

Separation of Crotonic Acid and 2-Pentenoic Acid Obtained by Pyrolysis of Bio-Based Polyhydroxyalkanoates Using a Spinning Band Distillation Column

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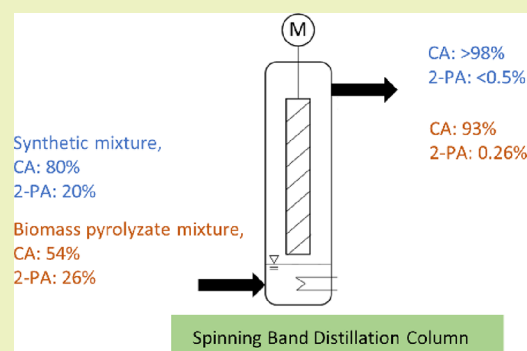
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ABSTRACT: Searching for renewable alternatives to produce platform chemicals, various biomasses have shown great potential as feedstock for value-added chemicals. For instance, biomass obtained by aerobic digestion of wastewater is rich in the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Pyrolysis of PHBV yields a mixture of crotonic acid (CA) and 2-pentenoic acid (2-PA). Application of CA and 2-PA as bio-based monomers requires purification. Purification by distillation is challenging as the high melting point of CA (72 °C) in combination with the high polymerization potential limits the temperature window for distillation severely. This study has experimentally explored the use of a spinning band distillation column (SBC) under vacuum operation to separate these acids. The thermodynamic feasibility for distillation was first studied by measuring vapor–liquid equilibrium data at relevant pressures of 50 and 100 mbar. The separation in the SBC was accomplished at 50 mbar and 40–110 °C for about 5 h. A successful recovery of CA with a high purity of >98% was achieved using a synthetic mixture of acids with a mass ratio of 80/20 (CA/2-PA). Actual pyrolyzate mixtures obtained by pyrolysis of the biomass and extracted pure PHBV were also fed to the distillation column and resulted in separation of CA with purities of 96 and 93%, respectively.

KEYWORDS: crotonic acid, 2-pentenoic acid, pyrolyzates, bio-based monomers, spinning band distillation column



INTRODUCTION

There is a pronounced growth in industrial interest for renewable and environmentally sustainable pathways to produce chemicals. Driven by the desire to move away from linear economic models based on the supply of fossil fuel-based materials, renewable sources for chemicals are being explored. Major classes of bio-based chemicals include bio-based solvents,^{1,2} bio-based platform chemicals,³ bio-based carboxylic acids,^{4–6} and bio-based polymers.^{7–9} In most cases, the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) copolymer is the main bio-based copolymer that can be obtained during fermentation of volatile fatty acid (VFA)-enriched wastewater. Starting from wastewater as an inexpensive feedstock for the microorganisms can result in a low-cost bio-based pathway to produce PHBV. However, the drawback of wastewater as feedstock for PHBV production is a varying product composition and quality, which are important characteristics of the produced PHBV. It is because during the fermentation process in the mixed microbial cultures (MMCs), VFAs with an even number of carbons will be converted to poly(3-hydroxy butyrate) (PHB). The ones with an odd number will be converted into a PHBV copolymer with varying hydroxy valerate (HV) contents.¹⁰ It is possible to adjust the composition of the wastewater prior to the fermentation to

produce polymers with certain properties. However, controlling the feed would increase the cost of the bio-based production pathway. For a process based on fermenting a mixture of odd and even VFAs, PHBVs with varied properties are the main bio-polymers produced in the MMCs without controlling the feed composition. An alternative to direct use, the PHBV grown without well-controlled conditions in MMCs can be pyrolyzed to produce their corresponding 2-alkenoic acids. Crotonic acid (CA) and 2-pentenoic acid (2-PA) are the main pyrolyzates during pyrolysis of the PHBV, originating from hydroxy butyrate (HB) and HV monomers, respectively.

CA, or *trans*-2-butenoic acid, is mainly used in the synthesis of copolymers. Among the known copolymers based on CA, crotonic acid-vinyl acetate is the main copolymer, with the trade names of Cevian, Gelva, Mowilith, and Vinac,¹¹ which are used in cosmetic and hair styling products. Apart from this,

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CA finds further applications in industries such as coatings, paint, textile, binders, adhesives, flocculants, ceramics, and agrochemicals.¹² The esters of 2-PA can be used in flavoring essences, and its current application is mainly in medicine studies.^{13,14} The ongoing market of these unsaturated carboxylic acids is limited due to their complex production routes. Therefore, providing a relatively straightforward and bio-based pathway is expected to enhance their market.

Although the synthesis of CA via PHB/PHBV thermal decomposition has been examined over the last decades,^{12,15–20} its separation from complex pyrolysis mixtures has not been well studied. A fluidized bed setup was developed by Mullen et al.²¹ to pyrolyze the PHB/switchgrass blend and yield CA-enriched bio-oil on a pilot scale. In situ fractionation of the pyrolyzate mixture was achieved by multistep condensation using water-cooled (4 °C) condensers connected to an electrostatic precipitator. Considering the melting point of CA (72 °C), cooling a vapor stream containing CA to 4 °C will result in condensation as well as partial precipitation. An optimum CA yield of 45% was achieved from a mixture of 10% PHB and 90% switchgrass with fine PHB particles at 375 °C. However, recovery of CA from the total pyrolysis liquid was not significant with this multistep separation procedure.

Recently, Parodi et al.²² developed a thermolytic distillation process to pyrolyze PHB and PHB-enriched biomass at 170 °C under vacuum conditions at 150 mbar to produce CA. The pyrolysis of PHB occurs simultaneously with the separation of volatile pyrolyzates such as CA during thermolytic distillation. The researchers recovered CA with a yield of 58% and a purity of 92% using this integrated method from MMC-based biomass containing 30 wt % PHB on a dry basis. Indeed, pyrolysis of MMC-based PHB/PHB-enriched biomass with this method can increase both the yield and purity of CA. However, in the case of MMC-based PHBV/PHBV-enriched biomass, the vapor stream will also contain 2-PA, originating from the HV monomers. Therefore, an additional purification is required to separate these carboxylic acids.

Considering various separation techniques for the desired fractionation, membranes might work, and low-temperature membrane solutions are available for bio-based saturated volatile fatty acids.^{23–25} However, because the vapor stream is prone to polymerization due to the unsaturation in the fatty acids CA and 2-PA, and the solidification of CA at 72 °C is a factor to be considered as well, operating a membrane separation for the vapor fractionation appears difficult. Given the high temperature from the pyrolysis, distillation appears as the most attractive primary separation since high-temperature liquid–liquid extraction with these reactive monomers would impose a risk of unwanted chemical reactions. While crystallization appears strong given the large difference in the melting points, it only applies at lower temperatures and therefore may be the secondary separation technique.

Therefore, in this work, we studied the possibility to do the separation of the CA/2-PA mixture by distillation due to the relative volatility. The natural boiling points of CA and 2-PA are 184.7²⁶ and 200–203 °C,²⁷ respectively. The described study is composed of an equilibrium study to determine the thermodynamic feasibility of the distillation and a multistage distillation study in a novel spinning band distillation column (SBC).^{28,29} The core idea of an SBC is the use of rotating internals as opposed to using packed or tray columns. The advantages of SBCs over the other two mentioned columns are their low holdup, very low pressure drop, and still high

separation efficiency. Usually, this type of fractionating column is used for analytic purposes with small amounts particularly. Because of the CA and 2-PA from PHBV, we face a separation system with a very limited amount of available chemicals, and the low holdup is ideal. The acids are not only polar but also organic molecules with a small hydrocarbon chain, and since the polytetrafluoroethylene (PTFE) spinning band is proven to improve the separation efficiency for several organic systems,^{30,31} it is also expected that the PTFE band is suitable for this system. Spinning bands, which stir mainly the vapor phase and also hinder the vapor flow directly to the top, are suited for operation under vacuum conditions.²⁹ By using vacuum conditions, it is possible to shift the mixture to temperatures, where a separation becomes possible (at too high temperatures, the acids are not stable).

In the current study, the used SBC was operated batch-wise, where the feed mixture was placed in the reboiler and boiled up. CA was collected in the distillate outlet, while 2-PA remained in the final bottom product. The use of the SBC in vacuum operation was first explored for the distillation of a model mixture prepared with a commercial CA and 2-PA system. Afterwards the purification of the acids from an actual pyrolyzate mixture obtained by pyrolysis of PHBV-enriched biomass and extracted pure PHBV was investigated using the same distillation column to demonstrate the proof of concept for distillative purification of CA.

MATERIAL AND METHODS

Chemicals. Crotonic acid ($\geq 98\%$), *trans*-2-pentenoic acid ($\geq 98\%$), acetone (99.5%), 1,2,4,5-tetrachloro-3-nitrobenzene, and chloroform-D were purchased from Sigma-Aldrich. The water used was ultrapure (Milli-Q, with a resistance of 18.2 $\mu\Omega$ cm at 25 °C).

VLE Measurement for the CA/2-PA Mixture. Initially, the VLE measurement of the CA and 2-PA mixture was performed in a Fischer Labodest VLE 602 ebulliometer. Due to the high melting point of CA (72 °C), crystallization occurred in the cold spots of the ebulliometer resulting in inaccurate VLE data for the samples with a high concentration of CA. Therefore, an equilibrium cell was developed to perform the isobaric-VLE study, which is depicted in Figure 1. First, about 15 mL of the mixture of the acids was prepared with a desired ratio of the acids ($0 < x < 1$) and placed in the heating mantle. The mixture was heated and stirred using a magnetic stirrer. The temperatures of the gas and liquid phases were measured using Pt-100 sensors with an accuracy of ± 0.5 °C. The pressure was set at

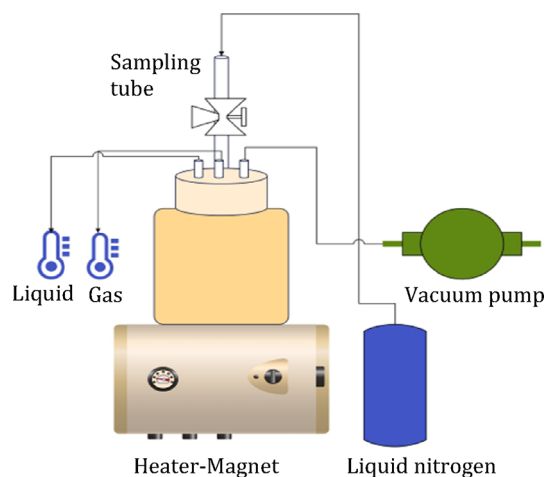


Figure 1. Schematic view of the custom-designed VLE measurement setup.

either 100 or 50 mbar using a vacuum pump PC 3001 VARIO select (Vacubrand GmbH, Wertheim, Germany). For each mixture at the set pressure, the power of the heater was increased until there was no change in the temperature of the acid mixture upon further increasing the heater set point. Afterward, the mixture was kept at that temperature for about 40 min to ensure equilibrium conditions (this was experimentally validated). Subsequently, a small glass tube was cooled by liquid nitrogen. By opening the valve, the glass vial was carefully moved into the vapor phase through a mounted septum. As the valve was opened only after placing the glass tube, the reduced pressure in the system could be maintained. Then, samples were taken from the vapor and liquid phases. The vapor phase sample was collected by freezing the vapor phase on the cooled vial. The samples were dissolved in Milli-Q water to be analyzed by high performance liquid chromatography (HPLC).

The experimental isobaric-VLE data was fitted using the Aspen Plus V12.1 regression tool to predict the parameters of the non-random two-liquid (NRTL) model.

Thermal Stability Study. The thermal stability of the acids during the distillation process was examined. About 5 g of the CA/2-PA mixture was prepared in a vial with a mass ratio of 80 to 20. Afterward, the vial was subjected at 110 and 145 °C for a certain contact time in the range of 0–10 h. The samples were taken before and after heating and analyzed by proton nuclear magnetic resonance (¹H-NMR) to investigate the isomerization and polymerization of the acids. 1,2,4,5-Tetrachloro-3-nitrobenzene was added as an internal standard. The peaks were identified using ChemDraw 20.0 software.

Distillation of the CA/2-PA Mixture Using the Spinning Band Column. The distillation in the SBC from NORMAG (now Pfaunder Group, Ilmenau, Germany) was performed in a batch-wise operation mode inside of a mobile fume-hood. The PTFE spinning band consists of seven segments of each 95.8 mm height, screwed together, thus adding up to a length of 670.6 mm active separation length. The whole band was mounted to a bearing with a downside direction and driven by a stirrer motor (IKA Eurostar 200, Staufen, Germany) connected by a shaft at the top side. The rotation speed of the spinning band was set to 50 rpm for the whole time. The column's heating jacket is located over the whole column, except for the sump. It was preheated to 110 °C by a glass heat exchanger connected with a thermostat (ministat125cc, Huber, Offenburg, Germany).

The most crucial part was to ensure that the column was operated under a high vacuum condition of 50 mbar. Therefore, the vacuum pump PC 3001 VARIO select (Vacubrand GmbH, Wertheim, Germany) was connected to the reflux condenser via a cold trap. To begin the distillation process, first, the column's heating jacket was filled with silicone oil (Lauda Ultra 350) to preheat the distillation column to 110 °C. Moreover, deionized water was fed into the column to heat up the column from the inside, evaporated, and then removed from the system at the top outlet.

The feed mixture ran down the column in the gap between the glass wall of the column and the spinning band, guided by the helical band. By rotation of the band, a thin liquid film was formed on the glass wall and continuously refreshed by the rotation. The vapor streaming upward follows along the path of the spinning band and continuously contacts the liquid film. This effect is similar to an Archimedean screw, where the rotation induces upward force to the liquid. Flooding is always caused because of an excessive accumulation of liquid at a specific location that negatively affects the desired separation process. It occurs due to the liquid level being too high, either due to high rotation speed or the evaporation rate. At this point, the vapor cannot pass through the gap and a high pressure drop and flooding along the column occur, similar to conventional industrial scale columns.^{30,31} Since mass transfer in the column takes place primarily in the falling film on the glass wall, it is particularly important to minimize the heating loss as much as possible. Due to this, the DN25 glass column was insulated with a DN50 vacuum double jacket over the whole active separation area. Moreover, aluminum cladding and a combination of 10 mm Spaceloft and 30 mm rockwool insulation surrounded the whole column during operation, as seen in Figure 2.

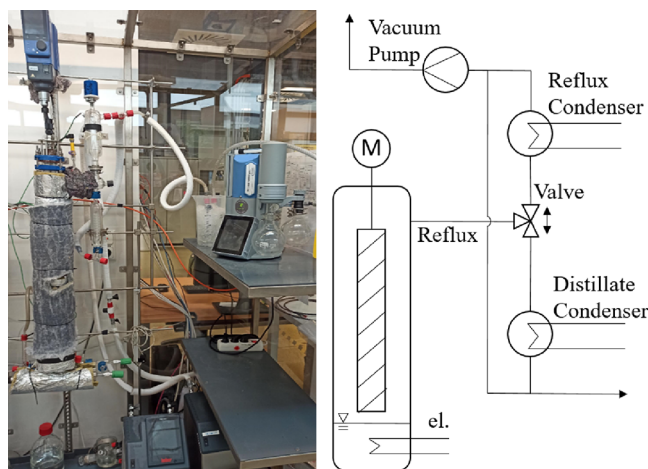


Figure 2. Experimental setup of the insulated vacuum distillation plant in batch operation mode, the right side scheme of a batch distillation column adapted after.³²

The vapor leaves the column at its top, enters the reflux condenser, and condenses there. Depending on the valve's position (see Figure 2), the condensate flows back into the column (when the reflux value is larger than zero) or is led to the distillate condenser and leaves the column as the top product.

Analysis. High Performance Liquid Chromatography (HPLC). The concentrations of CA and 2-PA were measured using HPLC [Agilent Hi-Plex H column (300 × 7.7 mm) with a refractive index detector on an Agilent 1200 series HPLC system; mobile phase, 5 mM H₂SO₄ solution; a column temperature of 65 °C at a flow rate of 0.6 mL min⁻¹].

Gas Chromatography–Mass Spectroscopy (GC-FID/MS). The acid mixture samples were dissolved in acetone and analyzed using GC–MS (GC-7890A, MS-5975C Agilent Technologies system) equipped with an Agilent HP-5MS HP19091S-433 capillary column (60 m, ID 0.25 mm, film thickness: 0.25 μm). The column was packed with 5% phenyl methylpolysiloxane. Helium was used as carrier gas with a constant flow of 1.95 mL·min⁻¹. The oven temperature was programmed from 45 °C (4 min) to 280 °C at a heating rate of 3 °C min⁻¹ and was held at 280 °C for 20 min. The injector and the column to MS interface were maintained at constant temperatures of 250 and 280 °C, respectively. A sample of 1 μL was injected into GC. MS was operated in electron ionization mode, and ions were scanned in an *m/z* range from 15 to 500.

Proton Nuclear Magnetic Resonance (¹H-NMR). The final purity of CA collected as a top product was further evaluated by ¹H-NMR. Moreover, to study whether or not polymerization and isomerization occur during distillation of these unsaturated acid mixtures, thermal stability experiments were performed in which the samples were analyzed by ¹H-NMR as well. All the samples were dissolved in deuterated chloroform and analyzed by ¹H-NMR using a Bruker Ascend 400 (400.1316005 MHz).

Karl–Fischer Titration (KFT). The water content of the condensate was determined by the Karl–Fischer titration using a Metrohm 787 KFTitrino. Hydranal composite 5 was titrated from a 20 mL burette filled with a mixture of methanol and dichloromethane in a volume ratio of 3 to 1. The sample was analyzed in triplicate with a relative error less than 1%.

RESULTS AND DISCUSSION

VLE Study for the CA/2-PA Mixture. The isobaric-VLE behavior of the acid's mixture was investigated under reduced pressures of 50 and 100 mbar. To test the performance of the newly developed VLE setup, the isobaric-VLE data for the CA/2-PA mixture with a mass ratio of 10 to 90 was first measured using a Fischer Labodest VLE 602 ebulliometer. At this

composition, also, the ebulliometer could be applied, while at high CA compositions, the crystallization in the cold zones of the ebulliometer caused operational problems. Then, VLE data of the same mixture was obtained with the custom-designed setup. As shown in Table 1, the difference in mass fraction of

Table 1. Comparison of the Performance of the Fischer Labodest VLE 602 Ebulliometer and Custom-Designed Equilibrium Cell, Using the CA and 2-PA Mixture with a Mass Ratio of 10:90, at 50 mbar and 110 °C

x	$y_{\text{Ebulliometer}}$	y_{Cell}
0.10	0.203 ± 0.012	0.216 ± 0.020

CA in the vapor phase (y) obtained by both apparatuses for the same mixture was only 0.0125. Therefore, it can be concluded that the newly designed setup provides comparable isobaric-VLE data to the Fischer Labodest VLE 602 ebulliometer. Thus, the isobaric-VLE data was collected for CA/2-PA mixtures at various compositions ranging up to pure CA using the custom-designed VLE equilibrium cell.

The x - y and T - xy diagrams of the mixture are shown in Figures 3 and 4, respectively. Based on the VLE-results, it can

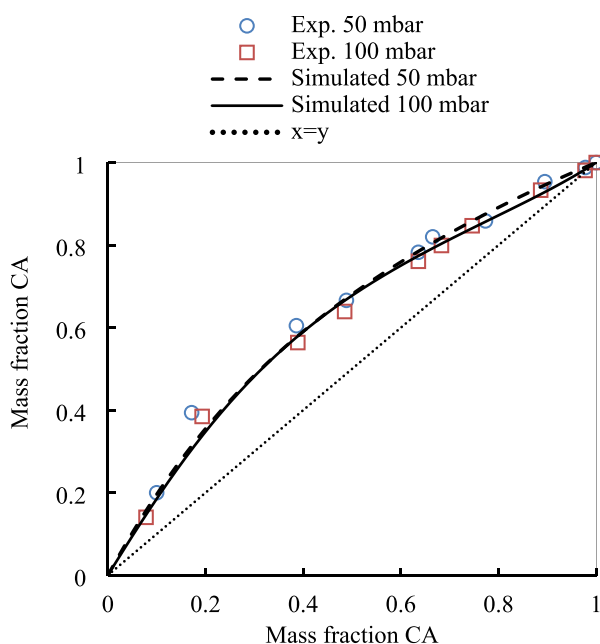


Figure 3. y - x diagram for the CA/2-PA mixture at 50 and 100 mbar.

be concluded that ordinary distillation appears to be a feasible method to separate the CA and 2-PA mixture as no azeotrope is observed, and appropriate relative volatility is shown without severe pinch point(s).

A data regression of the experimental VLE data was made using the Aspen Plus V12.1 regression tool to predict the binary interaction parameters of the NRTL model. The parameter C_{ij} was fixed at 0.3, which is found to be a suitable value for the carboxylic acid mixture.³³ The other parameters were modeled using the default equations in the simulator and the convergence algorithm of Britt–Leucke with a tolerance of 0.0001. The estimated NRTL binary parameters are given in Table 2. These parameters can be used to design a distillation process for separation of the CA/2-PA mixture.

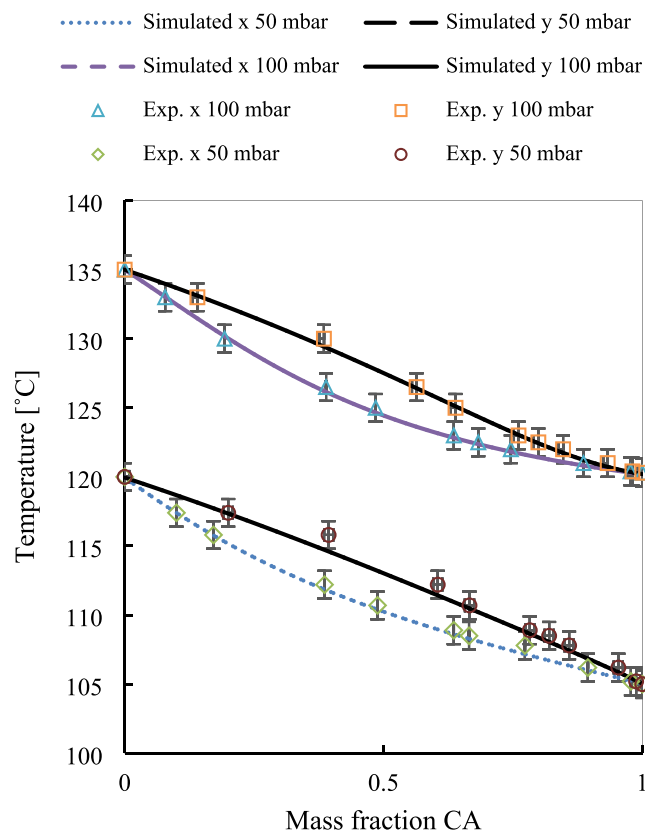


Figure 4. T - xy diagram for the CA/2-PA mixture at 50 and 100 mbar.

Table 2. Estimated NRTL Parameters for the CA/2-PA Mixture over the Temperature Range of 101–127 °C^a

parameter	value
A_{ij}	19.499
A_{ji}	-6.369
B_{ij}	-7036.650
B_{ji}	2147.260
C_{ij}	0.3 (fixed)

^aBy regression of experimental isobaric-VLE data at 50 and 100 mbar using the Aspen Plus V12.1 regression tool. The standard deviations of VLE data obtained by the equilibrium cell are about 0.0006 and 0.005 for x and y , respectively.

As shown in Figures 3 and 4, there is a very good agreement between the experimental data and the model predictions based on the NRTL model that was fitted on the data obtained at 50 and 100 mbar. The relative volatility of CA over 2-PA is similar at both experimental pressures, and no significant improvement was achieved at lower CA compositions with reducing the pressure by a factor of 2. However, as can be clearly seen from the graph, the increase in vapor phase mass fraction (y) at highly concentrated CA mixtures ($x > 0.6$) is considerable when the pressure reduced from 100 to 50 mbar. It seems that there is a pinch point at $x > 0.9$ at a pressure of 100 mbar while being much less pronounced or even absent at 50 mbar. Since the lower pressure is also beneficial in terms of product stability (the acids tend to polymerize at higher temperatures), a minimum achievable vacuum pressure was applied in the subsequent SBC studies, allowing us to obtain the highest purity of CA in the top product and limiting as much as possible the polymerization.

Theoretical Stages for Full Separation. Using the McCabe–Thiele method and NRTL-based fitted y - x diagram of 50 mbar, the total number of stages was calculated at a reflux ratio of 2. The results are shown in Figure S1 in the Supporting Information file. Accordingly, the total number of equilibrium stages is almost 9, including the partial condenser. Based on this analysis, and the results obtained in a previous study where the SBC was developed,^{28,29} performing a distillation in the SBC setup to obtain CA with high purity appears to be well feasible. However, this stage construction should be taken as first orientation for process design but has to be validated for scale-up purposes.

Investigation of Thermal Stability of the CA/2-PA Mixture. CA and 2-PA are unsaturated carboxylic acids that can undergo dimerization (eventually polymerization) and isomerization at elevated temperature.³⁴ Thus, thermal stability analysis of the CA/2-PA mixture was investigated under applied distillation conditions. A mixture of CA/2-PA (mass ratio of 20:80) was exposed to elevated temperatures of 110 and 145 °C for contact times up to 10 h. The ¹H-NMR spectrum of the samples before and after heating is shown in Figure 5. In the first trial, the actual distillation process was simulated in which the acid mixture was subjected to 110 °C and 50 mbar for 5 h. As can be seen from the graphs, a peak appears at around 1.3 ppm, which corresponds to CA dimers, according to the ChemDraw ¹H-NMR spectrum prediction tool. By performing the experiments at the ambient pressure, similar results are found. By increasing the temperature to 145 °C, the isomerization and polymerization can be accelerated as these reactions mainly happen at the elevated temperature.³⁴ For the sample that was subjected to high temperature for 10 h, a few more peaks are visible at 0.89, 2.5, 5.3, and 6.9 ppm. Based on ChemDraw prediction, the peak at 0.89 ppm is related to the methyl group of the dimers of 2-PA. Meanwhile, the peaks at 2.5, 5.3, and 6.9 can be corresponded to the dimers of both acids. In terms of the isomer of both acids, their methine group shift should occur one at around 5.9 ppm and another one at about 6.5 ppm.¹² The peak at 5.9 ppm is overlapped for all the isomers. There is no distinguishable peak at around 6.5 ppm. However, it is only an estimation, and the peak might be shifted in the real mixture. It could be that the peak at 6.9 ppm is the overlapped methine group of the acids, isomers, and dimers. Overall, it can be concluded that during distillation of the CA/2-PA mixture at 110 °C and 50 mbar for about 5 h, 2-pentenoic acid is thermally stable, while for CA, a small quantity of the acid undergoes dimerization reaction. Due to the complexity of the simulated mixture after heating, containing the acids, their corresponding isomers and dimers, and overlapping their ¹H-NMR peaks, the quantifications of the isomers and dimers were not possible.

Separation of CA/2-PA by Distillation. The distillation column is operated under reduced pressure of about 50–60 mbar. When the column's bottom temperature reaches a stable 100 °C, a mixture of CA/2-PA was prepared at a mass ratio of 80 to 20, preheated and filled into the bottom of the column.

The process was run for about 5 h, and during this time, the temperature was monitored in the top, the middle, and the bottom of the column, the pressure in the bottom was monitored, and the reflux was controlled by alternating the opening and closing of the valve toward the distillate exit. From the profiles shown in Figure 6, it can be concluded that the temperature at the bottom was stable at around 108–110 °C. The temperature in the middle of the column started

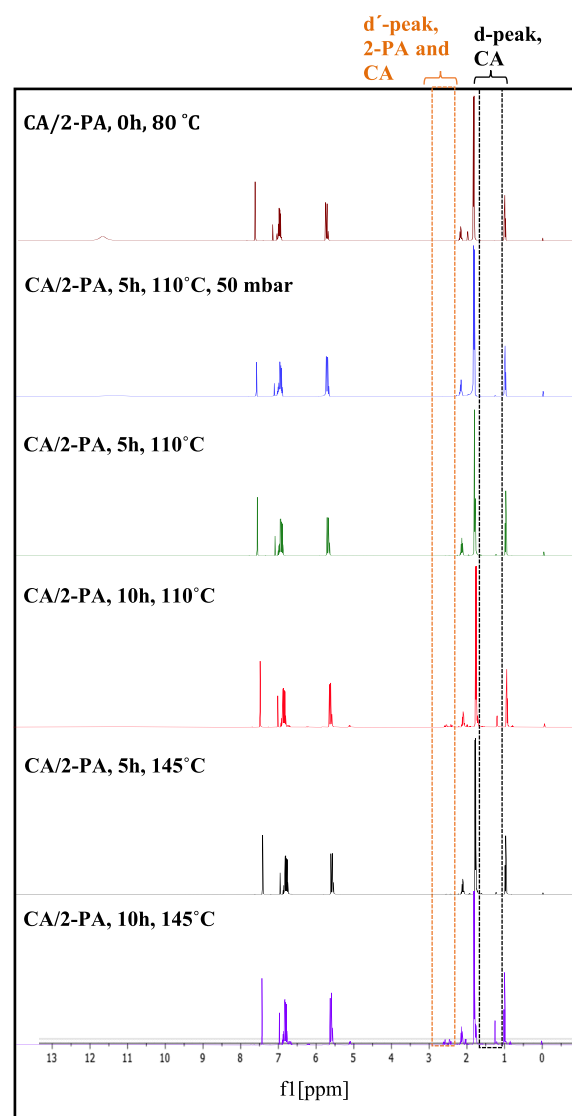


Figure 5. ¹H-NMR spectrum of the CA/2-PA mixture at 110 and 145 °C; the d-peak corresponds to the $-\text{CH}_3$ group of the CA dimer, and the d'-peak corresponds to the $-\text{CH}_2$ group of the dimers of both CA and 2-PA.

significantly lower at about 75 °C, and after about 20 min, the temperature rose to about 102 °C, just under the bottom temperature, and stayed there during the next hours. This temperature is well in agreement with the VLE behavior reported in Figure 4.

While, initially, the temperature in the top of the column was also 75 °C, like in the middle section of the column, during the first hour of operation, the temperature dropped to 40 °C at an infinite reflux operation. It takes a long time for the vapor from the bottom to reach the top because on its way upward, the spinning band there is a small front of crystals forming that needs to be brought upward. The temperature rise marks the point at the experiment where the vapor gradually arrives at the top section. After the vapor has arrived, the reflux ratio was increased to 0.5 s^{-1} , which occurred approximately after 3 h. Then, the middle section temperature increases slightly to 106 °C.

The decrease in the reflux means that the cooler now divides one part of the liquid back into the column and the other to the distillate cooler. Then, the top temperature almost

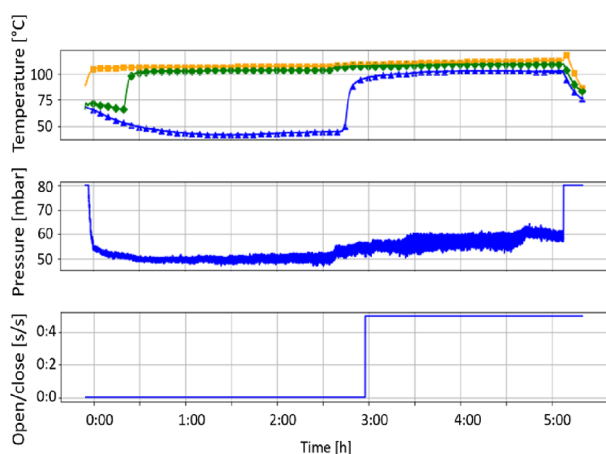


Figure 6. Temporal course of the distillation process, showing (top diagram) temperatures in the bottom temperature in yellow, mid-section temperature in green, and top temperature indicated in blue; (middle diagram): bottom pressure in the distillation column; (bottom diagram): the reflux ratio, depicted as the ratio of valve open time divided by valve closed time. The valve opens the distillate exit.

immediately increased to 100 °C. This occurs because the temperature sensor only measures the liquid phase temperature, and with zero reflux, there was no liquid phase present. During process operation, the bottom pressure remained relatively constant at around 50–60 mbar. For the first 3 h of operation of this batch-wise distillation, no distillate product was obtained since the vapor phase had not yet arrived at the column top.

Furthermore, the overall mass balance of the process is not closed. Of a 146.8 g feed in the beginning of the process, afterward, 78.26 g at the bottom and 40.94 g of the top product were obtained, resulting in an average mass loss of 27.6 g (18.80% of the feed mixture). We found the pH of the washing water to be around 3–4. Hence, a sample of washing water was analyzed by HPLC, which established that, indeed, a fraction of CA left the condenser in the vapor phase. However, its quantity is <1 g, which is not that significant. We assume that the main fraction of the lost mass remained in the middle section of the column in the form of crystals remaining on the spinning band and column wall. Moreover, some amount might be still attached to the gaskets as well as maybe in the tubes behind the condensers. Furthermore, a part should be accounted for the lost mass during handling such as in collecting the top products from the condensers.

Regarding the separation efficiency, as depicted in Table 3, the GC–MS analysis of the top and bottom product confirms the successful separation of the acid mixture. The top product is mainly CA with a purity of >98%. To ensure about the 2-PA content in the top product, ¹H-NMR analysis was also conducted to calculate the purity. The GC–MS and ¹H-NMR spectra are given in the Supporting Information.

Table 3. Separation of the CA/2-PA Mixture with a Mass Ratio of 80/20 at 5 h by Distillation Using an SBC

P (mbar)	T (°C)	top/bottom	composition (wt %)		
			CA	2-PA	water
50	110	top	98.2	<0.5	<1
		bottom	61	30	<1

According to ¹H-NMR and GC–MS, the 2-PA content in the top product is less than 0.5 wt %. The water content is <1 wt % based on KFT analysis. Thus, it can be concluded that distillation is definitely an appropriate technology to recover CA with high purity from the CA and 2-PA mixture.

Purification of CA Obtained by Pyrolysis of PHBV/ PHBV-Enriched Biomass by Distillation. Although the separation of CA and 2-PA is successfully done using the commercial acids in the SBC, the actual mixture obtained by pyrolysis of either the extracted PHBV or the PHBV-enriched biomass contains not only these acids but also other side products. Therefore, it is worthwhile to investigate the purification of CA using the actual mixture. The pyrolysis was performed following the procedure reported in our previous paper.³⁵ Briefly, a certain quantity of the PHBV-enriched biomass was separately loaded in the oven and pyrolyzed at around 240 °C under a nitrogen flow rate of 0.15 L min⁻¹. In the case of using the extracted PHBV, pyrolysis was conducted under a reduced pressure of 50 mbar at 220 °C. Finally, the pyrolyzate (the vapor phase) was condensed and collected to be applied in the distillation process. Due to the scale of the pyrolysis setup and limited amount of the bio-based materials, it was not possible to produce high quantity of pyrolyzate, which can be applicable in the SBC. Therefore, a certain quantity of the CA/2-PA mixture was added to the pyrolyzate mixtures, allowing a proper amount of feed to be used in the SBC. Table 4 represents the distillation results for

Table 4. Recovery of CA from the Pyrolyzate Mixtures Obtained by Pyrolysis of Pure MMC-Based PHBV and PHBV-Enriched Biomass Using an SBC at 50 mbar, 110 °C, and 5 h

feed (CA/2-PA) (wt %)	material used for pyrolysis	top/bottom	composition (wt %)		
			CA	2-PA	water
80/20 + 2% Py _{PHBV}	PHBV	top	96	0.06	<1
		bottom	65	22	<1
80/20 + 6% Py _{Biomass-PHBV}	PHBV-enriched biomass	top	93	0.26	<1
		bottom	60	25	<1

these mixtures. The purities of CA gained using the pyrolyzate mixture of PHBV and PHBV-enriched biomass are 96 and 93%, respectively. Compared to CA achieved by distillation of the commercial chemicals, there is a slight reduction in the purity of CA obtained from the pyrolyzate mixture distillation. This can be explained by other possible volatile side products, originating from the pyrolysis step. According to GC–MS, isocrotonic acid, 4-pentenoic acid, and 3-butenic acid are the main volatile byproducts that can end up in the top product and consequently decrease the purity of CA. Furthermore, the 2-PA purity that was obtained was much lower than the CA purity, which is due to the drying up of the vapor stream, which prohibited continued distillation. Future work on a continuous distillation process would allow us to also obtain 2-PA in high purity. Overall, the achieved purity is similar to the results obtained by Parodi et al.²² using MMC-based PHB in thermolytic distillation, meaning that a relatively pure CA production is also feasible using MMC-based PHBV, which can be an excellent candidate to reduce acid production cost through the bio-based pathway.

CONCLUSIONS AND OUTLOOK

The production of pure CA through thermal depolymerization of bio-based PHBV copolymer requires downstream purification steps because of the various side products, originating from each monomer. 2-PA is the main byproduct, arising from thermal decomposition of the HV monomer. Therefore, separation of the CA/2-PA mixture via distillation was investigated in this study. To assure thermal stability of these unsaturated acids, distillation must be performed under reduced pressure conditions. The results indicate that, indeed, distillation appears to be a feasible technique to recover CA with a purity of >98% from the CA/2-PA mixture using the SBC at 50 mbar. Moreover, the purification of CA obtained by pyrolysis of either PHBV-enriched biomass or extracted PHBV itself was also studied under the same applied conditions. It was found that CA can be recovered from pyrolysis oil with purities of 96 and 93% using the pyrolyzate mixture, obtained from pyrolysis of the PHBV-enriched biomass and extracted pure PHBV from the same biomass batch, respectively. Regarding the operation condition of the SBC for this mixture at semi-batch mood, in general, the distillation process under high vacuum is controllable. A stable operation can be achieved during distillation at several hours. Although the entire column was insulated, crystallization of CA still was observed at the top section of the column, which may be prevented by further improvement of the insulation. The observed product purity was very high. Further optimization potential could be offered by further increasing the temperature of the silicone oil at the bottom of the column. To minimize the mass loss in the process, potentially renewed gaskets might help to a small extent. Due to the vibrations of the rotation of the spinning band, it is assumed though that it can never be perfectly sealed. Maybe it would be possible to use vacuum distillation but no spinning band distillation to minimize vibrations. On the other hand, it could be investigated further whether after the process, the column can be washed with acetone and the product can be obtained out of the acetone as well and if that is feasible to do.

Considering all technical results on the CA and 2-PA separation, we conclude that it is certainly possible to separate these two acids by distillation after pyrolysis of PHBV. The future availability of much more starting materials from pilot-scale PHBV production and extraction studies at Paques Biomaterials BV will also enable studies on fully continuous distillation, which is expected to be easier to control. The distillation may be combined with crystallization of CA for the final purification. Further studies toward bio-based polymer production from these bio-based monomers could include a more general sustainability analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c07046>.

Estimating the number of stages using the McCabe–Thiele method; GC–MS spectrum of purified CA by vacuum distillation using the SBC; ¹H-NMR spectrum of purified CA by vacuum distillation using the SBC (PDF)

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V.E.: experimental methodology development, VLE and thermal stability experimenting, data analysis, and writing the original draft. L.M.N.: distillation column experimenting, writing, reviewing, and editing. T.K.: distillation column experimenting, reviewing, and editing. N.K.: supervision, formal analysis, editing, and reviewing the manuscript. B.S.: supervision, formal analysis, editing, reviewing the manuscript, and funding acquisition.

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ABBREVIATIONS

2-PA	2-pentenoic acid
CA	crotonic acid
GC-FID/MS	gas chromatography-flame infrared detector/mass spectroscopy
GC–MS	gas chromatography–mass spectroscopy
HB	hydroxy butyrate
¹ H-NMR	proton nuclear magnetic resonance
HPLC	high performance liquid chromatography
HV	hydroxy valerate
KFT	Karl–Fischer titration
MMC	mixed microbial culture
NRTL	non-random two-liquid model
PHB	poly(3-hydroxy butyrate)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PTFE	polytetrafluoroethylene

PyPHBV	pyrolyzate mixture of PHBV
PyBiomass-PHBV	pyrolyzate mixture of PHBV-enriched biomass
SBC	spinning band column
VFA	volatile fatty acid
VLE	vapor liquid equilibrium

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