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RESEARCH ARTICLE

# REVISED Ethyl lactate production by reactive distillation – optimization of reaction kinetics and energy efficiency

[version 2; peer review: 2 approved]

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## Abstract

**Background:** Ethyl lactate is an environmentally benign solvent, which could substitute petrol-based volatile organic compounds (VOCs) in many applications if production costs are reduced. It is usually produced by the esterification of lactic acid with ethanol – two important chemical building blocks of biorefineries that are available at industrial scale. Reactive distillation is a promising alternative production process, which utilises process intensification to increase energy efficiency and space-time yield by enhancing the reaction kinetics.
**Methods:** In this work, process intensification of ethyl lactate production by means of distillation was analysed with special focus on the efficient separation of water. Different setups were evaluated. The feedstock requirements were studied and the process was optimized regarding reaction kinetics in experiments on laboratory level. The preparation of anhydrous starting mixtures for ethyl lactate formation was tested in batch experiments and applied to reactive distillation. The simultaneous distillation was optimized and assessed for its energy efficiency. For this purpose, integrated reactive distillation was compared to a simple setup for distillation enhanced esterification.
**Results:** It was found that an optimized serial setup of reactors and distillation steps can offer similar process intensification at a lower distillate rate compared to simultaneous reactive distillation and is therefore more energy efficient. Moreover, the serial setup is more flexible and straight-forward to regulate and scale-up.
**Conclusions:** Based on the experimental results, the optimal setup and parameters of a continuous process for ethyl lactate production by distillation enhanced esterification was presented.

## Keywords

ethyl lactate, reactive distillation, process intensification, biorefinery

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**REVISED** **Amendments from Version 1**

The authors would like to thank the reviewers for the time and effort dedicated to reviewing our paper. Version 2 contains the following changes in response to their insightful suggestions:

- Clarifications regarding the context and novelty of the work were made.
- The methods and validation of the experiments were described more precisely.
- The initial reaction rates were calculated for batch experiments to increase comparability of the kinetics results.
- The mass balances of the continuous process and the composition of the individual streams were presented, based on additional experimental data. Hydrolyzed lactic acid feedstock was prepared using an adapted experimental procedure to address reservations regarding lactic acid oligomers.

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## Plain language summary

Ethyl lactate is an environmentally-friendly and safe chemical, which is produced from biological resources. It could replace conventional petrol-based solvents in many products such as paints and cleaning agents, which could improve air quality and contribute to the reduction of carbon dioxide ($CO_2$) emissions. However, the production cost of ethyl lactate has to be reduced for these applications. In this article we present the research we did into the development of an alternative process for the production of ethyl lactate from ethanol and lactic acid, which is called reactive distillation. It is an efficient process that could save energy and equipment costs. We considered different experimental setups and investigated the influence of feedstock composition and different technical process parameters in laboratory experiments. It was important to reduce the water content of the feedstock to achieve good performance results. We concluded that a series of process steps is more efficient than an integrated design in a single apparatus. Based on these results process design for a larger production scale is being continued.


## Introduction

Ethyl lactate is an environmentally benign solvent, which is typically produced from bio-based feedstock. It exhibits very low toxicity, is not ozone-depleting and is readily bio-degradable (Pereira *et al.*, 2011). Ethyl lactate shows favorable solvency properties for many applications. It has the potential to substitute petrol-based volatile organic compounds (VOCs) in a vast range of applications if production costs are reduced (de Jong *et al.*, 2010). Ethyl lactate is especially interesting for applications that include the release of solvent into the environment, such as coatings, paints and domestic cleaning products. According to the EU emission inventory report, domestic solvent use and coating applications together accounted for 27% of the total non-methane volatile organic compound (NMVOC) emissions in the EU in 2017 (European Environment Agency, 2019). Substituting conventional solvents by ethyl lactate could offer health and environmental benefits.

Ethyl lactate is usually produced by the esterification of lactic acid with ethanol using an acid catalyst. Both reactants are important building blocks of biorefineries that are available at industrial scale. Production processes for ethyl lactate have been patented (Martino-Gauchi & Teissier, 2004; Martino-Gauchi & Teissier, 2007; Tretjak *et al.*, 2006; Tretjak & Teissier, 2004) and industrialized (Rosales-Calderon & Arantes, 2019). However, these processes are characterized by low reaction rates and consequently, high capital and operating costs. A number of alternative processes are being developed, the most promising being membrane processes and reactive distillation (see Figure 1) (Pereira *et al.*, 2011). These processes utilize the effect of process intensification.

By removing the side product water from the mixture during reaction, the equilibrium limitation of conventional batch reactors is overcome. The chemical equilibrium gets re-established following the law of mass action. Therefore, lactic acid conversion above the batch equilibrium can be reached. The driving force is retained at a high level and the reaction kinetics is enhanced. (Keller, 2014) As a result, the energy efficiency and space-time yield of such processes are considerably higher.

The production of ethyl lactate by reactive distillation has been previously studied by Asthana *et al.* (2005), who tested the simultaneous esterification and separation of ethanol and water in a single apparatus and reached a lactic acid conversion of >90% and a ethyl lactate yield of 73%, but accepted high amounts of oligomers in the raw product stream, which required an additional process unit for refining. Gao *et al.* (2007) optimized operation parameters and reported an ethyl lactate yield of 53%.

The production of ethyl lactate is not a straight-forward reactive distillation task, where one of the reaction products exhibits the lowest or highest volatility of the quaternary mixture. Total acid conversion and the recovery of pure ester product cannot be easily achieved by optimization of column operation conditions (Asthana *et al.*, 2005). Using a distillation column with a reflux ration RR>0 in the case of ethyl lactate formation would concentrate ethanol in the distillate and consequently, retain water in the system. In the present work this undesired effect was omitted by a redesign of the reactor equipment. Different experimental setups for distillation enhanced esterification without column were tested. The process was optimized by experiments at laboratory level. The target was to reach close to entire lactic acid conversion and ethyl lactate yield, while keeping losses by oligomerization and the energy demand as low as possible. Special focus lay on the feedstock requirements and the efficient separation of water. Calculations regarding material and energy balances were added. Based on the results, the optimal setup for continuous

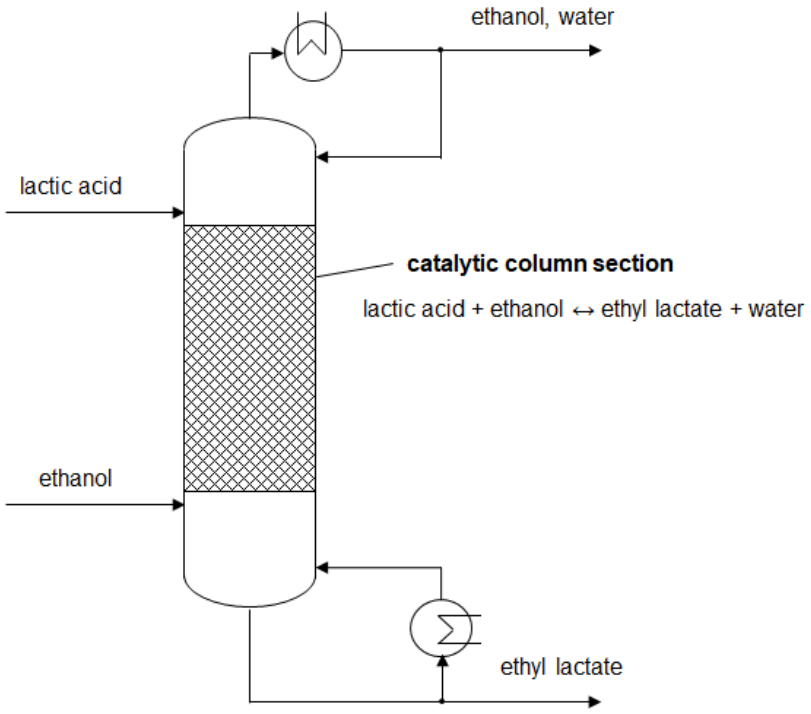



**Figure 1. Schematic illustration of ethyl lactate production by reactive distillation.**

ethyl lactate production by distillation enhanced esterification was proposed. The described actions were taken in preparation for piloting.

A heterogeneous catalyst was used to enable easy separation. Amberlyst resins were chosen, because they show favorable catalytic properties at low water concentrations (Nguyen *et al.*, 2018) and are commonly used in literature (Pereira *et al.*, 2011). Three different cation-exchange resins were tested in batch experiments.

Delgado *et al.* (2007) found that the positive effect of excess ethanol on the equilibrium constant is declining. A molar reactant ratio of $n_{EtOH}/n_{LA}$= 3/1 was proposed as optimal value in literature (Asthana *et al.*, 2005), according to which the starting mixtures of all experiments in this work were prepared.

Technical grade input chemicals (especially lactic acid feedstock) contain high amounts of water, which is undesired in the process. As side-product of the esterification reaction, water limits reaction rate and lactic acid conversion. The reaction kinetics of the esterification of lactic acid with ethanol has been studied extensively, using different lactic acid concentrations from dilute (approx. 20 w%) to concentrated lactic acid (88 w%). Pereira *et al.* (2011) gave a comprehensive review of kinetics studies literature. However, the concentration range above commercially available 88 w% lactic acid solutions has not yet been considered.

Due to its bifunctional structure, lactic acid undergoes intermolecular self-esterification and tends to form oligomers in concentrated solutions (Asthana *et al.*, 2005). For example, in technical (88 w%) lactic acid solutions at equilibrium, 33% of lactic acid equivalents are present in the form of oligomers (Vu *et al.*, 2005). However, oligomerization is suppressed by the presence of ethanol. If a technical grade (88 w%) lactic acid solution is mixed with ethanol at a molar ratio $n_{EtOH}/n_{LA}$ =1, the oligomer content at equilibrium is reduced to 2.4 mol%, and at a ratio of $n_{EtOH}/n_{LA}$ =3 it is 0.4 mol%. (Pereira *et al.*, 2008) The feasibility of ethyl lactate formation with dehydrated feedstock was first tested in batch experiments and then applied to reactive distillation.

It is expected that the capacity for water removal increases with purity of the ethanol feed. Asthana *et al.* (2005) suggested that an azeotropic ethanol-water feed mixture could be used to produce ethyl lactate via reactive distillation, which would have significant economic advantages. In this work the influence of ethanol feed purity was tested in reactive distillation experiments on laboratory level.

In reactive distillation, where the heterogeneously catalyzed esterification reaction is combined with a simultaneous separation operation, several effects can act limiting to lactic acid conversion:

- The chemical reaction at the catalytic site – characterized by the concentration of the components and the catalytic capacity of the catalyst particles.

- Mass transport between catalyst and bulk phase – For Amberlyst resins this step can be neglected at moderate stirrer speed (Chakrabarti & Sharma, 1993; Delgado *et al.*, 2007).
- Distillation: The separation of water from the bulk phase can potentially be the rate-determining step. To determine the optimal operation conditions, a variation of the stripping agent (ethanol feed purity) and distillate rate was performed.

## Methods

### Materials

Lactic acid (88 w%) was purchased from Carl Roth (Austria), ethanol of two purity levels (96% and 99.9%) was purchased from Australco (Austria). The cation-exchange resins Amberlyst 15, Amberlyst 46 and Amberlyst 48 (Dow, Germany) were used as acid catalysts.

### Analytics

Samples of the reaction mixture of 2 mL volume were cooled to ambient temperature immediately and stored at approx. 281 K for analytical measurements. Lactic acid, ethanol and ethyl lactate were quantified by HPLC measurements. A Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) was used with 5 mM sulfuric acid (aqueous solution) as mobile phase. Lactic acid and ethyl lactate were detected with an UV sensor (Agilent G1315B at 224 nm), ethanol was detected by a refractive index sensor (Agilent G1362A). The composition of binary mixtures of ethanol and water (distillate) was determined by density measurements using an oscillating U-tube device (DMA 35, Parr).

### Experimental procedures

In a first set of experiments the influence of the catalyst and the initial composition were studied in batch experiments. The aim of these initial tests was to determine the optimal starting conditions for reactive distillation. Based on these results, a semi-batch process for simultaneous reactive distillation was optimized. The effect of ethanol feed purity and heat duty was evaluated. Finally, the simultaneous reactive distillation process at optimized conditions was assessed regarding its energy efficiency and economic viability. For the conventional process used in industry there is a lack of publicly available data regarding its energy demand and operation costs. Therefore, a simple serial setup for distillation enhanced esterification was used as a reference. All experiments were conducted at least in duplicate, the main findings were conducted at least in triplicate and are represented by means and standard deviations (SD).

***Batch experiments.*** The evaluation of different catalysts and starting mixtures was done in batch experiments. Ethanol and lactic acid were mixed thoroughly in a 0.25 L round bottom flask equipped with a reflux condenser at an initial molar ratio of $n_{EtOH}/n_{LA}$ = 3 (0.17 kg reaction mixture). The mixture was heated to reflux temperature (355 K) using a thermal oil bath. A reference sample was taken as a starting point before the catalyst was added to the mixture (weight fraction $w_{cat}$ = 0.1). The initial reaction rate $r_0$ was calculated from the change of lactic acid concentration in the first 0.5 h of reaction. Three different cation-exchange resins were tested as catalysts for ethyl lactate formation using commercial grade lactic acid (88 w%) and ethanol (96%). Amberlyst 46 showed the highest catalytic activity under the studied conditions and was used in all following experiments.

The influence of the initial water content on the esterification reaction was studied using different starting mixtures as listed in Table 1. For batch No. 1 an 80 w% lactic acid solution was provided by adding deionized water to a commercial lactic acid solution. In batch No.2 the technical grade lactic acid solution was used directly. For batch No.3 and No.4 highly concentrated lactic acid solutions were prepared by a pre-treatment via vacuum distillation at 2 kPa and 353 K using a rotary evaporator (R205, Büchi). The final content of water was determined by a mass balance. The distillate was checked for its lactic acid content, which was <5 w% in all experiments. It is not expected that significant oligomerization occurred during the pre-treatment. However, the oligomer content present in technical grade lactic acid was most certainly concentrated and remained unavailable for ethyl lactate formation. The lactic acid conversion was calculated from the change of the lactic acid monomer concentration.

***Reactive distillation experiments.*** A conventional distillation apparatus was used to execute the reactive distillation experiments (Figure 2). The starting mixture (0.17 kg) was prepared from highly concentrated lactic acid (100 w%) and ethanol (99.9 vol%) at an initial molar ratio of $n_{EtOH}/n_{LA}$ = 3 as in

**Table 1. Starting mixtures for batch kinetics experiments.**

| Batch No. | Ethanol purity (vol%) | Lactic acid purity (w%) | Initial water fraction (mol/mol) |
|---|---|---|---|
| 1 | 96 | 80 | 0.29 |
| 2 | 96 | 88 | 0.19 |
| 3 | 96 | 100 (pre-treated) | 0.09 |
| 4 | 99.9 | 100 (pre-treated) | 0.00 |

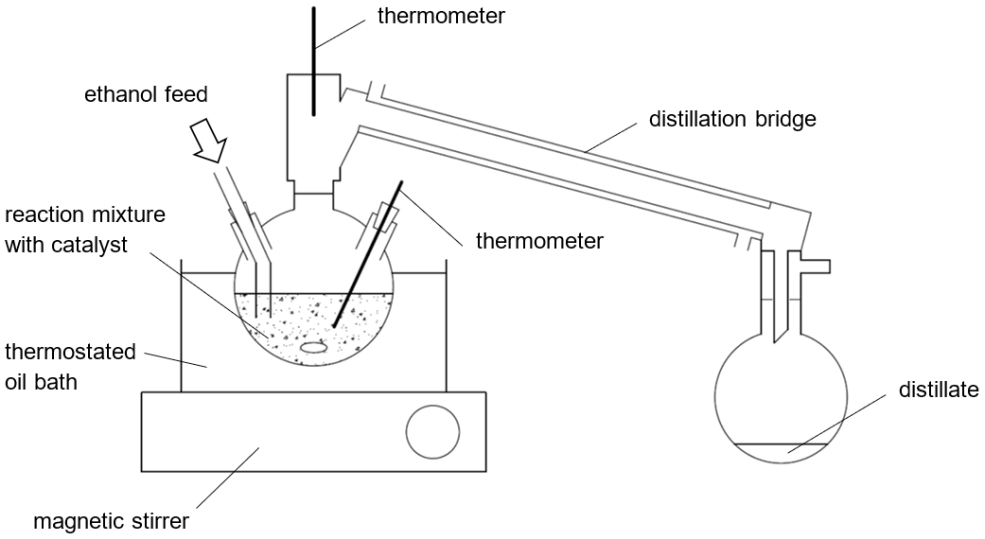



**Figure 2. Schematic illustration of the experimental setup.**

batch No. 4 (Table 1). The reactive mixture was magnetically stirred in a 0.25 L round bottom flask. The flask was heated using a thermal oil bath. When the boiling point of the mixture was reached, a reference sample was taken before the catalyst was added (Amberlyst 46, weight fraction $w_{cat}$=0.1). Distillate was continuously removed by a distillation bridge and collected in a flask. Every 20 minutes the volume and density of the collected distillate were measured. The distillate flux was calculated form the mass of distillate collected per period of time. The ethanol weight fraction of the distillate was determined according to its density. The ethanol feed flux required to compensate for ethanol losses into the distillate and maintain the initial molar reactant ratio constant was calculated and the corresponding amount of ethanol was added manually every 10 minutes.

The effect of ethanol feed purity and heat duty on the reaction kinetics were studied considering two purity levels of ethanol as stripping agent (96% and 99.9%). The heat duty was controlled by setting the oil bath temperature in the range of 373-385 K, which was kept constant (±0.1 K) throughout each experiment. The effective specific heat duty $\dot{q}_{eff}$ was determined indirectly from data of the feed and distillate flux using an energy balance. It was calculated according to Equation 1, where $m_r$ is the mass of the reaction mixture, $\dot{m}_F$ is the feed flux, $h_F$ is the specific enthalpy of the feed, $\dot{m}_D$ is the distillate flux and $h_D$ is the specific enthalpy of the distillate. The specific enthalpy of the feed and distillate was calculated according to its composition from values of the individual components from literature (Haar *et al.*, 1988; Majer & Svoboda, 1985; Pedersen *et al.*, 1975). All measured values and calculations for each specific experiment can be found in the underlying data.

$$\text{Eq. 1:} \quad \dot{q}_{eff} = \frac{1}{m_r}(\dot{m}_D \cdot h_D - \dot{m}_F \cdot h_F)$$

***Serial setup of reaction and distillation.*** A serial setup of batch reactors and distillation steps was used as benchmark to assess simultaneous reactive distillation. The starting mixture (0.17 kg) was prepared from highly concentrated lactic acid (100 w%) and ethanol (99.9 vol%) at an initial molar ratio of $n_{EtOH}/n_{LA}$ = 3 as in batch No. 4 (Table 1). Batch reaction was conducted as described above (in section *Batch experiments*). In each step the reaction was carried out until approaching equilibrium. Then, the mixture was cooled to ambient temperature and catalyst was remove by filtration (paper filter). Ethanol and water were removed by vacuum distillation (10 kPa, 333K, Büchi R205). Mass and composition of the distillate were measured. The amount of ethanol removed was replaced by fresh ethanol as a feed. Two levels of ethanol feed purity (96% and 99.9%) were evaluated. The obtained mixture was used as starting mixture for the next batch reaction step.

***Design of a continuous process.*** A serial setup of two reactors and an intermediate distillation steps was found as optimal setup in the previous experiments. To determine the mass balances for a continuous production process, starting mixtures were prepared from hydrolyzed lactic acid. To this end, technical grade lactic acid was diluted with deionized water to a 27 w% solution and equilibrated in a batch reactor with 10 w% Amberlyst 46 for 24 h at 363 K. At this concentration, oligomers account for <3 w% of the total lactic acid content at equilibrium (Vu *et al.*, 2005). The solution was then dehydrated following the usual pre-treatment procedure via vacuum distillation at 2 kPa and 318-353 K using a rotary evaporator

(R205, Büchi), whereas the total time above 323 K was 0.25 h. The solution was cooled to ambient temperature and ethanol (99.9%) was added immediately in a molar ratio of $n_{EtOH}/n_{LA}$ = 3. Using the obtained starting mixture, the experiment was conducted as described in section *Serial setup of reaction and distillation*. In the calculation of the mass balances, it was assumed that oligomers accounted for 3% of the total lactic acid content and remained unreacted throughout the process.

## Results and discussion

### Batch experiments

***Influence of catalyst.*** Three different catalysts were evaluated in batch experiments for the esterification of lactic acid with ethanol at a catalyst weight fraction of $w_{cat}$=0.1 at reflux temperature (355K). The reaction kinetics are shown in Figure 3. The initial reaction rates are presented in Table 2. Amberlyst 46 showed the highest catalytic activity under the studied conditions. Using this resin, 98% of the equilibrium conversion was reached within 2 h. It should be stressed that Amberlyst 46 has a lower density (600 g/L) than Amberlyst 48 (820 g/L) and Amberlyst 15 (780 g/L). Hence, the volume fraction of catalyst used in the experiments was Amberlyst 46 > Amberlyst 15 > Amberlyst 48.

***Influence of the starting mixture.*** A variation of the starting mixture regarding the initial water fraction was done in batch experiments at a catalyst weight fraction of $w_{cat}$=0.1 (Amberlyst 46) at reflux temperature (355K). Table 3 shows the equilibrium values and initial reaction rate for all considered concentration levels.

A low initial water fraction was beneficial to the equilibrium conversion as well as the reaction kinetics. When dehydrated starting mixtures were used the chemical equilibrium was reached after 1 h at 71% lactic acid conversion, compared to

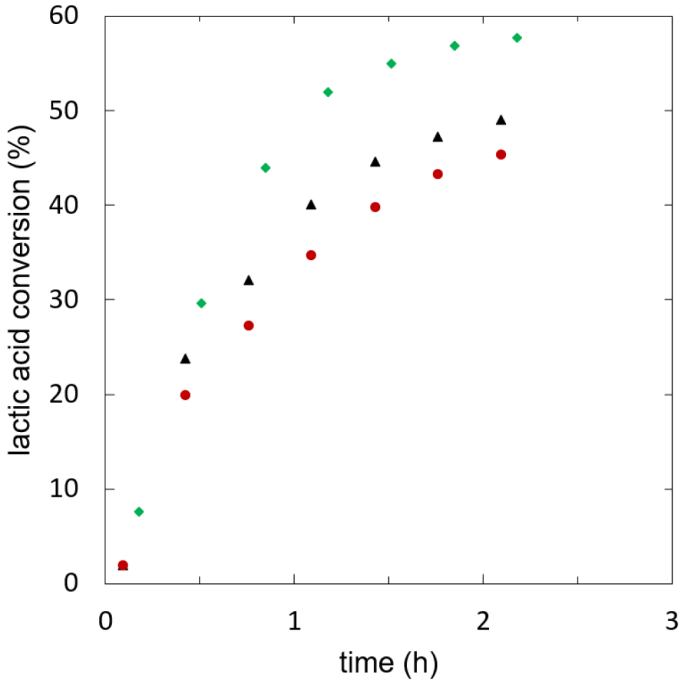



**Figure 3. Batch esterification of lactic acid with ethanol using different heterogeneous catalysts ($w_{cat}$=0.1): Amberlyst 15w (▲), Amberlyst 46 (◆), Amberlyst 48 (●).**

**Table 2. Initial reaction rate of batch esterification of lactic acid with ethanol using different catalysts.**

| Type of catalyst | Initial reaction rate $r_0$ (mol $L^{-1}$ $h^{-1}$) |
|---|---|
| Amberlyst 15 | 1.94 |
| Amberlyst 46 | 2.11 |
| Amberlyst 48 | 1.67 |

**Table 3. Equilibrium values for batch esterification of lactic acid with ethanol using different starting mixtures.**

| Initial water fraction $x_{w,0}$ (mol/mol) | Initial reaction rate $r_0$ (mol $L^{-1}$ $h^{-1}$) | Lactic acid conversion at equilibrium $X_{LA,Eq}$ (-) | Time to equilibrium $t_{Eq}$ (h) |
|---|---|---|---|
| 0.00 | 3.02 | 0.71 | 1 |
| 0.09 | 2.69 | 0.65 | 2 |
| 0.19 | 2.11 | 0.59 | 2.5 |
| 0.29 | 1.79 | 0.56 | 5 |

59% lactic acid conversion after 2.5 h when using commercial grade chemicals (19 mol% initial water fraction). Figure 4 shows lactic acid conversion over time.

Removing water from lactic acid feed before mixing with ethanol showed notable advantages. The challenges of the reactive separation process can be significantly reduced due to very low water content of starting mixtures. When preparing the starting mixture, the earliness of mixing is of major importance. Preferably, lactic acid is mixed with ethanol immediately after dehydration. By this, the formation of lactic acid oligomers can be suppressed. Oligomerization of lactic acid (and the hydrolysis of oligomers, respectively) proceeds relatively slow compared to ethyl lactate formation (Pereira *et al.*, 2008). Therefore, it should be prevented in order to avoid limitations in the supply of lactic acid monomers during ethyl lactate formation.

### Reactive distillation experiments

Ethanol was used as stripping agent for removing water during semi-batch reactive distillation experiments. The influence of the distillate rate and the corresponding heat duty on the reaction kinetics was evaluated. Figure 5 shows lactic acid conversion over time.

As shown in Figure 6, the kinetics was improved by increasing the heat duty until reaching an optimum. When the heat duty was increased further no significant change in the reaction kinetics was observed. In experiments the optimal kinetics was reached at 141.8 W/kg specific effective heat duty and 0.488 kg/kg h specific distillate rate, whereas the optimum for the heat duty is expected around 127 W/kg. The separation of water from the bulk phase is not expected to limit the reaction kinetics at optimal conditions, as increasing separation capacity did not additionally enhance the reaction.

The influence of ethanol feed purity was evaluated at a specific effective heat duty in the range of 140-155 W/kg. Figure 7 shows the reaction kinetics of ethyl lactate formation in reactive distillation experiments using ethanol of two different purity levels (96% and 99.9%) as stripping agent. When 96% ethanol was used, reactive distillation performed similarly to batch reaction, whilst the conversion was below the batch equilibrium. A conversion of 70% was reached after 1 h. Then, the reaction proceeded further and the batch equilibrium was overcome. After 3.1 h a conversion of 75% was reached. A switch of the stripping agent to dehydrated ethanol after the first reaction phase was tested, which increased the reaction rate. Using dehydrated ethanol as a stripping agent from the start lead to superior reaction kinetics even below the batch equilibrium. A conversion of 90% (SD = 0.77%) was reached after 2.27 h of reaction. The overall feed ratio was 4.1 kg ethanol/kg lactic acid. At this operation point the optimum of the reaction kinetics for integrated reactive distillation was found.

The obtained reaction kinetics was superior to similar processes reported in the literature, where a lactic acid conversion of about 90% was reached after 4 h (Khunnonkwao *et al.*, 2012; Tanaka *et al.*, 2002). This can be explained by the reduced water content of the feedstock used in this work.

### Serial setup of reaction and distillation

A serial setup of batch reactors and distillation units was used as a benchmark to assess the simultaneous reactive distillation under optimal conditions. In a first step the reaction was carried out until approaching batch equilibrium. A lactic acid conversion of 69% (SD = 0.47%) was reached after 0.83 h. Ethanol and water were almost entirely removed in a vacuum distillation step and replaced by dehydrated ethanol (99.9%). The starting mixture for the second reaction step was almost water-free again. The reaction was intensified and the chemical equilibrium was obtained after 0.5 h of reaction at 86% (SD = 0.30%) lactic acid conversion. After a second distillation and replacement step, 91% (SD = 0.97%) lactic acid conversion was reached at 1.8 h total reaction time. In the second distillation step a significant amount of ethyl lactate was detected in the distillate (<10 wt%), which was in a similar range as the additional ethyl lactate formed in reaction 3. In Figure 8 the series of batch reaction and distillation is compared to the simultaneous reactive distillation under optimal conditions. Both processes showed similar reaction kinetics. The serial setup is more favorable in terms of efficiency, as the overall feed ratio was 3.8 kg ethanol/kg lactic acid for 90% conversion compared to 4.1 kg/kg for the simultaneous process. If two reaction steps are considered the overall feed ratio

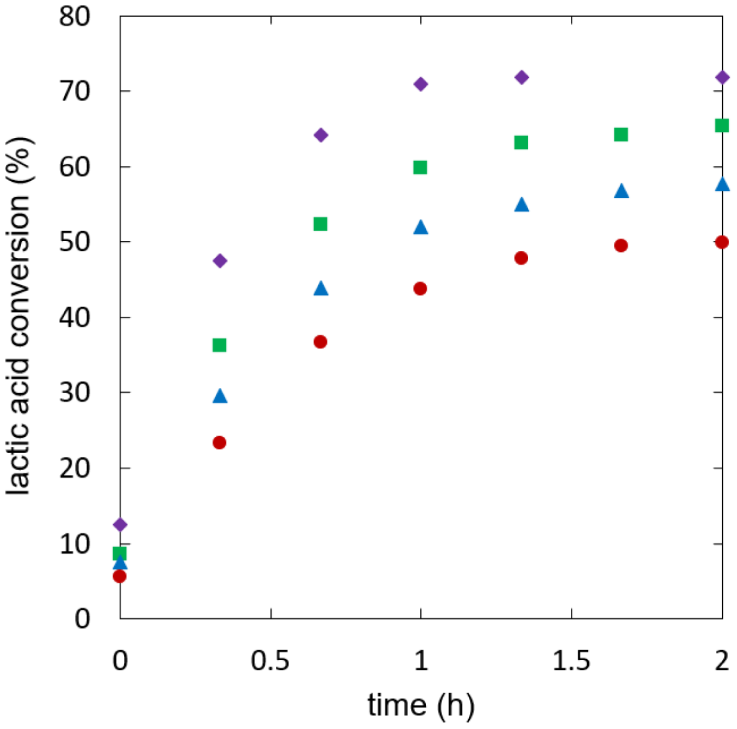



**Figure 4.** **Reaction kinetics of ethyl lactate formation in batch experiments using different starting mixtures, initial water fraction (mol/mol): 0.00 (◆), 0.09 (■), 0.19 (▲), 0.29 (●).**

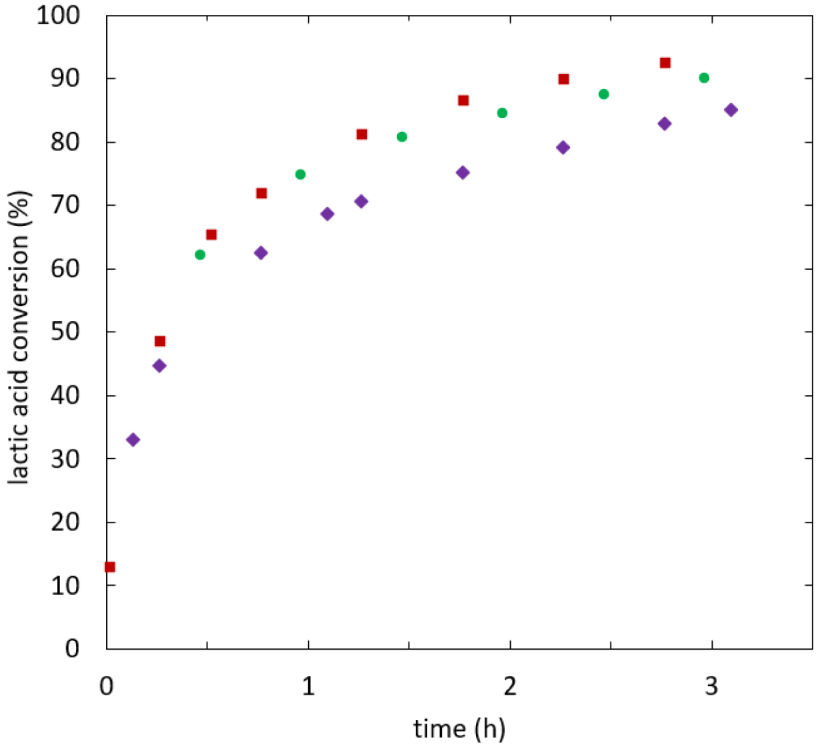



**Figure 5.** **Reaction kinetics for ethyl lactate formation in semi-batch reactive distillation, specific effective heat duty (W/kg): 112.6 (◆), 121.5 (●), 141.8-209.7 (■).**

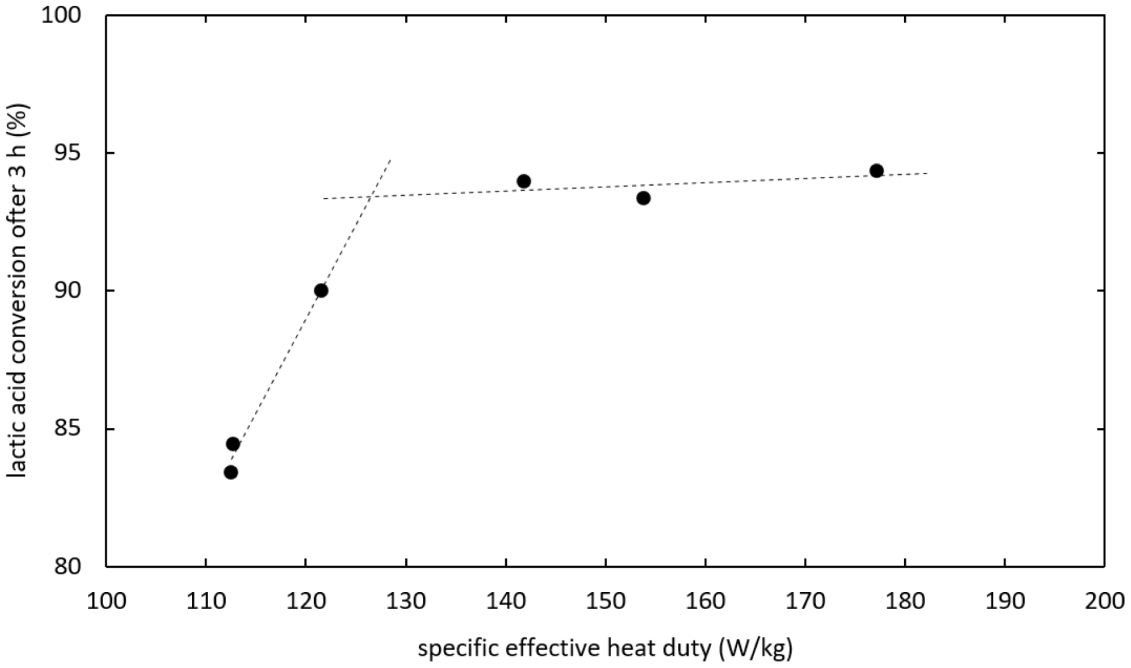



**Figure 6.** **Influence of heat duty on ethyl lactate production via reactive distillation.**

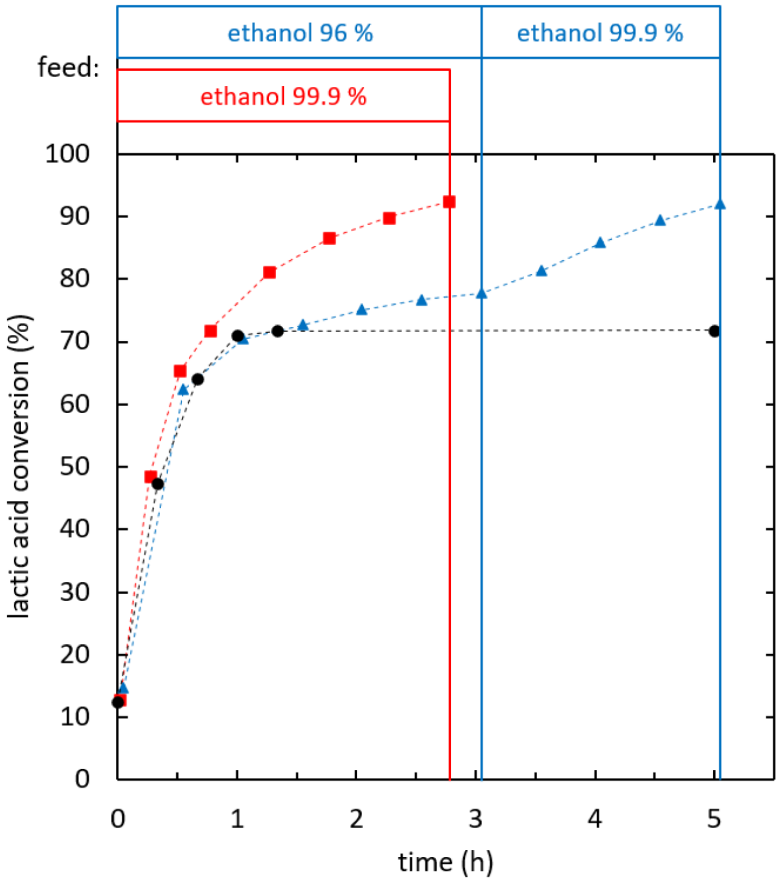



**Figure 7.** **Influence of ethanol feed purity on ethyl lactate production via reactive distillation (■) and (▲), batch reaction (●).**

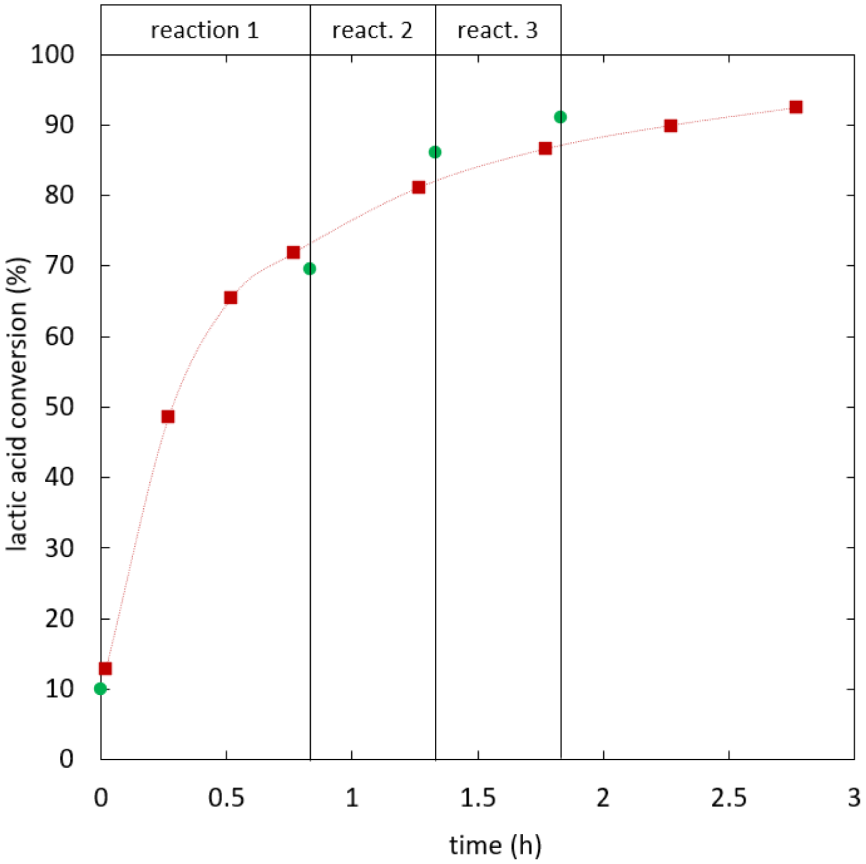



**Figure 8. Integrated reactive distillation (■) compared to a serial setup of batch reactions and distillation steps (●) at 99.9% ethanol feed purity.**

was 2.6 kg/kg compared to 3.2 kg/kg required to reach 86% lactic acid conversion in integrated reactive distillation.

The influence of feed purity in the serial process was tested. The same procedure as described above was used; however, 96% ethanol was added in the replacement steps. The results were compared to combined reactive distillation with the same feed purity in Figure 9. The reaction kinetics of both processes was similar. Ethyl lactate was detected in the distillate of both intermediate distillation steps.

## Design of a continuous process

In typical reactive distillation technology the process is intensified by the simultaneous separation of products during the reaction. However, ethyl lactate production is not a straightforward optimization task. Neither of the reaction products exhibits the highest, nor the lowest volatility of the multi-component system. In this case optimal separation is obtained without reflux, using ethanol as stripping agent for the side-product water.

Even at optimal reaction conditions the required residence time for 90% lactic acid conversion was determined to be >2 h. Reactive distillation in a vertical column would therefore require either an extensive column height, or a very low flow rate in the vertical direction that could only be attained by special column installations.

In a horizontal setup of tubular reactors, which enables simultaneous distillation, low flow rates could easily be established. However, such a setup would require a complex regulating and heating system and many feed points for ethanol. Membrane reactors would probably offer a more efficient option if simultaneous separation was envisaged.

In this work a different approach to process intensification by means of distillation is proposed. The flow sheet of the continuous process is shown in Figure 10. A concept with two tubular reactors, an intermediate distillate replacement step and the downstream separation of ethanol and water offers favorable reaction kinetics and high reactant conversion while keeping losses of ethyl lactate into the distillate at a low level. A second intermediate distillation step is not recommended, because the losses of ethyl lactate into the distillate would be of similar magnitude as the additionally formed ethyl lactate in a third reaction step. Special attention should be given to the design of the lactic acid pre-treatment and the intermediate distillation equipment. Rapid separation at

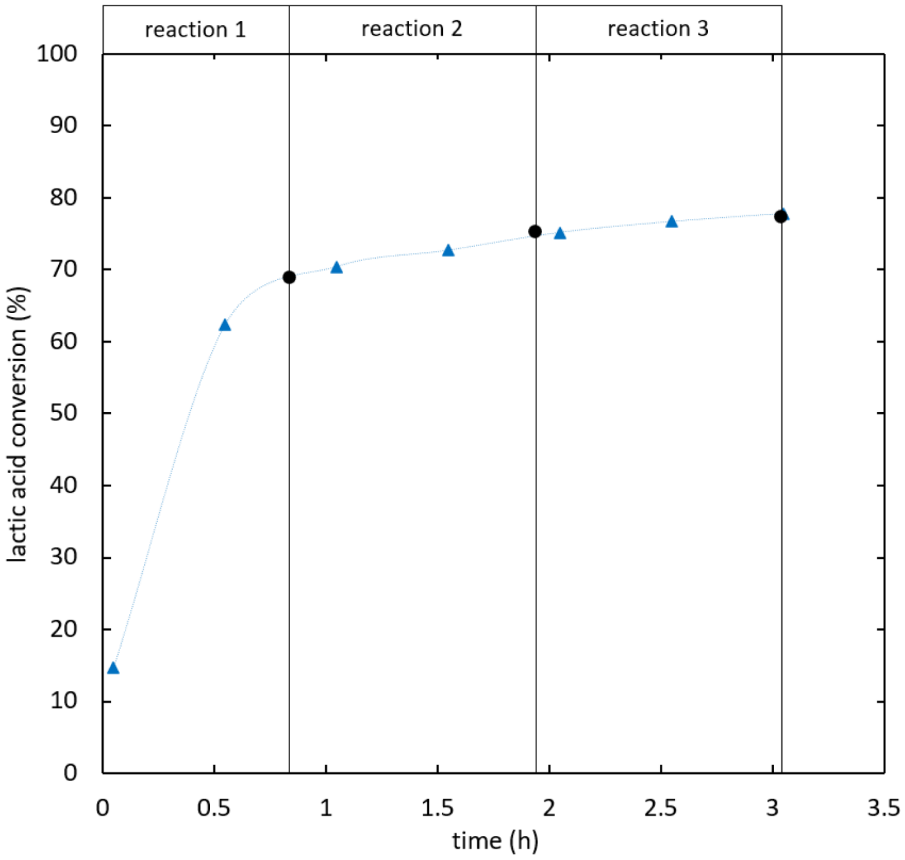



**Figure 9. Integrated reactive distillation (▲) compared to a serial setup of batch reactions and distillation steps (●) at 96% ethanol feed purity.**

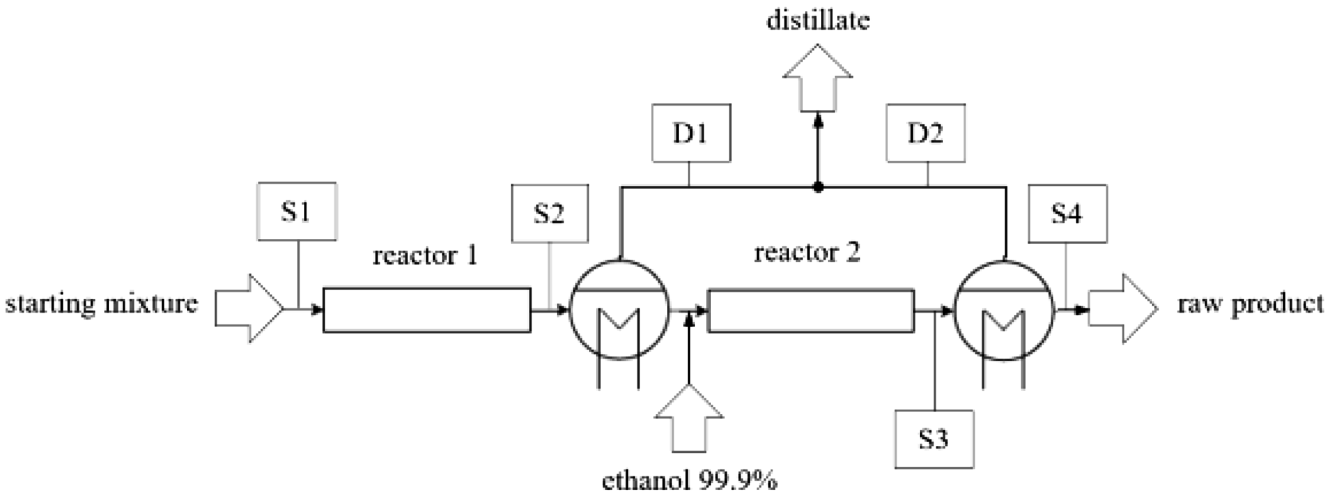



**Figure 10. Schematic flowsheet of a continuous process for ethyl lactate production via distillation enhanced esterification of lactic acid with ethanol.**

moderate conditions and the earliness of mixing with ethanol are important in order to suppress oligomerization of lactic acid kinetically. The mass balances presented in Table 4 were determined experimentally, using hydrolyzed lactic acid feedstock. The proposed setup can be built compactly, is easily scalable and offers very efficient operation. An additional

**Table 4. Mass balances of the continuous process presented in Figure 10.**

| stream | specific mass flux (kg/kg ethyl lactate output) | weight fraction (kg/kg) | | | | |
|---|---|---|---|---|---|---|
| | | lactic acid | ethanol | ethyl lactate | water | oligomers |
| S1 | 2.51 (SD=0.06) | 0.37 (SD=0.022) | 0.63 (SD=0.022) | 0.00 (SD=0.000) | 0.02 (SD=0.003) | 0.01 (SD=0.001) |
| S2 | 2.51 (SD=0.06) | 0.11 (SD=0.006) | 0.48 (SD=0.013) | 0.33 (SD=0.004) | 0.07 (SD=0.003) | 0.01 (SD=0.000) |
| D1 | 1.26 (SD=0.09) | 0.00 (SD=0.000) | 0.86 (SD=0.009) | 0.01 (SD=0.005) | 0.13 (SD=0.009) | 0.00 (SD=0.000) |
| S3 | 1.20 (SD=0.08) | 0.06 (SD=0.013) | 0.49 (SD=0.011) | 0.43 (SD=0.002) | 0.01 (SD=0.001) | 0.01 (SD=0.000) |
| D2 | 1.30 (SD=0.10) | 0.00 (SD=0.000) | 0.94 (SD=0.004) | 0.04 (SD=0.002) | 0.02 (SD=0.002) | 0.00 (SD=0.000) |
| S4 | 1.17 (SD=0.05) | 0.12 (SD=0.024) | 0.00 (SD=0.001) | 0.85 (SD=0.024) | 0.00 (SD=0.000) | 0.02 (SD=0.000) |

purification step is required to remove residual lactic acid form the raw product stream and obtain commercial grade ethyl lactate.

The use of dehydrated ethanol (99.9%) is crucial to the effective separation of water. Significant process intensification could only be achieved using a dehydrated ethanol feed as stripping agent. For efficient operation of the process – especially from an economic perspective – a unit for the recovery of ethanol from the distillate is required. Dehydration of ethanol is a well-established process in industry and economically viable at a large scale. It can be done either by adsorption of water on a molar sieve, or by membrane processes such as pervaporation (Baeyens *et al.*, 2015; Jyothi *et al.*, 2019; Vane, 2008).

## Conclusion

In this work the optimal setup and parameters for the production of ethyl lactate by distillation enhanced esterification were determined. The reactor design for reactive distillation was reassessed, considering the disadvantages of distillation columns in the separation of water from the mixtures present in the process. Different setups for distillation enhanced esterification without column were evaluated. The feedstock requirements were evaluated. Removing water from lactic acid feedstock solutions before mixing with ethanol was tested in batch experiments and applied to reactive distillation. These starting mixtures showed significant advantages that reduced the challenges of the reactive separation task.

A semi-batch process for simultaneous reactive distillation was optimized regarding reaction kinetics and energy efficiency. A lactic acid conversion of 90% (SD = 0.77%) was reached after 2.3 h reaction time. The reaction kinetics was superior to similar processes reported in the literature, where a lactic acid conversion of about 90% was reached after 4 h (Khunnonkwao *et al.*, 2012; Tanaka *et al.*, 2002) This can be explained by the reduced water content of the feedstock used in this work.

Integrated reactive distillation under optimal conditions was assessed for its energy efficiency and economic viability. For this purpose, the simultaneous process was compared to a serial setup of reactors and distillation steps. Similar process intensification at a lower overall feed ratio (3.8 kg ethanol/kg lactic acid for 91% conversion (SD = 0.97%), 2.6 kg/kg for 86% conversion (SD = 0.30%)) was reached with the serial setup. It was found that a decoupled process of reaction and separation steps can be operated more efficiently. Based on these results the optimal design of a continuous production process for distillation enhanced esterification was presented. The mass balances were determined experimentally using hydrolyzed lactic acid feedstock.

Particular attention in the upscaling must be given to the design of equipment for the preparation of the starting mixture and the intermediate distillation step. Rapid separation of water at moderate conditions and the earliness of mixing with ethanol are crucial in order to suppress oligomerization of lactic acid kinetically. Lactic acid oligomers are formed and hydrolyzed in relatively slow reactions compared to ethyl lactate formation (Pereira *et al.*, 2008). It is assumed, that the oligomer content of the starting mixture remains inaccessible throughout the process and should therefore be as low as reasonably possible. Lactic acid is usually produced by fermentation and concentrated from a dilute solution after downstream processing. Commercial lactic acid (88 w%) contains significant amounts of oligomers due to retention in the concentrated form. In an integrated production of ethyl lactate the presence of oligomers in the feedstock could be diminished by immediate processing after dehydration.

It was found that dehydrated ethanol (99.9%) feedstock is necessary to establish significant process intensification. For efficient operation the recovery of ethanol from the distillate is essential. Dehydration of ethanol is a well-developed process and, in many cases, already established at sites that

produce ethanol as a fuel additive. Moreover, shared infrastructure such as a bonded warehouse for ethanol and safety measures of an ex-proof production environment could reduce costs of integrated ethyl lactate production. Low operation costs are expected due to efficient separation of water, as well as low investment costs for compact equipment due to high space-time-yield. The process is easily scalable and could be integrated into existing or new biorefinery concepts. The flexibility of a biorefinery could be enhanced as ethyl lactate production does not require enantiomeric purity of lactic acid feedstock and could therefore compensate for quality variations of chemical building blocks. Due to these synergies, the presented process is especially interesting for integrated ethyl lactate production in versatile biorefineries that produce both feedstocks, ethanol and lactic acid.

## Data availability

### Underlying data

Zenodo: Underlying Data of "Ethyl lactate production by reactive distillation – optimization of reaction kinetics and energy efficiency". http://doi.org/10.5281/zenodo.4916874 (Stipsitz *et al.*, 2021).

Data are available under the terms of the Creative Commons Attribution 4.0 International license (CC-BY 4.0).

### Acknowledgements

The authors would like to thank Kompetenzzentrum Holz GmbH for assistance with the sample analytics.

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# Open Peer Review

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**Version 2**

Reviewer Report 30 September 2021

https://doi.org/10.21956/openreseurope.15118.r27669

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✔ **Juan Gabriel Segovia-Hernandez**
Chemical Engineering Department, Campus Guanajuato, Universidad de Guanajuato, Guanajuato, Mexico

Once the authors have addressed the comments of the reviewers, the paper has improved and it can be accepted for indexing.

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** process intensification, control, optimization

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.**

Reviewer Report 30 September 2021

https://doi.org/10.21956/openreseurope.15118.r27670

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✔ **María Teresa Sanz**
Department of Biotechnology and Food Science, University of Burgos, Burgos, Spain

I have no further comments to add. Authors have answered the proposed questions and I think the topic is of interest to be indexed.

***Competing Interests:*** No competing interests were disclosed.

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.**

**Version 1**

Reviewer Report 02 August 2021

https://doi.org/10.21956/openreseurope.14821.r27277

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**María Teresa Sanz**
Department of Biotechnology and Food Science, University of Burgos, Burgos, Spain

The authors propose a new configuration to produce ethyl lactate from the esterification reaction of lactic acid with ethanol by combining different steps of reaction and subsequent removal of ethanol and water. The content of water was proved as an important parameter to determine the lactic acid conversion. The topic is of interest due to the properties of ethyl lactate as solvent. However, some issues could be better explained.

The authors presented a good introduction section regarding previous studies and describing the presence of oligomers by using commercial lactic acid of 88 wt %. However, during the development of the manuscript no results were presented about the presence of oligomers, that probably would be concentrate in the ethyl lactate rich stream. Results are only reported as lactic acid conversion but a characterization in terms of chemical composition of the different streams is missing for the three experiments carried out by the authors: batch experiments, reactive distillation experiments and serial set up of reaction and distillation.

Please, specify the analytical procedure to check the final content of water (0.00 mol/mol) for pre-treated lactic acid.

When using the 100 (pre-treated) lactic acid the authors stated that when mixing with ethanol the formation of oligomers is suppressed. But 88 wt% commercial lactic acid has already important amounts of oligomers that would be concentrated after water removal.

Please, in equation 1, indicate how the specific enthalpy of the feed and distillate was evaluated.

In Figure 3, the effect of the type of catalyst is plotted. It seems that the initial reaction rate is quite similar for all the three catalyst studied, but the equilibrium conversion seems to be different. To assess this effect, longer kinetic reaction could have been carried out. Could the authors explain the effect of catalyst on equilibrium conversion?

Please, in Table 2, include the initial reaction rate since according to the authors “a low initial

water fraction was beneficial to the equilibrium conversion as well as the reaction kinetics". The values of $r_o$ could help in the description of the results.

The authors proposed a combined intensified process based on different steps of reaction and separation of water/ethanol and then a subsequent reaction step by replacing the removed ethanol. It would have been very interested for the work to report the exact composition of the different streams plotted in Figure 10. According to the manuscript, lactic acid, ethanol and ethyl lactate were quantified by HPLC (and water and ethanol by density measurements), but no results were presented. Did the authors observe any difference between ethanol composition by HPLC and density measurements?

A final comparison of different intensification process such as esterification process combined with pervaporation to remove water by using hydrophilic membranes would have been useful.

**Is the work clearly and accurately presented and does it cite the current literature?**
Yes

**Is the study design appropriate and does the work have academic merit?**
Yes

**Are sufficient details of methods and analysis provided to allow replication by others?**
Partly

**If applicable, is the statistical analysis and its interpretation appropriate?**
Not applicable

**Are all the source data underlying the results available to ensure full reproducibility?**
Partly

**Are the conclusions drawn adequately supported by the results?**
Partly

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** process intensification, biomass valorization, pressurized fluids

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.**

Author Response 24 Sep 2021

**Peter Stipsitz**

Dear Dr. Sanz, thank you very much for the constructive review of our work. We really appreciate your suggestions for improvement. In the following paragraphs we address your individual comments.

*Please, specify the analytical procedure to check the final content of water (0.00 mol/mol) for pre-treated lactic acid."* The final content of water was determined by a mass balance. The distillate was checked for its lactic acid content, which was <5 w% in all experiments. *"When using the 100 (pre-treated) lactic acid the authors stated that when mixing with ethanol the formation of oligomers is suppressed. But 88 wt% commercial lactic acid has already important amounts of oligomers that would be concentrated after water removal. (...) It would have been very interesting for the work to report the exact composition of the different streams plotted in Figure 10."*

It is correct, that the oligomers of commercial lactic acid were concentrated in the experiments presented in version 1. It is expected that the oligomers remained unavailable for ethyl lactate formation. The lactic acid conversion was calculated from the change of the lactic acid monomer concentration. In version 2 we present the mass balances of the continuous process and the composition of the individual streams, based on new experimental data. For these experiments hydrolyzed lactic acid feedstock was prepared using an adapted experimental procedure.

*"Please, in equation 1, indicate how the specific enthalpy of the feed and distillate was evaluated."*

The specific enthalpy of the feed and distillate was calculated according to its composition from values of the individual components. References to the literature values were added to the manuscript, which are also listed in the underlying data file. All measured values and calculations for each specific experiment can be found in the underlying data.

*"In Figure 3, the effect of the type of catalyst is plotted. It seems that the initial reaction rate is quite similar for all the three catalyst studied, but the equilibrium conversion seems to be different. To assess this effect, longer kinetic reaction could have been carried out. Could the authors explain the effect of catalyst on equilibrium conversion? (...) Please, in Table 2, include the initial reaction rate since according to the authors "a low initial water fraction was beneficial to the equilibrium conversion as well as the reaction kinetics". The values of $r_0$ could help in the description of the results."*

We listed the initial reaction rates $r_0$ in Table 3 and the additional Table 2 to increase comparability of the kinetics results. The equilibrium conversion was independent of the type of catalyst. After 24 h of reaction the same equilibrium conversion was reached with all three catalysts. Within the time shown in Figure 3 the equilibrium was not yet reached. Equilibrium values are presented in Table 3.

***Competing Interests:*** No competing interests were disclosed.

Reviewer Report 22 July 2021

https://doi.org/10.21956/openreseurope.14821.r27279

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**Juan Gabriel Segovia-Hernandez**
Chemical Engineering Department, Campus Guanajuato, Universidad de Guanajuato, Guanajuato, Mexico

Several details must be clarified before the paper is ready for indexing.

1. The authors should explain in detail how they carried out each of the experiments. There are a lot of information loss that would not allow anyone interested to reproduce the experiments shown in the paper. Authors need to be more explicit in the execution of the experiments and give more detail to be reproduced.

2. It is necessary to conduct a more detailed statistical study of the results. It is necessary to validate the experiments and their reliability. On the other hand, it is necessary to carry out a detailed statistical design of experiments to correlate all the variables analyzed to observe the effect of all of them and which of them have more or less impact on the case study. This information is lost in the document.

3. The results are of interest. But the authors need to establish an in-depth analysis to correlate the information obtained and to establish a firm conclusion from the results. The analysis is very superficial.

4. If it is not the goal of the work, but the authors should assess the economic impact of the proposal. Is it economically viable the proposal submitted by use in industry, for example?.

5. Authors should clearly establish which is the novelty of the work. What is really new in this paper? What is the difference with other previously published works on the subject?

**Is the work clearly and accurately presented and does it cite the current literature?**
Partly

**Is the study design appropriate and does the work have academic merit?**
Yes

**Are sufficient details of methods and analysis provided to allow replication by others?**
Partly

**If applicable, is the statistical analysis and its interpretation appropriate?**
No

**Are all the source data underlying the results available to ensure full reproducibility?**
Partly

**Are the conclusions drawn adequately supported by the results?**

Partly

***Competing Interests:*** No competing interests were disclosed.

***Reviewer Expertise:*** process intensification, control, optimization

**I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.**

Author Response 26 Jul 2021

**Peter Stipsitz**

Thank you very much for your review report. We appreciate your suggestions and will soon provide a new version of the manuscript, that addresses all of your comments.

***Competing Interests:*** No competing interests were disclosed.

Author Response 24 Sep 2021

**Peter Stipsitz**

Dear Dr. Segovia-Hernandez, thank you very much for the constructive review of our work. We really appreciate your suggestions for improvement. In the following paragraphs we address your individual comments.

1. *"The authors should explain in detail how they carried out each of the experiments. There are a lot of information loss that would not allow anyone interested to reproduce the experiments shown in the paper. Authors need to be more explicit in the execution of the experiments and give more detail to be reproduced."*

   In version 2 we described the methods and validation of the experiments more precisely.

2. *"It is necessary to conduct a more detailed statistical study of the results. It is necessary to validate the experiments and their reliability. On the other hand, it is necessary to carry out a detailed statistical design of experiments to correlate all the variables analyzed to observe the effect of all of them and which of them have more or less impact on the case study. This information is lost in the document."*

   In version 2 we described the validation of the experiments more precisely. All experiments were conducted at least in duplicate, the main findings were conducted at least in triplicate and are represented by means and standard deviations in the whole document. The concept of the experimental design was explained in an additional paragraph.

3. *"The results are of interest. But the authors need to establish an in-depth analysis to correlate the information obtained and to establish a firm conclusion from the results. The*

*analysis is very superficial."*

We elaborated the comparison of the different experimental setups and established a more precise conclusion. The optimal process for ethyl lactate production by distillation enhanced esterification was found.

4. *"If it is not the goal of the work, but the authors should assess the economic impact of the proposal. Is it economically viable the proposal submitted by use in industry, for example?"*

   Unfortunately, there is a lack of publicly available data regarding the energy demand and operation costs of the conventional process used in industry. Therefore, we compared two different setups for the process using experimental data. A simple serial setup for distillation enhanced esterification was used as a reference for assessing the integrated process. In the conclusion we added suggestions for the application of the proposed technology in integrated biorefineries.

5. *"Authors should clearly establish which is the novelty of the work. What is really new in this paper? What is the difference with other previously published works on the subject?"*

   In the introduction we described the concept and novelty of the work more precisely. The goal was to find the optimal process for ethyl lactate production by distillation enhanced esterification by comparing different experimental setups.

***Competing Interests:*** No competing interests were disclosed.