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A NOVEL PROCESS CONCEPT FOR THE PRODUCTION OF ETHYL LACTATE

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Abstract
A dynamic model of a reactive divided wall column is presented so as to analyse a novel process concept for the esterification of lactic acid with ethanol to ethyl lactate. The divided wall column is modelled by composing single packing columns to a Petlyuk-structure using different correlations for fluid dynamics and pressure drop. Besides, a variety of side reactions are considered such as the oligomerisation of lactic acid, and the esterification of their oligomers. Moreover, feasibility studies are carried out in order to show in detail the potential of the proposed process concept, in particular, the reactive dividing-wall column. For this purpose, the influence of different parameters like side draw flow rate and the liquid split are simulated to examine their impact on the ethyl lactate production.

Keywords: Reactive Distillation, divided wall column, lactic acid, ethyl lactate, process integration, hybrid process, gPROMS

1. Introduction

For the chemical synthesis of poly(lactic acid) PLA, highly purified lactic acid as monomer is required. However, the purification of lactic acid obtained from bacterial fermentation requires extensive purification operations due to its low vapour pressure, its tendency to undergo self-esterfication, and the presence of troublesome impurities[5]. One possibility for the purification consists in the esterfication of lactic acid with alcohol[16,8]. In this process, the volatile lactate ester can be separated by distillation, and the distilled lactate ester can hydrolyzed into lactic acid. Alternatively, reactive distillation can also be applied[6].

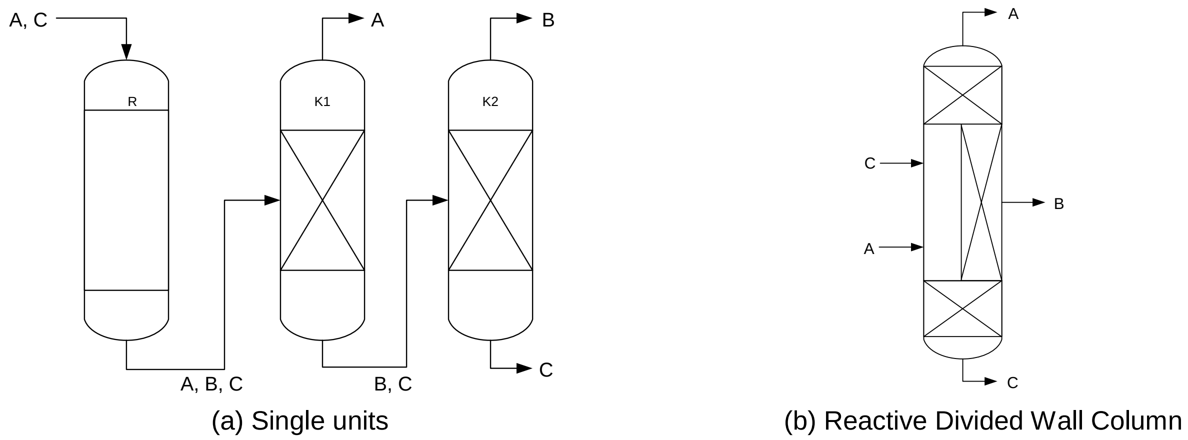
Ethyl lactate can be used in a broad variety of industrial cleaning and dissolving applications because of its good solvent properties[19,21]. In the past, different process alternatives have been proposed for its production such as reactive batch distillation[12], reaction with integrated pervaporation[4], reaction with vapor permeation[11], reactive-distillation[10], and semicontinuous distillation[1], the main idea being savings in capital, energy, and environmetal benefity through process integration. However, in aqueous solutions above 30 wt%, lactic acid forms dimers and higher oligomers, which complicates its use as reagent since the oligomers also undergo esterification[3]. That leads to a mixture of lactic acid mono- and oligomers and the corresponding esters. Currently, only one kinetic has been published, which considers also the oligomerisation[3]. Following the reaction, Ethyl Lactate has to be separated from a mixture with several compounds through rectification in two steps. With the use of a reactive divided wall column it is now possible to combine single units in order to save energy- and investment costs. Moreover, the oligomer esters, which are produced as side products, can be refined for sale, further converted to ethyl lactate, or can be used as plasticizers, but their use is not common. Therefore, it is more reasonable to process the by-products to ethyl lactate or to minimize the formation of oligomers by using diluted lactic acid solutions[2].

2. Process integration

In the chemical industry, the production of liquid products is normally divided in different single steps and units as e.g. reactors and rectification columns. Let us consider a mixture of component A and C which reacts to a component B. Here A represents the lightest and C the heaviest compound.

$$A + C \rightarrow B \qquad (1)$$

A first process concept is outlined in Figure 1(a). It denotes a cascade of a reactor (R) and two rectification columns (K1, K2) for the recovery of educts and the purification of the product B. The separation is needed if the reactants react only partly or one compound is added in a non-stoichiometric ratio.



(a) Single units (b) Reactive Divided Wall Column

Figure 1. Implementation of the Reactive Divided Wall Column

The first step of integration is the implementation of a reactive distillation column. Thereby the reactor (R) and the first distillation column (K1) are summarised into one unit. A positive side effect represents the increased conversion of equilibrium-limited reactions e.g. the esterification, which is caused by a continuous removal of the products from the reactive packing. Figure 1(b) shows a further step of integration by combining all three units in a reactive divided wall column (RDWC), the main idea being savings in capital, energy and environmental benefit through process integration. The classical concept of the divided wall column without a reactive packing was patented in 1949 by R. O. Wright for the Standard Oil Development Company[22].

The direct sequence of two distillation columns, as used in the classical concept Figure 1(a), is intuitive but in some cases thermally inefficient. For example when B is the major component and the split between A and B is similar to the split between B and C. In the first column (K1) some stages above the bottom, component B has a concentration maximum. Below this point, the component C is enriched and therefore component B becomes diluted. This remixing causes higher energy consumption since both components have to be separated again in the next column (K2). This problem can be eliminated by using the Petlyuk structure or directly a dividing wall column (see Figure 2). In the first column (prefractionator) the components A and C are separated whereas component B is distributed on the top- and bottom streams. The upper part of the second column (3, 4) performs then the separation of A and B, while the lower part (5,6) separates B and C. This is shown in Figure 2 where the reaction is additionally implemented through a reactive packing as prefractionator. Here the component C is added as liquid into the top while A is added as vapour into the bottom section of the reactive packing. These points can be seen in Figure 2 for the fraction of component B since it becomes diluted at these points.

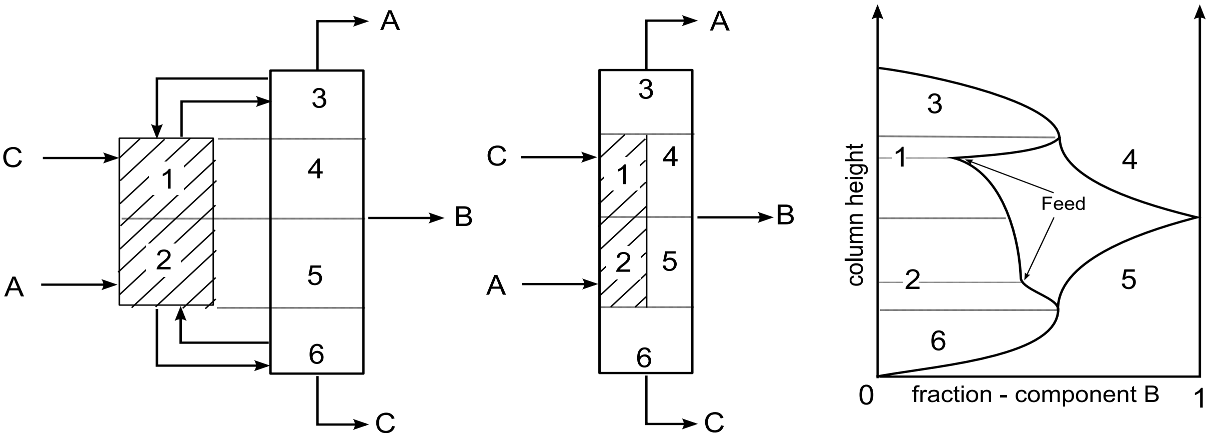


Figure 2. Concentration profile of a divided wall column with a reactive packing

However, this highly integrated process enables further synergistic effects such as lower energy consumption and reduced number of equipment units[14]. On the other hand, the accessible operating window will be reduced because of the integrated configuration[18]. The contemplation of all these subjects makes the choice of an optimal integration level difficult. Thus, an adequate model development of the reactive divided wall-column with their numerous and complex interactions represents a challenging task.

3. Process description

The esterification of lactic acid with ethanol consists of different reactions. These are: *esterification* of lactic acid, *oligomerisation* of lactic acid, *esterification* of the oligomers and *transesterification* of the oligomer esters directly to ethyl lactate. A pseudo-homogeneous kinetic of the esterification over Amberlyst 15 cation-exchange resin can be found in[3]. It represents the only publication with a kinetic study including the oligomerisation.

Table 1. List of the included components

Nr.	Abbr.	Name	Formula
1	W	Water	H_2O
2	EtOH	Ethanol	C_2H_5OH
3	L1	Lactic Acid	$C_3H_6O_3$
4	L2	Dilactic Acid	$C_6H_{10}O_5$
5	L3	Trilactic Acid	$C_9H_{14}O_7$
6	L1E	Ethyl Lactate	$C_5H_{10}O_3$
7	L2E	Ethyl Dilactate	$C_8H_{14}O_5$
8	L3E	Ethyl Trilactate	$C_{11}H_{18}O_7$

$$L_1 + EtOH \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} L_1E + H_2O$$

$$L_2 + EtOH \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} L_2E + H_2O$$

$$L_3 + EtOH \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} L_3E + H_2O$$

$$L_2 + H_2O \underset{k_4/K_4}{\overset{k_4}{\rightleftharpoons}} 2L_1$$

$$L_3 + H_2O \underset{k_5/K_5}{\overset{k_5}{\rightleftharpoons}} L_1 + L_2$$

The set of reactions above describes the lactic acid monomer esterification as well as the oligomer formation and esterification. All oligomers which are larger than dimers (L2 and L2E) are summarized as L3 and L3E.

3.1. Process concepts

A case based continuous process for the esterification of lactic acid with ethanol to ethyl lactate is depicted in Figure 3. Three major columns are needed: the primary reactive distillation column (R1) for the esterification of lactic acid, a vacuum distillation column (K1) to separate and purify the ethyl lactate from the oligomers and their esters and a second reactive distillation column (R2) for the post processing of the by-products which is in this case a transesterification. One more distillation column (K2) is needed to recycle ethanol by separating the water. Instead of a column it would also be possible to use an evaporation unit. As catalytic packing KATAPACK-S from Sulzer filled with Amberlyst 15 resin is used for the esterification.

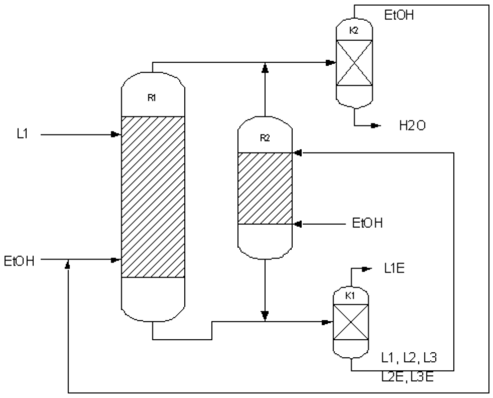
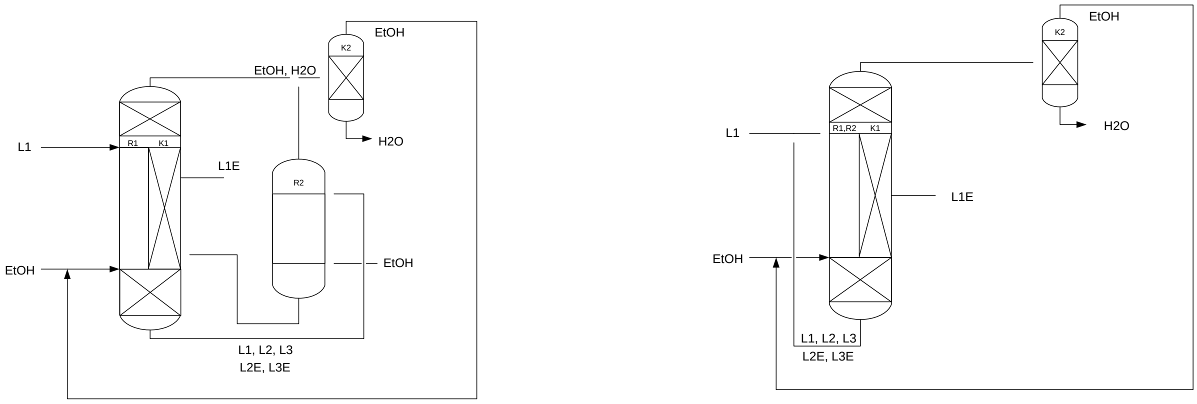


Figure 3. Conventional process concept with a reactive packing[2]

In this case base the use of a dividing wall column offers the possibility to several new combinations. First, it could be considered to combine the esterification and the purification in a dividing wall column as shown in Figure 4(a). This step saves one column but leads to several operational questions. It has to be examined which operation conditions such as pressure, temperature and liquid split on top of the dividing wall cause the highest ethyl lactate production. The next step is to include the transesterification into the divided wall column. Since the same catalyst is used, it is possible to feed back the bottom products to the reactive packing for the esterification as outlined in Figure 4(b). Compared to the case base continuous process in Figure 3, this configuration would combine three process units in one.



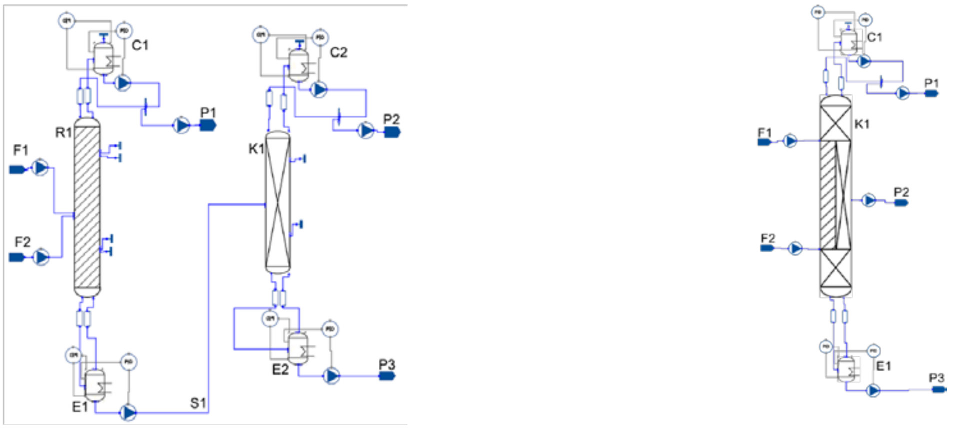
(a) Combined esterification and purification

(b) Combined esterification, purification and transesterification

Figure 4. Combination of single units into a reactive divided wall column

3.2. Dynamic process simulations

In this work, the model environment gPROMS is used to implement a dynamic model for the esterification (R1 – 12m packing) and the packing column for the purification (K1 – 6m) of ethyl lactate as used in the case base continuous concept shown in Figure 3. The upper feed is an aqueous solution of lactic acid (88 wt%) with a flow rate of 1kg/s and a Temperature of 340K. Pure ethanol is added in the feed below with a flow rate of 2kg/s and a Temperature of 350K.



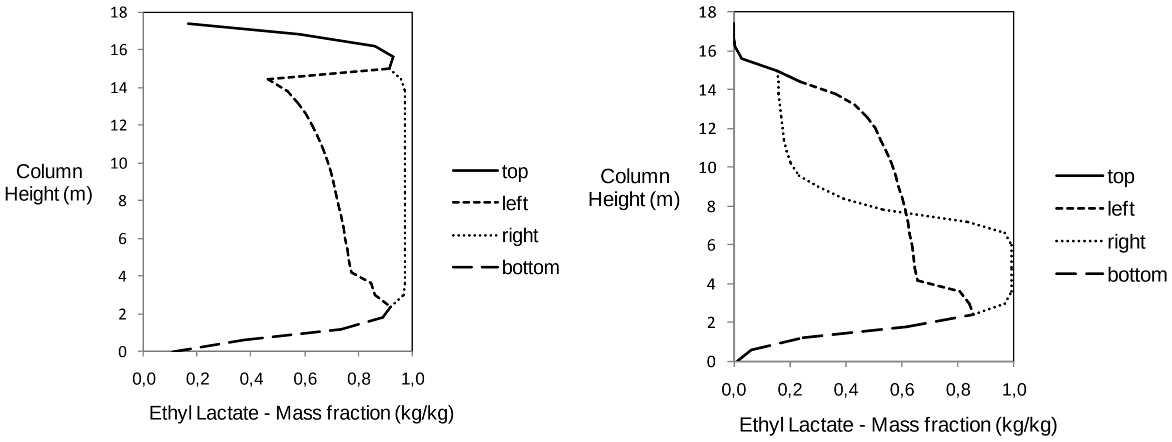
(a) Single Esterification and purification

(b) Combined esterification and purification

Figure 5. Implementation of the concepts in gPROMS

Based on a reactive dividing wall column it is now possible to combine esterification and purification in one unit. Figure 5(b) shows this process as implemented in gPROMS. The divided wall column is modelled with four KATAPAK-S packings. The packings on top (3m), on the right (12m) and in the bottom (3m) are only for distillation while the left packing (12m) is filled with Amberlyst 15 resin for the esterification. The feed properties are the same as in the case base process. The packings are modelled with an equilibrium approach and a HETP-value of 0.6.

Figure 6 shows the concentration changes of ethyl lactate in the divided wall column when it reaches its steady point. The evaporator has a Temperature of 500K and the condensator pressure is set to 1.0135bar. The removal P2 in Figure 8 (a) and (b) corresponds to 0.5 kg/s and 1 kg/s, respectively. As expected, the concentration profiles show a high concentration of ethyl lactate on the right side and a clearly visible reactive part on the left, where the two feed points can be seen. The ethyl lactate is distributed over the whole height of the column with a high purity at the side draw.



(a) P2 – 0.5 kg/s (b) P2 – 1 kg/s

Figure 6. Ethyl Lactate - Mass fraction in the reactive divided wall column

In[2] it is recommended to use the reactive packing for the esterification like a stripping column with nearly no reflux. Therefore, the liquid split in the divided wall column is set to a value, that only 1% of the liquid coming from the upper packing flows in the reactive packing on the left. In Figure 7, this ratio is slowly changed at t = 33 min until the liquid flow divides equally at t = 50 min and a share of 50% flows into the reactive section. In the Figure, the liquid mass flow of ethyl lactate (L1E), leaving the reactive packing, is plotted. It can be seen, that the mass flow of ethyl lactate first goes up, but after a while it declines and less ethyl lactate leaves the reactive packing.

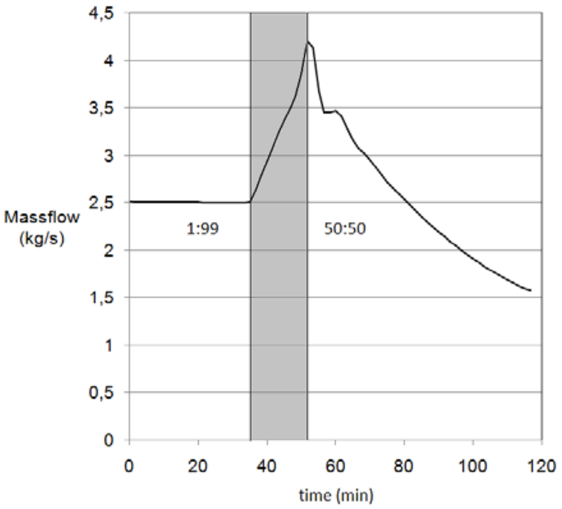


Figure 7. Influence of the liquid split

4. Conclusions

A novel process concept has been introduced for the esterification of lactic acid with ethanol to ethyl lactate. For this purpose, a dynamic model of a reactive divided wall column has been implemented as a Petlyuk structure in gPROMS. The combined esterification and purification of lactic acid to ethyl lactate in the reactive divided wall column were efficiently integrated by using a kinetic model which also describes the oligomerisation of lactic acid. Moreover, two process concepts for the implementation of a divided wall column have been presented and dynamic simulations have been carried out to analyse the feasibility of combining esterification and purification in a reactive divided wall column. The developed models proved to converge robustly for several simulation parameters and initial values.

Acknowledgements

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