	(kg)	mass
$\dot{n}$	(mol s <sup>-1</sup> )	molar flux
$n_i$	(mol)	amount of substance i
$p^{sat}$	(Pa)	saturated vapour pressure
$\dot{Q}_C$	(W)	heat duty of the condenser
$\dot{Q}_R$	(W)	reboiler duty
r	(mol s <sup>-1</sup> kg(cat) <sup>-1</sup> )	reaction rate
R	8.314 (J mol <sup>-1</sup> K <sup>-1</sup> )	universal gas constant
T	(K)	temperature
$T_b$	(K)	boiling point
v	(-)	reflux ratio
$\dot{V}$	(m <sup>3</sup> s <sup>-1</sup> )	volume flow rate

$V_m$	$(\text{m}^3 \text{mol}^{-1})$	molar volume
$w_i$	(-)	weight fraction of component i
$x_i$	(-)	mole fraction of component i in the liquid phase
$X_i$	(-)	liquid phase composition variable for reactive phase diagrams
$X_{\text{Lac}}$	(-)	lactic acid conversion
$Y_{\text{EL,Lac}}$	(-)	yield of ethyl lactate referring to lactic acid
$y_i$	(-)	mole fraction of component i in the vapour phase
$Y_i$	(-)	vapour phase composition variable for reactive phase diagrams
$\gamma_i$	(-)	activity coefficient of component i
$\eta$	(Pa s)	dynamic viscosity
$\vartheta$	(°C)	Celsius temperature
$v_i$	(-)	stoichiometric coefficient
$\rho$	$(\text{kg m}^{-3})$	density
$\rho_b$	$(\text{kg m}^{-3})$	bulk density
$\sigma$	$(\text{N m}^{-1})$	surface tension
$\tau$	(s)	mean residence time
$\phi_i$	(-)	fugacity coefficient of component i

## Indices

cat	catalyst
EL	ethyl lactate
est	estimated
EtOH	ethanol
L	liquid
Lac	lactic acid
max	maximal value
min	minimal value
r	reaction
req	required
W	water
0	initial state
*	state of chemical equilibrium

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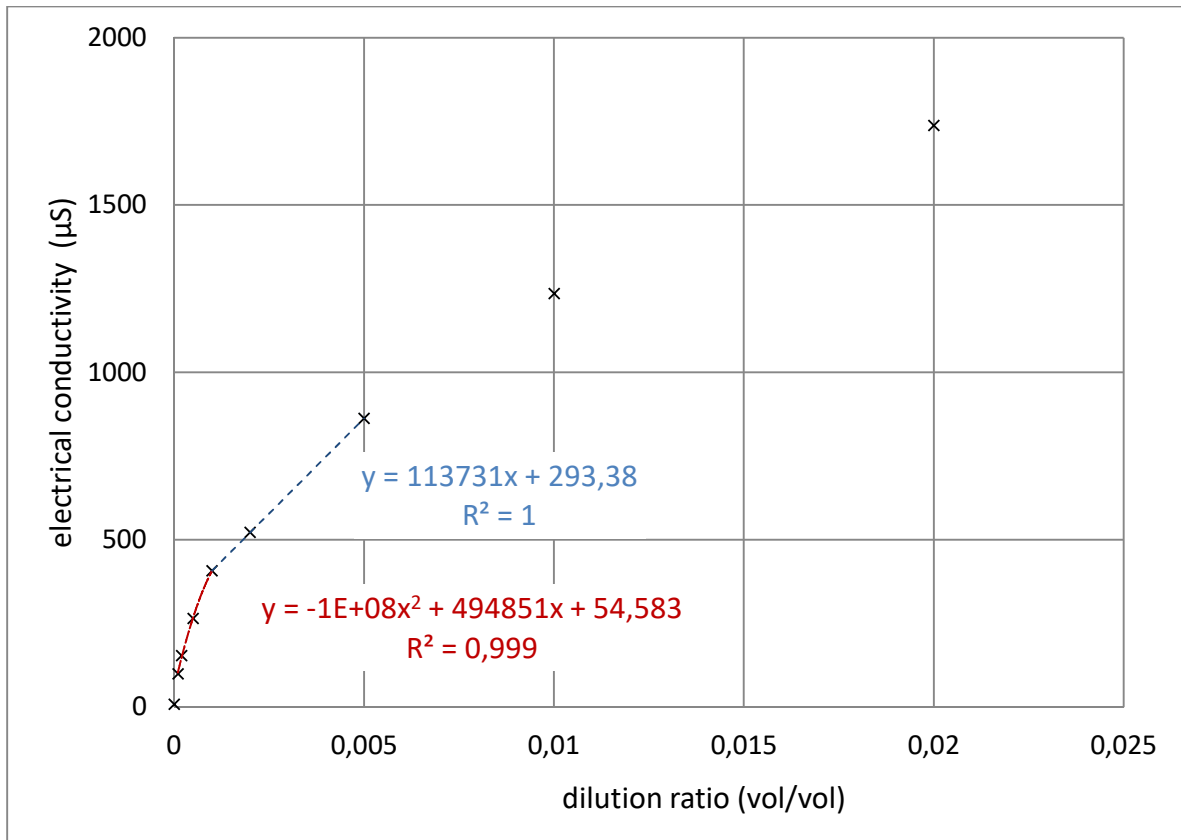
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# Appendix



*Calibration function for tracer (80 w% lactic acid) concentration by electrical conductivity (EC) measurements*