

Semicontinuous distillation of impurities for the production of butyl acrylate from bio-butanol and bio-acrylic acid



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ABSTRACT

Chemical production processes which use biosynthetic pathways typically experience variations in the concentration and composition of impurities contained in the products, due to the natural variability of biological behaviour. As a result, downstream processes which use these biosynthetic chemical products need to be quite flexible with respect to the impurity concentrations. In this study, a ternary semicontinuous distillation process is investigated, separating a mixture into three fractions, as a potential candidate for the purification of three different bio-based chemicals (bio-acrylic acid, bio-*n*-butanol, and bio-*n*-butyl acrylate) which are generated at various steps in the process to produce bio-*n*-butyl acrylate from bio-based feedstocks. In this model-based investigation, the performance of this approach is discussed in terms of the energy demand, product loss, and the cycle time. It is shown, that a single ternary semicontinuous system can be applied to purify several bio-based chemicals, allowing a simple increase or decrease of the desired final purity, while being able to handle natural variations of the initial compositions of the feed.

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1. Introduction

The chemical industry is still highly dependent on fossil raw materials, both for fuel production and for the production of bulk chemicals and specialty chemicals. Due to diminishing reserves of fossil fuels and other non-renewable materials, new pathways using sustainable bio-based resources are under investigation [1]. As a result, a shift from an oil-based to a bio-based chemical industry is anticipated.

Acrylic acid (AA) and its derivatives are important basic building blocks for the chemical industry which are growing in demand. For example, the worldwide production of these chemicals increased by 40% from 2003 to 2006 [2,3] and is anticipated to continue increasing by almost 5% per year until 2015 [4]. Butyl acrylate is one of the most important derivatives of acrylic acid and 30% of the global acrylic acid demand is used for its production [5]. *n*-Butyl acrylate (BA) is produced in an equilibrium-limited esterification reaction of *n*-butanol (BuOH) and acrylic acid, with water as co-product. The conventional process for the *n*-butyl acrylate

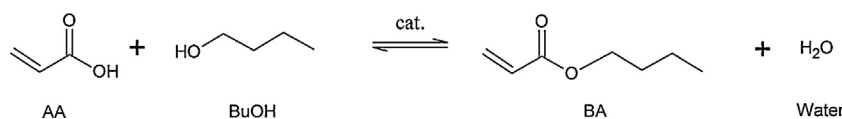
production was published by Bell [2] and is a homogeneously catalysed multistage process using two reactors for the conversion of the reactants followed by three distillation columns for product purification and reactant recovery. Niesbach et al. investigated a single-stage reactive distillation process for the production of *n*-butyl acrylate, significantly reducing the number of unit operations required and consequently the production costs for *n*-butyl acrylate [6–8]. Reactive distillation is a well known technology for achieving process intensification for various reactions, such as esterifications [6,9], transesterifications [10,11] or etherifications [12,13] and can also be used in combination with other unit operations, for example in combination with membranes [14]. In the studies of Niesbach et al., the concept of reactive distillation emerged as a promising future technology for the economic production of *n*-butyl acrylate. However, these studies assumed the feed products were pure (i.e., pure *n*-butanol and pure acrylic acid).

In reality, if *n*-butanol and acrylic acid are derived from a biological process, they will contain impurities which can alter the performance of the reactive distillation unit and subsequently end up in the final *n*-butyl acrylate product and can also vary from batch to batch due to seasonal changes in the biological raw material composition of the fermentation process. To identify the impact of the use of bio-based raw materials on distillation processes, Niesbach et al. [15] developed a 4-step methodology using the example of a reactive distillation column for the production of *n*-butyl acrylate. As a result of this methodology, potential impurities in bio-based

Abbreviations: AA, acrylic acid; AP, Aspen Plus™; BA, *n*-butyl acrylate; BuOH, *n*-butanol; FC, flow controller; HETP, height equivalent to a theoretical plate; HOC, Hayden O'Connell equation of state; IMP, impurity; LC, level controller; MV, middle vessel; RR, reflux ratio; UNIQUAC, universal quasichemical.

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Scheme 1. Reaction scheme of the esterification of acrylic acid and *n*-butanol.

reactants and potential side-reactions in the reactive distillation column were identified and their impact on the reactive distillation process for the production of *n*-butyl acrylate was shown. The impurities were investigated with concentrations up to 3000 ppm, based on component data sheets of basic *n*-butanol and acrylic monomer suppliers. It was concluded that a certain group of impurities (which are critical with respect to the product purity and must be removed) cannot be separated by changes in the operational parameters of the reactive distillation process. Therefore, additional purification steps are necessary.

One of the most suitable separation strategies for this situation is semicontinuous distillation. Semicontinuous distillation is a process intensification technique which can separate both light and heavy boiling components simultaneously, even with changing feed concentrations. In semicontinuous distillation processes, at least one middle vessel is tightly integrated with a distillation column operating in a particular forced cycle. This strategy can achieve multiple separation steps using only one column [16]. The potential of semicontinuous processes to achieve lower lifetime costs in comparison to batch and continuous distillation processes, also showing simulation results of batch and continuous processes in comparison to semicontinuous processes, was shown by Adams and Seider [16–18] and Pascall and Adams [19] for intermediate production rates such as those typically seen in biochemical processing. Semicontinuous processes have so far been studied for azeotropic distillation, ternary non-azeotropic distillation, extractive distillation, semicontinuous distillation with chemical reaction and pressure-swing distillation processes [16–23]. Within this study, a ternary semicontinuous separation is investigated.

Ternary semicontinuous separation processes allow for a separation of three fractions. The middle vessel (MV) receives a side-stream of the distillation column and the fresh feed while the column is fed with the contents of the middle vessel. In ternary semicontinuous processes, distillate and bottom products are removed continuously and the intermediate boiling component is recycled to the middle vessel and purified during the course of the cycle.

Within this study, the potential of a semicontinuous process for the further purification of high-purity bio-based raw materials is investigated. The potential of a semicontinuous distillation unit to act as a multipurpose unit, either separating the reactants upstream or the final products downstream of the reactive distillation column, is investigated. The esterification of acrylic acid and *n*-butanol for the production of *n*-butyl acrylate published by Niesbach et al. [6] serves as case study. The use of a semicontinuous process for the removal of impurities from the final product *n*-butyl acrylate as well as from reactants upstream of the reactive distillation column is shown. Simulation studies are performed to investigate the feasibility of semicontinuous processing for the purification of the various streams to allow for the production of bio-derived *n*-butyl acrylate with a sufficient purity. As the concentration of impurities in bio-based raw materials differs in dependency of the feedstock and even in different batches, the flexibility of this concept in respect to the impurity concentration is furthermore investigated. The performance of the use of a semicontinuous distillation for the removal of bio-based impurities is discussed in terms of the energy demand, product loss, and the cycle time.

2. Process

The chemical system investigated in this study is the equilibrium-limited esterification of acrylic acid and *n*-butanol to form *n*-butyl acrylate and water. The reaction scheme of this reaction is shown in Scheme 1.

This reaction is performed in the reactive distillation process shown in Fig. 1, which was optimised in earlier studies [6]. The optimisation study resulted in an economically optimised reactive distillation process for the synthesis and purification of *n*-butyl acrylate in a single step. However, for the optimisation, only the four main components (Scheme 1) were taken into account. In a subsequent study the impact of using bio-based raw materials was investigated and the impurities were identified, that disturb the performance of the reactive distillation process. These impurities can be categorised in impurities that were found in the two reactants and those, that result from side-reactions in the reactive distillation column. It was found, that the reactive distillation process is only able to operate in a given process window while still maintaining the desired product purity. For higher concentrations of impurities, a separation of the identified impurities using a semicontinuous distillation unit is investigated in this study, to still allow a production of *n*-butyl acrylate, fulfilling industrial purity specifications.

Impurities enter the process through the acrylic acid and *n*-butanol feeds and much of it ends up in the *n*-butyl acrylate product, which has a required industrial minimum purity of $w_{BA} \geq 0.9950$ [24], but typically higher purities around $w_{BA} \geq 0.9970$ are

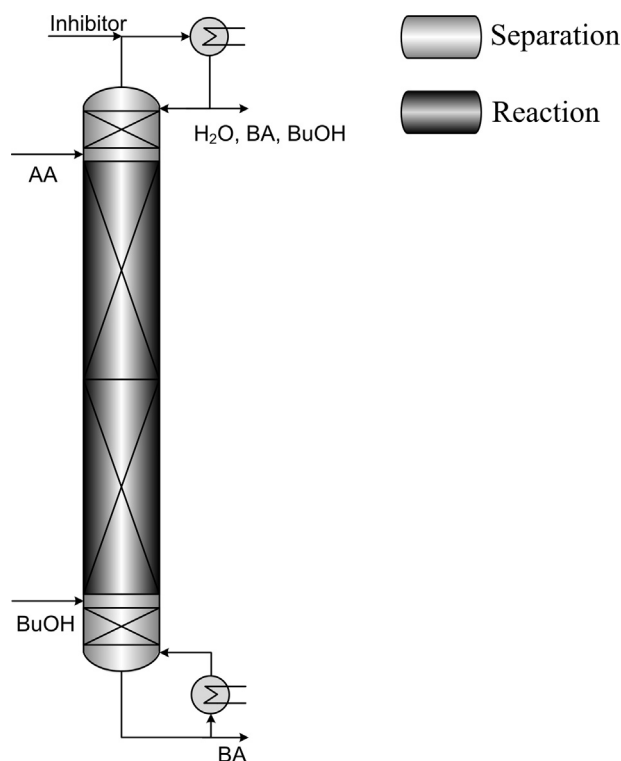


Fig. 1. Set-up of optimised reactive distillation process.

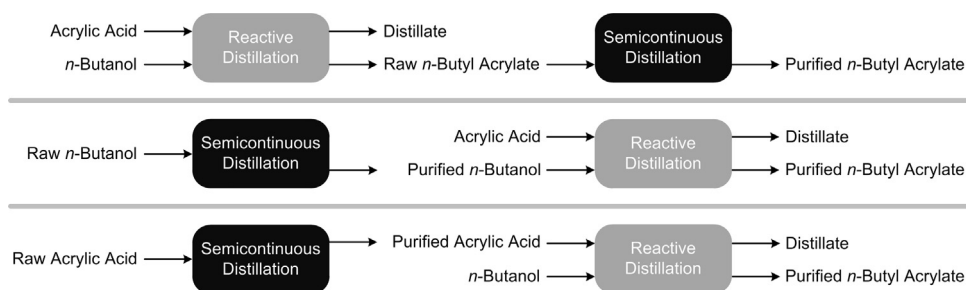


Fig. 2. Investigated process configurations for the production of purified bio-derived *n*-butyl acrylate.

achieved. Therefore, the impurities can be removed from either the *n*-butyl acrylate after production, or from the acrylic acid and *n*-butanol feeds before they are fed to the reactive distillation column and the most-feasible position for the application of the semicontinuous process may change with the type of impurities. In this work, both options are explored using semicontinuous distillation strategies as shown in Fig. 2.

As several esters are produced in the reactive distillation column from the impurities due to side-reactions with the main components and some of these esters are hard to separate from the final product, a removal of the impurities from the reactants avoids the formation of esters and simplifies the purification of the final product. However, it may still be easier to purify the BA product because only one separation system is required, whereas either two separation systems or an alternating operation of one system for the purification of either *n*-butanol or acrylic acid would be needed if the impurities were removed from the reactants first. Thus, both options are examined in this work.

Table 1 summarises the potential impurities that were identified in the reactants acrylic acid and *n*-butanol with their boiling points at 0.576 bar, the operation pressure of the reactive distillation process, and the set of impurities identified as critical for the *n*-butyl acrylate purity in the reactive distillation process [15]. The impurities were identified in a 4-step methodology, investigating the impurities resulting from the bio-derived reactants and potential side-reactions occurring in the reactive distillation process [15]. Those impurities were clustered based on similarity in thermodynamic and physical property data and simulation studies were performed to identify their influence on the *n*-butyl acrylate purity after the reactive distillation process [15]. In this investigation, a reduction from 14 initial impurities to eight impurities was performed after step-2 and of these eight impurities, four were found to be the most critical in respect to the purity of *n*-butyl acrylate in the reactive distillation process [15]. As the last reduction from eight to four impurities was only performed for a processing of these components in the *n*-butyl acrylate reactive distillation process, all eight impurities resulting from the clustering after step-2 are taken into account in this study.

In the following sections, a feasibility study for the use of a ternary semicontinuous distillation process for the removal of the abovementioned impurities from the three investigated streams is presented. The results of simulations of the semicontinuous process are presented, using simulation results (feed and product compositions) of a reactive distillation process, that were already published in earlier studies [6,15].

2.1. Thermodynamic and physical properties

Reliable pure component and mixture property data is essential to ensure accurate simulation results. Thermodynamic and physical property data in this work is calculated using the Aspen Properties™ package within Aspen Plus™ and Aspen Dynamics™.

The physical and thermodynamic pure-component and mixture property data for the components investigated within this simulation study are taken from Aspen Properties™ and are compared to literature data. For the determination of the liquid phase activity coefficients in Aspen Properties™, the UNIQUAC model is used [26]. The Hayden O'Connell equation of state is applied to account for nonidealities in the gas phase [27]. The selected models for the determination of the other pure component and mixture property data are summarised in the Table S-1 in the supplementary material.

Vapour pressure and vapour–liquid equilibria are of particular importance for the simulation of any distillation column. If large deviations between Aspen Properties™ equilibria predictions and literature data are found, new parameters are determined using regression of the literature data. A description of the selected methods can be found in an earlier work [15]. A comparison of experimental and simulated data for the vapour pressures of the impurities identified in *n*-butyl acrylate and an example for a comparison of a vapour–liquid equilibrium with experimental data are shown in Figs. 3 and 4. The selected UNIQUAC binary interaction parameters are summarised in Table S-2 in the supplementary material.

2.2. Process description

The semicontinuous process is designed to achieve a designated final purity of the target product, either *n*-butyl acrylate, acrylic acid or *n*-butanol. All three of these already possess a high purity of $w_{BA} \geq 0.9900$ before entering the semicontinuous process, but a further separation of impurities is necessary to achieve the industrial specification for the final product *n*-butyl acrylate ($w_{BA} \geq 0.9970$).

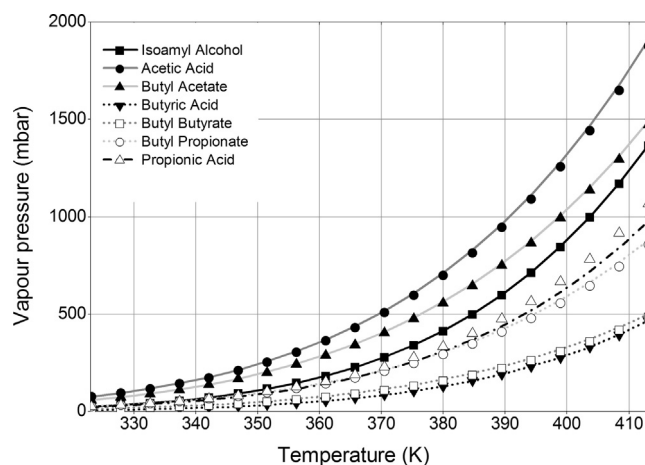


Fig. 3. Vapour pressures of the impurities identified in *n*-butyl acrylate. Symbols represent the literature data taken from Yaws [29] and lines represent the simulated results of the Aspen Properties™ simulations.

Table 1
Potential impurities identified by Niesbach et al. [15] for the two feed streams and the final product stream of the reactive distillation column for the production of BA with respective boiling points at $p = 0.576$ bar taken from Yaws [25]. The last three columns show, for which stream the impurity is taken into account.

Component	IUPAC name	Formula	CAS number	T_b (K)	AA-feed	BuOH-feed	BA-product
Isobutanol	2-Methyl-1-propanol	$C_4H_{10}O$	78-83-1	366.6		+	
Acetic acid	Acetic acid	$C_4H_4O_2$	64-19-7	374.2	+	+	+
Butyl acetate	Butyl acetate	$C_6H_{12}O_2$	123-86-4	381.2			+
Isoamyl alcohol	3-Methyl-1-butanol	$C_5H_{12}O$	123-51-3	388.5		+	+
Propionic acid	Propanoic acid	$C_3H_6O_2$	79-09-4	394.8	+		+
Butyl propionate	Butyl propanoate	$C_7H_{14}O_2$	590-01-2	400.1			+
Butyl butyrate	Butyl butanoate	$C_8H_{16}O_2$	109-21-7	419.0			+
Butyric acid	1-Butanoic acid	$C_4H_8O_2$	197-92-6	419.6		+	+

The same setup for the semicontinuous process is used for all three separation tasks to demonstrate a flexible field of application for a single semicontinuous process unit. The column consists approximately 4.2 m of Sulzer BX™ structured separation packing with an HETP value of 0.14 m, which is equivalent to 28 equilibrium stages, not including the condenser and the reboiler. For the investigation presented in this manuscript the structured packing Sulzer BX™ is used, which is also used for the separation section of the reactive distillation process [6]. A total of 30 equilibrium stages are chosen to demonstrate the separation efficiency at moderate column heights.

Table 2
Design of the semicontinuous distillation process.

Design variable	Value
Equilibrium stages	28
Packing type	Sulzer BX™
Packing height	4.2 m
Feed position	Below stage 14
Column diameter	0.547 m

The feed from the middle vessel is fed to the middle of the column at a height of 2.1 m (equivalent to a position between the 14th and the 15th equilibrium stage from the top of the column) and a sidestream is collected at the same height, which is recycled to the middle vessel. The operating parameters for the different operation modes are summarised in Section 3.2 for the *n*-butyl acrylate simulation and Section 3.3 for the acrylic acid and *n*-butanol purifications. The process flowsheet of the semicontinuous process used for the removal of the impurities is shown in Fig. 5 and the most important design information is summarised in Table 2. The target component, either *n*-butyl acrylate, *n*-butanol or acrylic acid is purified and separated from the light boiling and heavy boiling impurities. The middle vessel in this ternary semicontinuous process is attached to both, the side stream of the distillation column and the fresh feed stream. The purified product can be obtained from the middle vessel using the drain during the end of each cycle. The whole campaign within one operating cycle of the semicontinuous process consists of three operating modes.

In the first operating mode, the middle vessel is fed with the feed to be separated—in this case, raw *n*-butyl acrylate containing the impurities. When the desired liquid level in the middle vessel is reached, the valve for the raw *n*-butyl acrylate closes and

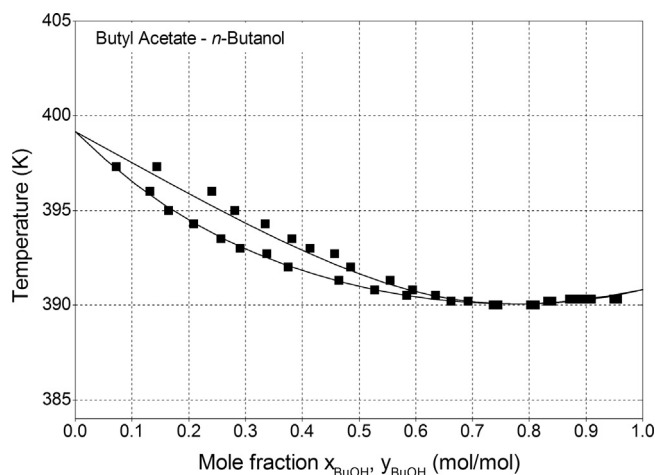


Fig. 4. Vapour–liquid equilibrium of the binary system butyl acetate – *n*-butanol at 1.01 bar. Symbols represent the literature data taken from Shim et al. [28] and lines represent the simulated results of the Aspen Properties™ simulations.

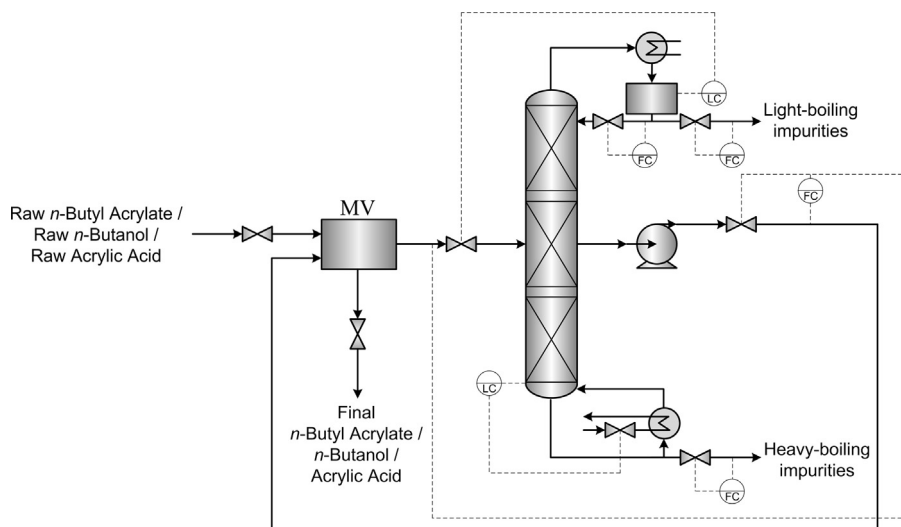


Fig. 5. Semicontinuous process configuration.

the second operating mode begins. In the second operating mode, light-boiling impurities are removed at the top (containing some of the main component) and the heavy-boiling impurities (also containing some of the main component) are removed at the bottom of the column. The side stream is recycled to the middle vessel. During this time, the concentration of the main component in the middle vessel gradually increases, and the distillate and bottoms molar flow rates are maintained constant, although the impurity content of those streams will gradually decrease. The second operating mode is maintained until the desired purity specification for the main component in the middle vessel is achieved.

As soon as the desired specification is reached, the third mode begins. In the third mode, the contents of the middle vessel are quickly removed via the drain at the bottom of the middle vessel until the middle vessel is almost empty. Then, the cycle restarts with the first operating mode. However, the column continues to function, and the distillate and bottom product molar flow rates remain constant during this mode as well. Within the simulations, the middle vessel is emptied to 8% of the maximum liquid level when the purified product is removed and refilled to 96% of the maximum liquid level during the charging phase, according to investigations by Pascall and Adams [19]. A detailed description of the dynamic simulation of the semicontinuous process is given in Section 2.4.

2.3. Process control

The control of this semicontinuous process is configured in such a way that quick and efficient transitions between the operating modes are possible. A detailed discussion of possible control configurations for ternary semicontinuous processes was published by Pascall and Adams [19] and will not be discussed in detail within this publication.

As shown in Fig. 5, the side draw flow rate is controlled using information about the feed flow rate and composition using a strategy known as the ideal side-draw recovery arrangement, which was developed by Adams and Seider [18]. In this strategy at each time instance, the flow valve of the side draw is adjusted such that the total molar flow rate of the side draw is equal to the total molar flow rate of the main component in the feed (i.e., the total flow rate of the feed times the mole fraction of the main component). This configuration has been shown to result in reduced cycle times in comparison to configurations without controlling the side stream flow rate [16].

The distillate and bottom product molar flow rates are kept constant by manipulating their respective flow valves. In contrast to other investigations of semicontinuous processes (e.g., Pascall and Adams [19]), the concentrations of the impurities in the distillate and bottom product only vary slightly within the cycles. This is a result of the very small distillate and bottom product streams resulting from small concentrations of the impurities in the raw butyl acrylate up to 2000 ppm for each impurity (see Section 3). Therefore, a control system to maintain the impurity concentration in the top and bottom stream is not used. Besides the distillate and bottom product mass flow, the reflux ratio is kept constant throughout each simulation. For future investigations of this configuration, further degrees of freedom can be investigated by additionally varying the reflux ratio within a dynamic campaign.

Furthermore, the level of the reflux drum is kept constant by adjusting the feed flow rate and the level in the reboiler is maintained by adjusting the reboiler heat duty.

2.4. Process simulation

The distillation column is modelled using the equilibrium-based RadFrac model included in Aspen PlusTM and Aspen DynamicsTM.

Besides the design variables already described in Section 2.2, additional design variables need to be set in order to allow for a dynamic simulation of the process. The overall pressure drop for the column is set to 0.1 bar. The size of the column, the size of the middle vessel, the size of the reflux drum as well as the size of the sump were determined using the design heuristics published by Luyben et al. [30]. The pressure drops for the valves are set to 0.1 bar, except for the raw feed valve and the valve of the column feed, which are operated with a pressure drop of 0.05 bar. The column diameter is chosen based on the Aspen PlusTM sizing function and is set to 0.547 m.

Flooding and weeping behaviour is checked during the simulation studies using a flooding approach from Eckart [31,32] and neither flooding nor weeping conditions in any of the presented simulations were experienced.

Column top pressure, distillate-to-feed ratio, reflux ratio and the side stream to feed ratio are varied throughout the simulation studies to investigate the impact of these changes on the processes behaviour. Furthermore, the feed composition and the final purity achieved in the semicontinuous process are varied. Detailed explanations of the chosen operating parameters for the operation modes are summarised in Section 3.2 for the *n*-butyl acrylate simulations and Section 3.3 for the acrylic acid and for the *n*-butanol simulations.

The start-up procedure for the dynamic simulations in Aspen DynamicsTM was performed according to the descriptions published by Pascall and Adams [19]. Proportional integral controllers are used within this study. The controller parameters are tuned to ensure a stable operation throughout the cycles. An event-driven task is set-up to control the switch between the different modes within each cycle. Subsequently, the dynamic model is used to perform the simulation studies.

3. Results of semicontinuous process simulations

In this section, the design and the results of the three different operation modes are presented. In total, almost 320 dynamic simulations were performed for the investigation of the presented operation modes and parameter studies. The simulation studies are performed to demonstrate the feasibility of the use of semicontinuous distillation processes for the removal of small concentrations of bio-based impurities. Furthermore, the flexibility of these processes in respect to the use of the same semicontinuous setup for the purification of raw materials with varying initial impurity concentrations is shown and the use of a semicontinuous distillation unit as a multipurpose process for the purification of different raw materials is demonstrated. Therefore, within the simulation studies, the reflux ratio, column top pressure and the size of the distillate and bottom product mass flow (by the variation of the distillate-to-feed ratio and the side-stream to feed ratio) are varied. Furthermore, simulations with different initial impurity concentrations and different final specifications for acrylic acid, *n*-butanol and *n*-butyl acrylate are performed. To allow for a comparison of results of different case studies, the total amount of purified product should not differ significantly in the different simulations. To meet this requirement, five complete cycles are performed in each simulation. The performance criteria used for the evaluation are described in Section 3.1.

Figs. 6–8 summarise the results of one of the simulations of the *n*-butyl acrylate case study. The initial concentration of *n*-butyl acrylate for this simulation is $w_{BA} = 0.9930$, containing 1000 ppm of each of the seven impurities listed in the right column of Table 1. This simulation is performed with a reflux ratio of $RR = 200$, a column top pressure of $p = 0.576$ bar (the column top pressure of the reactive distillation column [6]), and distillate and bottom product

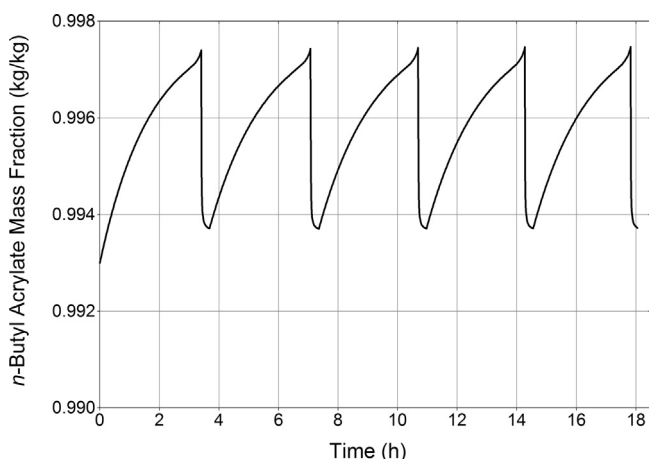


Fig. 6. *n*-Butyl acrylate purity in the middle vessel as a function of operating time for the purification of raw *n*-butyl acrylate with a purity of $w_{BA} = 0.9930$ to a final purity of $w_{BA} = 0.9970$ with a reflux ratio of $RR = 200$ and a column top pressure of $p = 0.576$ bar.

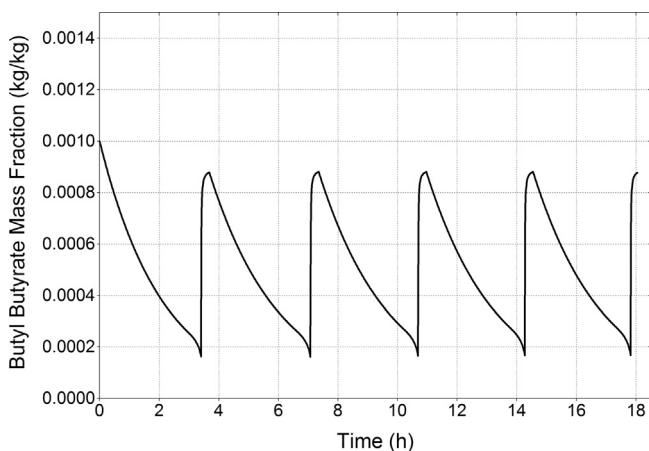


Fig. 7. Butyl butyrate mass fraction in the middle vessel as a function of operating time for the purification of raw *n*-butyl acrylate with a purity of $w_{BA} = 0.9930$ to a final purity of $w_{BA} = 0.9970$ at a reflux ratio of $RR = 200$ and a column top pressure of $p = 0.576$ bar.

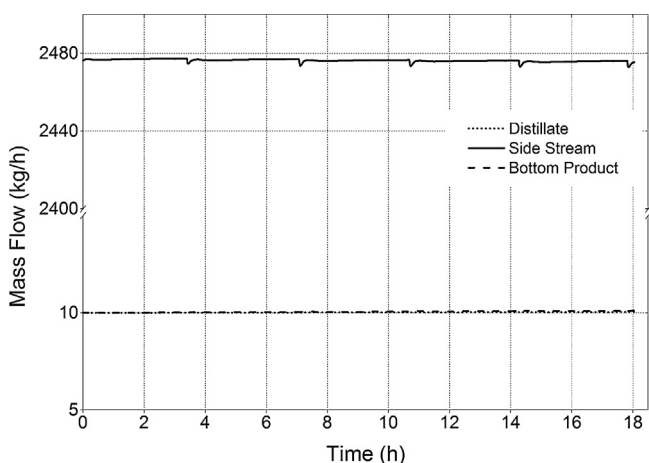


Fig. 8. Mass flows of distillate, side stream and bottom product for semicontinuous process as a function of operating time for the purification of raw *n*-butyl acrylate with a purity of $w_{BA} = 0.9930$ to a final purity of $w_{BA} = 0.9970$ at a reflux ratio of $RR = 200$ and a column top pressure of $p = 0.576$ bar.

mass flow setpoints of 10 kg h^{-1} (achieved with controllers that adjust the distillate-to-feed ratio and the side-stream to feed ratio). In the distillate stream, the weight fraction of the main component is $w_{BA} = 0.8142$ and in the bottom stream the weight fraction of the main component is $w_{BA} = 0.7207$ in average over all five cycles. In this study, a final purity of $w_{BA} = 0.9970$ *n*-butyl acrylate is achieved. Fig. 6 shows the *n*-butyl acrylate concentration as a function of operating time. Throughout each cycle, the concentration of *n*-butyl acrylate increases. As soon as the desired purity is reached, the product is removed from the middle vessel and the middle vessel is charged with raw *n*-butyl acrylate, causing the decrease in concentration. Note that the middle vessel is not completely emptied in between the cycles to ensure that flow to the distillation column continues uninterrupted. Also, note that the initial concentration of the first cycle is slightly lower compared to the cycles two to five because the initial concentration is a sort of initial guess. However, as shown in Fig. 2, a stable limit cycle is reached in the second cycle.

Fig. 7 shows the concentration of the heavy-boiling impurity butyl butyrate in the middle vessel over time. The trends for most of the other impurities follow essentially the same shape, and so only one is shown for clarity. As butyl butyrate is removed at the bottom of the semicontinuous process, the concentration in the middle vessel decreases until the desired purity for *n*-butyl acrylate is achieved and the cycle is restarted.

In Fig. 8, the corresponding mass flows of the distillate, the bottom product and the side stream are shown. As can be seen from this figure, the majority of the feed stream is leaving the column at the side-stream location in the middle of the column. This is a result of the low impurity concentrations in the feed. The light- and heavy-boiling impurities are removed in the small distillate and bottom product streams at the top and the bottom of the column.

A detailed analysis of the results for the *n*-butyl acrylate case study is shown in Section 3.2.

Figs. 6–8 are representative results for the simulations of all three case studies, demonstrating the stability of the dynamic process throughout several cycles and thus demonstrating the successful implementation of the control system for the semicontinuous distillation set-up.

3.1. Performance criteria

To evaluate the simulations within the different case studies, three performance criteria are defined and used in this study as an intuitive way of characterising and comparing the many case studies. For all studies shown within this paper, the cumulative energy demand, the cumulative amount of purified product and its composition and the cumulative amount of distillate and bottom product and its composition are monitored for five complete cycles. Investment costs are not used, as the same semicontinuous distillation unit was used as a multipurpose unit for all three operation modes. These cumulative values are used for the calculation of the performance criteria. The first performance criterion, the specific heat duty is shown in Eq. (1).

$$\text{Specific heat duty} = \frac{\text{Reboiler heat duty (kWh)}}{\text{Total product mass produced (kg)}} \quad (1)$$

The specific heat duty allows an estimation of the necessary energy demand of the reboiler per kg of purified product. The heat duty of the condenser is not taken into account for the calculation of this criterion and energy savings by a potential heat integration are not investigated.

The second criterion used to evaluate the process performance within this study is the specific loss of target product in the distillate

Table 3

Varied parameters and investigated ranges for *n*-butyl acrylate case study, taking all seven impurities into account. The values marked in bold are base-case values that are kept constant while the other parameters are varied during the simulation studies.

Parameter	Investigated range
Reflux ratio	200 , 300, 600
Column top pressure (bar)	0.2, 0.4, 0.576
Top/bottom mass flow (kg h ⁻¹)	5, 7.5, 10
Initial BA purity (wt.-frac.)	0.9930, 0.9948, 0.9965
Final BA purity (wt.-frac.)	0.9970, 0.9980, 0.9990

and bottom product streams as shown in Eq. (2).

Specific product loss

$$= \frac{\text{Product loss}_{\text{distillate}} (\text{kg}) + \text{product loss}_{\text{bottom product}} (\text{kg})}{\text{Total product mass produced} (\text{kg})} \quad (2)$$

The product used for the abovementioned calculations is either acrylic acid, *n*-butanol or *n*-butyl acrylate, depending on the considered case study.

Beside the loss of product and the energy demand of the process, the cycle time is used as the third performance criterion, as the length of the cycles is an indication for the yearly throughput of the plant. Also, because a stable limit cycle is not obtained until the second cycle, the cycle time of the second cycle is used for the evaluation purposes.

3.2. Purification of *n*-butyl acrylate

For the *n*-butyl acrylate simulation studies, seven different impurities are taken into account, namely: isoamyl alcohol, acetic acid, butyl acetate, butyric acid, butyl butyrate, butyl propionate and propionic acid (see Table 1). In an earlier investigation, these impurities were found to accumulate in the final product *n*-butyl acrylate within the reactive distillation process [15]. The investigated ranges for the operating parameters of the semicontinuous process, for the initial and for the final purity of *n*-butyl acrylate are summarised in Table 3.

The reflux ratio is varied between RR = 200, 300 and 600. These large values are results of the small total size of the distillate stream. Therefore, even at high reflux ratios of RR = 600, the total reflux flow is moderate compared to the feed flow. The results of changes in the column top pressure are investigated at $p = 0.2, 0.4$ and 0.576 bar. The highest pressure of $p = 0.576$ bar results from the operating pressure of the reactive distillation column upstream to this semicontinuous process [6]. The other investigated pressures are lower, as higher pressures result in higher temperatures and hence in a higher risk for a polymerisation of *n*-butyl acrylate [8]. As the raw material contains only small fractions of the impurities, the investigated distillate and bottom product flows are small in comparison to the side-stream. In this study, mass flows of $\dot{m}_{\text{Top,Bot}} = 5 \text{ kg h}^{-1}$, 7.5 kg h^{-1} and 10 kg h^{-1} are investigated with a distillate and bottom product mass flow of the same size within each simulation. An impurity concentration of $w_{\text{Imp}} = 500 \text{ ppm}$, 750 ppm and 1000 ppm is studied for each impurity, resulting in initial purities for *n*-butyl acrylate of $w_{\text{BA}} = 0.9930, 0.9948$ and 0.9965 . For the final purities of *n*-butyl acrylate, the industrial specification of $w_{\text{BA}} = 0.9970$, as well as higher purities of $w_{\text{BA}} = 0.9980$ and $w_{\text{BA}} = 0.9990$ are investigated. The values highlighted in bold in Table 3 are the base-case parameters that are kept constant during the investigation of the other parameters in this simulation study.

The average concentration of *n*-butyl acrylate in the distillate stream is $w_{\text{BA}} = 0.8693$ for all experiments with a distillate and bottom product flow of $\dot{m}_{\text{Top,Bot}} = 10 \text{ kg h}^{-1}$, resulting in an average impurity concentration of $w_{\text{Imp}} = 0.1307$ in the distillate. In

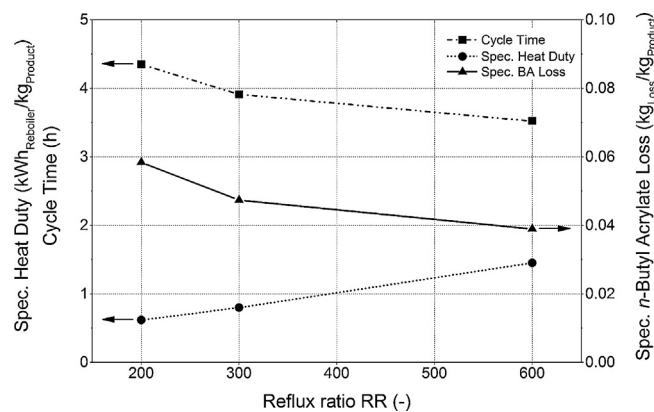


Fig. 9. Specific heat duty, specific *n*-butyl acrylate loss and cycle times for the purification of *n*-butyl acrylate from an initial purity of $w_{\text{BA}} = 0.9948$ to a final purity of $w_{\text{BA}} = 0.9980$ as a function of the reflux ratio.

the bottom product, the average *n*-butyl acrylate concentration is $w_{\text{BA}} = 0.7916$, leading to an average impurity concentration of $w_{\text{Imp}} = 0.2084$. For a distillate and bottom product flow of $\dot{m}_{\text{Top,Bot}} = 7.5 \text{ kg h}^{-1}$, the average *n*-butyl acrylate concentration slightly increased to $w_{\text{BA}} = 0.8848$ for the distillate and $w_{\text{BA}} = 0.8356$ for the bottom product. A further decrease of the distillate and bottom product flow to $\dot{m}_{\text{Top,Bot}} = 5 \text{ kg h}^{-1}$ does not result in significant changes of the amount of impurities in the distillate and bottom product, ending up with average *n*-butyl acrylate concentrations of $w_{\text{BA}} = 0.8730$ for the distillate and $w_{\text{BA}} = 0.8202$ for the bottom product. The resulting total loss of *n*-butyl acrylate per mass of purified product is given in this section.

For an increasing reflux ratio, the specific heat duty increases by 57% from 0.62 kWh kg^{-1} for RR = 200 to 1.45 kWh kg^{-1} for RR = 600 (Fig. 9). This results from the increasing flow rate of internal liquid and vapour streams inside the column. The impact of the reflux ratio on the specific heat duty is significantly larger than its impact on the specific *n*-butyl acrylate loss (−33%) and the cycle time (−19%). In other words, increasing the reflux ratio improves both the yield and the cycle time, but with increasing energy demands. The optimal value for the reflux ratio will depend on the specific application of this process and depend strongly on the costs for heat and the costs for the loss of *n*-butyl acrylate product.

An example of the results for changes in the distillate and bottom product mass flow is shown in Fig. 10, showing a purification from an initial *n*-butyl acrylate concentration of $w_{\text{BA}} = 0.9930$ to a final concentration of $w_{\text{BA}} = 0.9970$. The base-case pressure ($p = 0.576$ bar) and the base-case reflux ratio (RR = 200) are used.

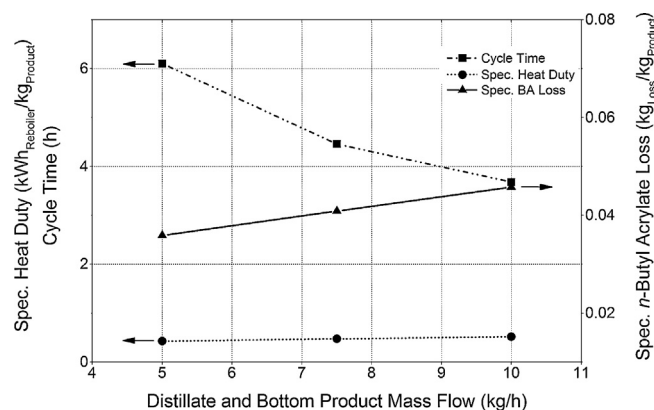


Fig. 10. Specific heat duty, specific *n*-butyl acrylate loss and cycle times for the purification of *n*-butyl acrylate from an initial purity of $w_{\text{BA}} = 0.9930$ to a final purity of $w_{\text{BA}} = 0.9970$ as a function of the distillate and bottom product mass flow.

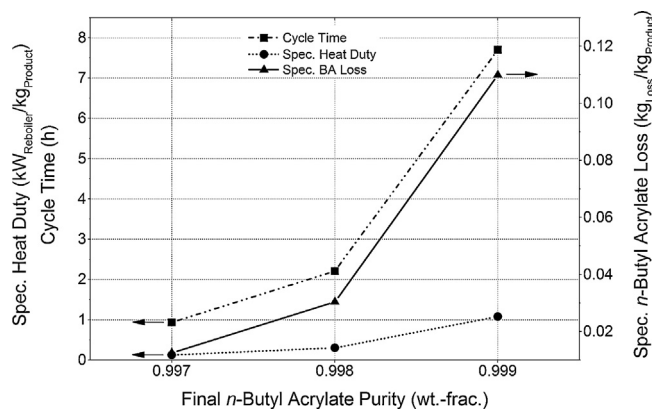


Fig. 11. Specific heat duty, specific *n*-butyl acrylate loss and cycle times for the purification of *n*-butyl acrylate from varying initial purities for *n*-butyl acrylate to a final purity of $w_{BA} = 0.9980$ as a function of the initial *n*-butyl acrylate purity.

As shown in Fig. 10, the cycle time is most significantly impacted by changes in the distillate and bottom product mass flows. As product mass flows increase, the impurities are also removed more quickly, and thus the desired purity for *n*-butyl acrylate is reached in a shorter time. For example, the cycle time decreases by as much as 40% by increasing the distillate and bottom mass flow from 5 kg h^{-1} to 10 kg h^{-1} . However, the tradeoff is that this also results in both higher specific heat duty (more energy spent per kg of product recovered) as well as higher *n*-butyl acrylate concentrations in these streams (more specific *n*-butyl acrylate loss, from 3.6% to 4.6% over the same range). These results from the increased internal column flow rates caused by the higher distillate flow rates with the same reflux ratio.

For the purification of bio-based raw materials, a process with a high flexibility is necessary, as both the composition of the different impurities and the concentration of these impurities can differ depending on the feedstock of the fermentation process and from batch to batch. Fig. 11 shows how the three performance criteria are affected by changes in the initial impurity concentration in raw *n*-butyl acrylate. In each case, a final purity of $w_{BA} = 0.9980$ is achieved, demonstrating that the process is flexible with regard to batch-to-batch changes in purities. For the example shown in Fig. 11, a decrease of the *n*-butyl acrylate purity in the feed from $w_{BA} = 0.9965$ to $w_{BA} = 0.9930$ results in an increase of the cycle time from 2.2 h to 8 h with proportional increases for the specific heat duty and the specific *n*-butyl acrylate loss. In contrast to continuous purification processes, a decrease of the initial purity of the raw materials in a semicontinuous process can be compensated by an increasing cycle time, without the need to change the other operating parameters.

In addition to flexibility with respect to varying feed concentrations, the semicontinuous process can also handle batch-to-batch setpoint changes in the final purity for the target product. Fig. 12 shows the results of simulations with an initial *n*-butyl acrylate concentration of $w_{BA} = 0.9965$ and base-case values for the three operating parameters. By just increasing the cycle time of the process, an increased final purity for the target product can be achieved. Due to the asymptotic slope of the results towards infinity at an *n*-butyl acrylate purity of 1, the costs drastically increase at very high purities.

The last parameter investigated in this simulation study is the column top pressure. The optimised reactive distillation column operates at a top pressure of $p = 0.576$ bar, as larger pressures cannot be realised due to constraints imposed by the chosen catalyst and the polymerisation tendency of some components [8]. Beside the operating pressure of the reactive distillation column, two lower pressures, $p = 0.2$ bar and 0.4 bar, are investigated. Although a

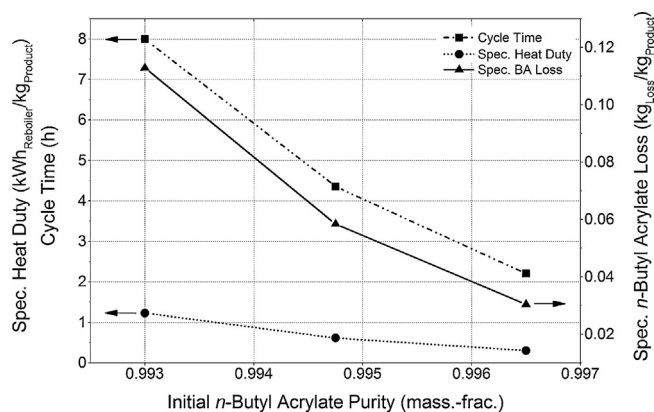


Fig. 12. Specific heat duty, specific *n*-butyl acrylate loss and cycle times for the purification of *n*-butyl acrylate from an initial purity of $w_{BA} = 0.9965$ to varying final purities as a function of the final *n*-butyl acrylate purity.

reduced pressure also reduces the boiling temperatures in the column, a clear trend for the heat duty as a function of the pressure is not found. Instead, all three performance criteria exhibit a minimum at the medium pressure of $p = 0.4$ bar. To further investigate this trend, the percentage removal of the seven investigated impurities in the purified *n*-butyl acrylate as a function of the column top pressure is shown in Fig. 13.

In the simulations shown in this figure, a purification of raw *n*-butyl acrylate with an initial concentration of $w_{BA} = 0.9930$ to a final concentration of $w_{BA} = 0.9980$ is studied with impurity concentrations in the raw feed of 1000 ppm per impurity. Three key conclusions can be made from the results. First, the components butyric acid, butyl butyrate, propionic acid and butyl acetate are almost completely removed from *n*-butyl acrylate using the semi-continuous distillation process for the whole investigated pressure range. Of these components, butyl acetate is removed together with the distillate, while butyric acid, butyl butyrate and propionic acid are removed together with the bottom product. Second, butyl propionate, which is fed with a concentration of 1000 ppm in raw *n*-butyl acrylate, is not removed at all using this process. This is a result of the vapour pressures of *n*-butyl acrylate and butyl propionate which are essentially identical to each other for the investigated pressure range. Third, the separation efficiency for isoamyl alcohol and acetic acid changes strongly with pressure, but with opposing trends. At higher pressures, the separation of isoamyl alcohol,

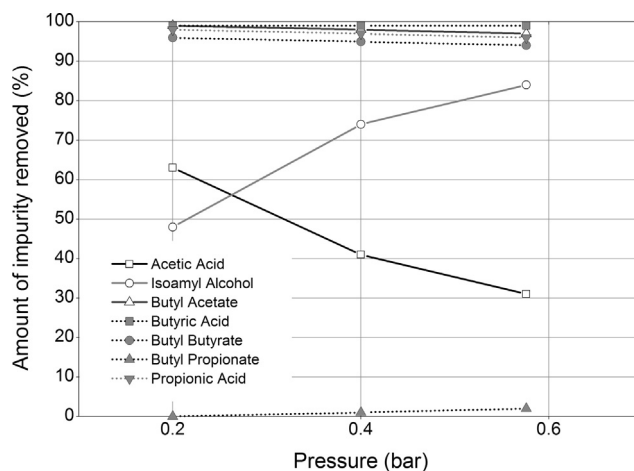


Fig. 13. Amount of removed impurity in purified *n*-butyl acrylate for the purification of an initial purity of $w_{BA} = 0.9930$ (1000 ppm per impurity) to a final purity of $w_{BA} = 0.9980$ as a function of the column top pressure.

which is separated together with the distillate, is advantageous, as the difference in the boiling temperature between *n*-butyl acrylate and isoamyl alcohol increases with increasing pressure. However, the opposite is true for the heavy-boiling component acetic acid, which is more favourable at lower pressures due to the presence of a heavy-boiling azeotrope between *n*-butyl acrylate and acetic acid. Although the difference in boiling temperature between *n*-butyl acrylate and acetic acid increases with pressure, the fraction of acetic acid in the azeotropic composition decreases with increasing pressure, and thus the separation of acetic acid at lower pressures is advantageous.

Therefore, two additional cases for the purification of *n*-butyl acrylate are simulated. In both cases, butyl propionate is not added to the raw *n*-butyl acrylate, assuming that it is not produced in the reactive distillation process. The first case is simulated at $p = 0.2$ bar without adding butyl propionate and isoamyl alcohol. The initial purities for *n*-butyl acrylate are kept constant in comparison to the study taking all seven impurities into account ($w_{BA} = 0.9930, 0.9948, 0.9965$). This allows a comparison of the results to the main case, as the same amount of impurities needs to be separated for the same final purities. The five remaining impurities are added at equal concentrations achieving a final mass fraction of one. In the second case, a simulation at $p = 0.576$ bar is performed without adding butyl propionate and acetic acid, which is difficult to separate at higher pressures. The results for the purification and the product loss based on an initial purity of $w_{BA} = 0.9965$ for the three different cases are summarised in Fig. 14.

For these two case-studies, the average concentration of *n*-butyl acrylate for all simulations in the distillate and bottom product is $w_{BA} = 0.8472$ in the distillate and $w_{BA} = 0.7262$ in the bottom product, resulting in average impurity concentrations for the distillate and bottom product of $w_{Imp.} = 0.1528$ and $w_{Imp.} = 0.2738$, respectively.

The use of a semicontinuous process for the separation of an impurity mixture without butyl propionate significantly increases the efficiency of the process. The trends shown in Fig. 14 are also found for the specific heat duty and the cycle times and for the other two initial purities, which means that both investigated cases improve all performance criteria in comparison to the case, where all impurities are taken into account. For a purification to a final purity of $w_{BA} = 0.9990$, the specific heat duty was reduced by 55% for case 1 (Fig. 14) and by 61% for case 2, the specific *n*-butyl acrylate loss by 59% for case 1 and by 63% for case 2 and the cycle time by 54% for case 1 and by 61% for case 2. Besides a significant decrease of the energy consumption, the *n*-butyl acrylate loss

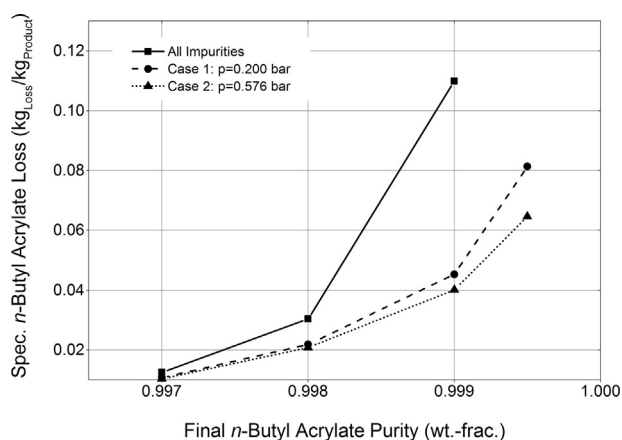


Fig. 14. Comparison of specific *n*-butyl acrylate loss for the case study with all impurities and the two case studies with five impurities each as a function of the final *n*-butyl acrylate purity with an initial purity of $w_{BA} = 0.9965$.

and the cycle times, higher final purities can also be achieved, if the process is used for suitable impurity compositions. For the simulations shown in Fig. 14, a final purity of $w_{BA} = 0.9995$ is additionally investigated, which cannot be achieved when the raw material contains significant amounts of butyl propionate. Depending on the concentrations of acetic acid and isoamyl alcohol in the raw material, a suitable operating pressure needs to be chosen to allow for an efficient separation of these components.

3.3. Purification of bio-based reactants *n*-butanol and acrylic acid

Besides the use of a semicontinuous distillation column for the removal of impurities from *n*-butyl acrylate downstream of the reactive distillation column, impurities can also be separated directly from the reactants acrylic acid and *n*-butanol upstream of the reactive distillation process. As a result, the formation of butyl propionate in the reactive distillation column, which cannot be separated from the final product *n*-butyl acrylate using the semicontinuous distillation process, can potentially be avoided. Within the investigations of the two reactants, the same semicontinuous distillation setup is used as for the purification of *n*-butyl acrylate, demonstrating that a single semicontinuous distillation column can potentially be used as a multipurpose unit for the purification of several bio-based chemicals (Fig. 5).

Within the reactant acrylic acid, the light-boiling impurity acetic acid and the heavy-boiling impurity propionic acid are identified [15] and separated using the semicontinuous distillation. The recovery of propionic acid would avoid the formation of butyl propionate in the reactive distillation column and therefore the complex separation from *n*-butyl acrylate. The recovery of acetic acid would also be advantageous, as the pressure sensitive separation from *n*-butyl acrylate would not be necessary. Within the reactant *n*-butanol, the light-boiling impurity isobutanol and the heavy-boiling impurities acetic acid, isoamyl alcohol and butyric acid are identified and their separation is investigated in this section. The recovery of isoamyl alcohol is especially advantageous because this would avoid the complex separation from *n*-butyl acrylate. A summary of the potential impurities in the studied bio-based chemicals within this paper is shown in Table 1.

The investigated ranges for the operating parameters of the semicontinuous process as well as the investigated initial and the final purities of *n*-butanol and acrylic acid are summarised in Table 4.

Within these simulation studies, the same ranges for the reflux ratio, the column top pressure and the distillate and bottom product mass flows are investigated in the same way as for the *n*-butyl acrylate case study shown in Section 3.2. Furthermore, the same final purities of $w_{AA,BuOH} = 0.9970, 0.9980$ and 0.9990 are investigated and an additional purity of $w_{AA,BuOH} = 0.9995$ is taken into account. The initial purities for this study are varied between $w_{AA} = 0.9960, 0.9972$ and $w_{AA} = 0.9986$ for acrylic acid and $w_{BuOH} = 0.9920, 0.9944, 0.9960$ and $w_{BuOH} = 0.9972$ for *n*-butanol, maintaining equally distributed concentrations of the impurities ranging from 700 ppm to 2000 ppm for each impurity in both case studies. As bio-based

Table 4

Operating parameters and investigated ranges for the *n*-butanol and acrylic acid case study, taking the respective impurities into account. The values marked in bold are base-case values that are kept constant while the other parameters are varied during the simulation studies.

Parameter	Investigated range
Reflux ratio	200 , 300, 600
Column top pressure (bar)	0.2, 0.4, 0.576
Top/bottom mass flow (kg h ⁻¹)	5, 7.5, 10
Initial AA, BuOH purity (wt.-frac.)	0.9920, 0.9944, 0.996, 0.9972
Final AA, BuOH purity (wt.-frac.)	0.9970, 0.9980, 0.9990, 0.9995

acrylic acid only contains two impurities in significant amounts and bio-based *n*-butanol contains four impurities, different initial reactant purities are investigated.

3.3.1. Purification of acrylic acid

The use of a ternary semicontinuous distillation system is simulated for the separation of acetic acid and propionic acid from a high-purity acrylic acid mixture. In this portion of the study, the operating parameters, initial purities and final purities summarised in Table 4 are investigated. The two impurities acetic acid and propionic acid are taken into consideration as impurities in acrylic acid, whereas acetic acid is light-boiling in comparison to acrylic acid and is supposed to be collected in the distillate and propionic acid is supposed to be collected in the bottom stream due to a heavy-boiling azeotrope formed by propionic acid and acrylic acid. In the simulation study using a ternary semicontinuous distillation process, only a slight purification is achieved for the acrylic acid stream compared to the initial impurities. For example, a purification of an initial concentration of $w_{AA} = 0.9960$ is only possible up to a final concentration of $w_{AA} = 0.9980$. The purified acrylic acid streams still contain large amounts of acetic acid for all simulations, whereas most of the propionic acid is removed. This is also reflected by the acrylic acid concentrations in the distillate and bottom product stream. The average acrylic acid concentration in the distillate for all simulations for the purification of acrylic acid is $w_{AA} = 0.9792$ and in the bottom product the average acrylic acid concentration is $w_{AA} = 0.8653$, demonstrating the low impurity concentrations in these streams and the big loss of acrylic acid. Fig. 15 shows the percentage removal of both impurities in the purified acrylic acid for the purification from an initial concentration of $w_{AA} = 0.9980$ (1000 ppm per impurity) to a final concentration of $w_{AA} = 0.9990$ as a function of the pressure for the three investigated column top pressures of $p = 0.2$, 0.4 and $p = 0.576$ bar.

Both impurities are fed with an initial concentration of 1000 ppm within this simulation. The reason for the poor purification performance of the semicontinuous distillation system is shown in Fig. 15. Despite a good recovery of the propionic acid, high final purities of acrylic acid cannot be achieved as acetic acid is only slightly removed from the acrylic acid. The removal of acetic acid is also not significantly improved by a variation of the other operating parameters.

3.3.2. Purification of *n*-butanol

The use of a ternary semicontinuous distillation system is simulated for the separation of isobutanol, acetic acid, isoamyl alcohol

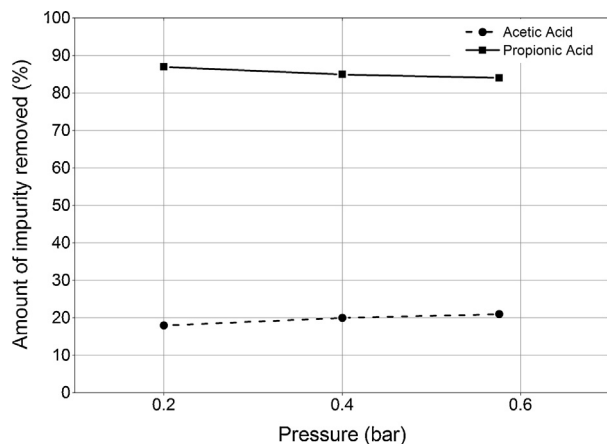


Fig. 15. Amount of removed impurity in purified acrylic acid for the purification of an initial purity of $w_{AA} = 0.9980$ (1000 ppm per impurity) to a final purity of $w_{AA} = 0.9990$ as a function of the column top pressure.

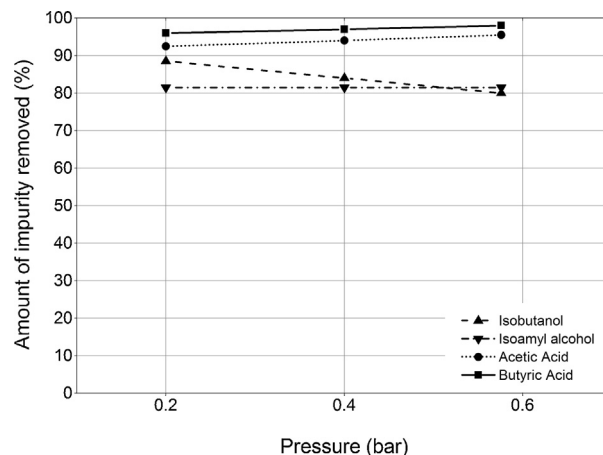


Fig. 16. Amount of removed impurity in purified *n*-butanol for the purification of an initial purity of $w_{AA} = 0.9920$ (2000 ppm per impurity) to a final purity of $w_{AA} = 0.9990$ as a function of the column top pressure.

and butyric acid from a high-purity *n*-butanol stream. The operating parameters, initial purities and final purities investigated in this case study are summarised in Table 4. For the separation of these four impurities, the ternary semicontinuous distillation column shows promising results, separating isobutanol at the top of the column and acetic acid, isoamyl alcohol and butyric acid at the bottom. A final purity of $w_{BuOH} = 0.9995$ is achieved even with the worst investigated initial purity of $w_{BuOH} = 0.9920$ with a cycle time of 8.7 h, a specific *n*-butyl acrylate loss of 0.109 kg kg^{-1} and a specific heat duty of 2.4 kWh kg^{-1} . Fig. 16 shows the results of a simulation with an initial purity of $w_{BuOH} = 0.9920$ to a final purity of $w_{BuOH} = 0.9990$. In this figure, the recovery rate of the four investigated impurities is shown as a function of the column top pressure. As the initial purity of this simulation is $w_{BuOH} = 0.9920$, the impurities are fed with a concentration of 2000 ppm each.

A significant separation of all impurities is achieved within this process. The separation of isoamyl alcohol is not affected by changing the operating pressure of the column, whereas the separation of the other three components can be improved by using the optimal column top pressure. As the concentration of isobutanol in the distillate increases with decreasing pressure, the recovery of isobutanol at lower pressures is advantageous. A better separation of butyric acid and acetic acid is achieved at higher pressures. For butyric acid, the difference of the boiling point in comparison to *n*-butanol increases with increasing pressure, allowing a better separation. The separation of acetic acid is also improved with increasing pressure, although the difference in the vapour pressures of *n*-butanol and acetic acid decreases with increasing pressure in the investigated operating range. This results from the heavy boiling azeotrope of acetic acid and *n*-butanol. The composition of this binary homogeneous azeotrope changes from $w_{\text{acetic acid}} = 0.395$ at $p = 0.576$ bar to $w_{\text{acetic acid}} = 0.363$ at $p = 0.200$ bar, allowing a better separation of acetic acid at higher pressures.

For the simulations varying the operational parameters as well as the initial and final purities of *n*-butanol, comparable results to the *n*-butyl acrylate case study are obtained, except for the variation of the pressure. Simulations of purification from an initial purity of $w_{BuOH} = 0.9920$ to a final purity of $w_{BuOH} = 0.9990$ are performed at different pressures, with results shown in Fig. 17. In the study, all impurities have identical feed concentrations.

The results indicate that the impact of the column top pressure on the final concentration of isobutanol is large in comparison to the impact of the pressure on the concentrations of the other components. A reduction of the cycle time (-16%), the specific heat

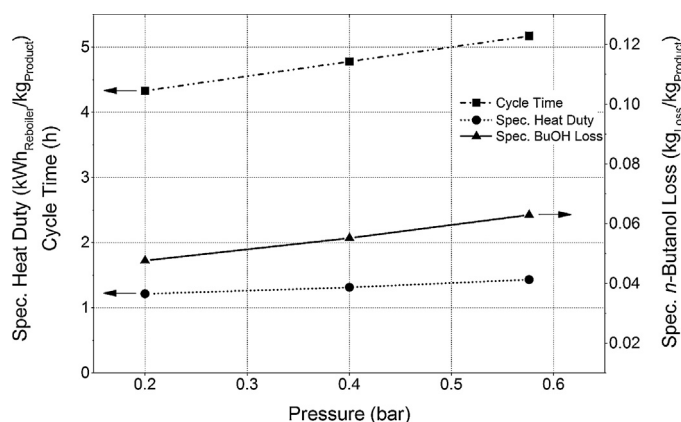


Fig. 17. Specific heat duty, specific *n*-butanol loss and cycle times for the purification of *n*-butanol from an initial purity of $w_{\text{BuOH}} = 0.9920$ to a final purity of $w_{\text{BuOH}} = 0.9990$ as a function of the column top pressure.

duty (–15%) and the specific *n*-butanol loss (–24%) is achieved by a pressure change from 0.576 bar to 0.200 bar.

The average concentration of the main component *n*-butanol found for these simulations is $w_{\text{BuOH}} = 0.9002$ in the distillate and $w_{\text{BuOH}} = 0.6246$ in the bottom product, demonstrating a good impurity separation, especially in the bottom product stream.

3.4. Analysis

The results for the purification of the two bio-derived reactants acrylic acid and *n*-butanol and of the final product *n*-butyl acrylate using a semicontinuous distillation system were presented in Section 3 of this investigation. The use of a semicontinuous process is shown for a mixture of various impurities and a separation of these impurities can be performed in a single semicontinuous distillation column. The ability of a semicontinuous distillation system to act as a multipurpose unit and purify various streams is shown. A main focus of this study is to evaluate the flexibility of this process to be able to handle varying impurity concentrations in respect to the composition and the concentration of the single impurities. It is shown that a semicontinuous process is able to maintain final purities without changes in operational parameters such as the reflux ratio or the column pressure, only by increasing or decreasing the cycle times. Furthermore, higher final purities can easily be achieved by longer cycle times without the necessity to change other operating parameters. Nevertheless, the boundaries of the semicontinuous process for these case studies are shown with respect to the separability of some of the investigated components. Based on the results shown in Section 3, the feasibility for the use of a semicontinuous distillation system for the presented case-studies were identified.

In the investigation for the purification of the final product *n*-butyl acrylate it was found, that six of the seven impurities can be separated using the semicontinuous technology, only butyl propionate cannot be removed using semicontinuous processing. The difficulty in removing butyl propionate results from almost identical vapour pressures of *n*-butyl acrylate and butyl propionate. Hence, for a successful implementation of semicontinuous processing downstream of the reactive distillation process, the formation of butyl propionate should be avoided, e.g., by removing the propionic acid upstream of the reactive distillation column. Besides these difficulties, an efficient simultaneous separation of isoamyl alcohol and acetic acid is not possible, as their separation efficiency strongly changes with pressure, but with opposing trends. Therefore, two additional cases were simulated with five impurities each, both without having butyl propionate as an impurity in

Table 5

Results of the presented study showing the investigated impurities and the main component they should be separated from in the investigated pressure range. “++” represents an amount of more than 90% of the impurity removed, “+” between 50% and 90% removed, “–” between 10% and 50% removed and “––” represents an amount of less than 10% removed.

Impurity	AA-feed	BuOH-feed	BA-product
Isobutanol		+	
Acetic acid	–	++	+/-
Butyl acetate			++
Isoamyl alcohol		+	
Propionic acid	+		++
Butyl propionate			--
Butyl butyrate			++
Butyric acid		++	++

the *n*-butyl acrylate stream and with either acetic acid or isoamyl alcohol, depending on the operating pressure of the column. In these studies it is shown, that significant savings in energy demand and product losses and reduced cycle times can be achieved, just by a change of the operational pressure in dependency of the impurities found in *n*-butyl acrylate. Therefore, the semicontinuous process is an attractive technology for the separation of impurities from the final product *n*-butyl acrylate, as long as only small amounts of propionic acid were found in the bio-based feed streams, leading to negligible concentrations of butyl propionate.

In the investigations for the purification of the two reactants upstream of the reactive distillation process, the feasibility of a semicontinuous process was only found for one of the two reactants. For bio-derived acrylic acid, the use of a semicontinuous process simultaneously removing the light-boiling and heavy-boiling impurities does not offer any advantages for the purification, as only a slight separation of acetic acid is achieved by this distillation process. Nevertheless, the removal of propionic acid using this technique shows promising results and avoids the formation of butyl propionate in the reactive distillation column. But as only one separation step is successfully performed in this process, the use of a normal distillation column or an alternative separation technique should be preferred to a semicontinuous system. For *n*-butanol, an efficient separation of impurities contained in bio-based *n*-butanol is achieved using a ternary semicontinuous distillation column, even at comparably low initial *n*-butanol purities of $w_{\text{BuOH}} = 0.9920$. A flexible purification is possible for the entire range of initial and final impurities tested, and the same semicontinuous distillation system can be used for several different purification tasks. The impact of changes in the operating parameters is essentially the same as it was for the *n*-butyl acrylate case study. However, in the final implementation of the proposed system, the reflux ratio, distillate mass flow rate, and bottom product mass flow rate should be determined by optimisation of the process economics, which are outside of the scope of this study. For this system, it is expected that low column pressures will be optimal since the separation of isobutanol is significantly improved, while the separation of the other impurities does not change significantly. A summary of the results obtained in this study, showing the single impurities and the main component they should be separated from, is given in Table 5. Impurities that are removed by more than 90% are marked with “++”, between 50% and 90% they are marked with “+”, from 10% to 50% they are marked with “–” and for a removal of less than 10% they are marked with “––”. For impurities that are removed by more than 50%, a use of the semicontinuous process concept for the separation of the impurity from this main component, for acrylic acid and *n*-butanol upstream of the reactive distillation process and for *n*-butyl acrylate downstream of the reactive distillation process, is potentially feasible.

To conclude, the semicontinuous process is an attractive technology for future bio-based separations, allowing a high flexibility in respect to initial and final purities within given boundaries.

4. Conclusion and future outlook

In this work, the application of a ternary semicontinuous distillation system to realistic batch purification problems that occur both upstream and downstream of a reactive distillation column used for the production of bio-derived *n*-butyl acrylate from *n*-butanol and acrylic acid was investigated using dynamic simulations. Additional purification is needed because industrial purity requirements for *n*-butyl acrylate cannot be achieved using the reactive distillation process as it currently exists. The semicontinuous process was used, as an additional continuous purification unit, such as a conventional distillation column, does not provide the flexibility to guarantee the product specification using bio-derived raw materials with changing impurity compositions. Ternary semicontinuous distillation processes simultaneously perform two thermochemical separation steps (which typically requires two distillation columns in continuous operation) in a single distillation column, facilitated by the tight integration with a middle-vessel.

In the analysis, the impacts of changes in key operational parameters and conditions (reflux ratio, distillate mass flow rate, bottom product mass flow rate, column top pressure, initial and final purities of each of the three primary products) on the performance of the process were investigated. It was determined that the semicontinuous process can successfully be used for removal of all impurities except two of the seven studied from *n*-butyl acrylate for the entire range of initial and final desired purities studied; butyl propionate cannot be removed thermally due to nearly identical vapour pressures with butyl acrylate, and only one of the pair of acetic acid or isoamyl alcohol can be removed in significant amounts depending on the pressure chosen. In addition, the use of a semicontinuous system for the purification of *n*-butanol shows promising results, since all impurities could be removed from the *n*-butanol using the same process configuration as the *n*-butyl acrylate system. However, the results indicate that the use of a semicontinuous process for the purification of bio-based acrylic acid, containing the two impurities acetic acid and propionic acid, is not feasible, as only the propionic acid and small amounts of the acetic acid are removed.

Furthermore, the results of the analysis indicate that, for the *n*-butyl acrylate and *n*-butanol systems studied, ternary semicontinuous distillation systems are flexible enough to handle batch-to-batch variations in both the initial concentrations of impurities and the final purity setpoint of the primary product, but do not require shut-down, cool-down, or start-up phases between them. This is a significant advantage over batch distillation. Furthermore, the distillate and bottoms products are removed continuously at near-steady state, meaning that this semicontinuous distillation strategy has both the steady-state processing advantages of continuous distillation and the batch-to-batch flexibility advantages of batch distillation. Furthermore, the same semicontinuous process can be used for several purification tasks, also allowing a high flexibility in respect to the chemical system. For an industrial application, the semicontinuous process can be used on demand if the desired product purity cannot be achieved due to high impurity concentrations. Although this work demonstrates the technical feasibility of removing most of the impurities from bio-derived *n*-butyl acrylate, an economic analysis was not within the scope and thus should be considered in future work to determine if this process should be commercialised.

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Appendix A. Nomenclature

Latin letters

\dot{m}_i	mass flow of flow <i>i</i> (kg h ⁻¹)
<i>p</i>	pressure (bar)
<i>T</i>	temperature (K)
w_i	weight fraction of component <i>i</i> in the liquid phase (kg kg ⁻¹)

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cep.2013.09.008>.

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