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## 1-Butanol Separation from Aqueous Acetone-Butanol-Ethanol (ABE) Solutions by Freeze Concentration

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**ABSTRACT:** The suspension freeze crystallization of aqueous 1-butanol solutions, synthetic acetone-butanol-ethanol (ABE) solutions, and ABE fermentation broth was studied as a novel concentration method that requires less energy than evaporation for water removal. The equimolar aqueous ABE solutions in a total molality range of  $0-5.05 \text{ mol/kg}_{(water)}$  were proven to be ideal solutions based on the freezing point depression obtained. An aqueous solution of 8 wt % 1-butanol and three different types of aqueous ABE solutions (3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW (wt %)) were concentrated for 80 min by suspension freeze crystallization in a subcooling range from 0.24 to 1.15 °C. Freeze crystallization enabled 1-butanol separation from the generated mother liquor, which split into two liquid phases after ice separation, i.e., a water-enriched phase and a 1-butanol-enriched phase. Ice yield values were higher for higher subcooling degrees and higher initial water content in the feed solutions. 1-Butanol yields separated from the mother liquors were 9.85%, 59.46%, and 22.46% for 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW, respectively, whereas two-stage freeze crystallization of the fermentation broths resulted in water removal with a maximum relative percentage of 29.5%.

#### 1. INTRODUCTION

The increasing environmental issues caused by human activities, especially industrial production, are global concerns that need to be not only addressed but also efficiently reduced. The most obvious solutions should be oriented toward the implementation of novel industrial technologies that lead toward green and sustainable production.

In March 2020, the European Commission accepted a new plan with objectives to promote the circular economy based on the sustainable consumption of renewable natural resources and production of biobased products.<sup>1</sup> Consequently, achieving this objective depends on the development and application of novel recovery methods for biobased products as well as recycling technologies that enable the recirculation of materials while ensuring efficient and environmentally safe production.

Biorefinery concepts based on biochemical conversion and/ or thermochemical conversion of forest and agricultural biomass into fuel, energy, and biochemicals and bioproducts have an important role in the promotion of the circular economy and sustainability.<sup>2,3</sup> The main challenge in the biorefinery field is the application of proper downstream processing that enables efficient separation and recovery of biochemicals produced from complex streams.<sup>4</sup>

Biobutanol, produced by the acetone-butanol-ethanol (ABE) fermentation of pretreated biomass with Clostridium strains, can be a good replacement for gasoline, due to its good

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#### Table 1. Compositions of ABE Fermentation Broths Used in Freeze Crystallization Studies

fermentation broth	composition									
	acetone		1-butanol		ethanol		acetic acid		butyric acid	
ID	g/L	mol/kg <sub>(water)</sub>	g/L	mol/kg <sub>(water)</sub>	g/L	mol/kg <sub>(water)</sub>	g/L	$mol/kg_{(water)}$	g/L	$mol/kg_{(water)}$
1	9.04	0.160	16.86	0.234	1.65	0.037	0.98	0.017	1.13	0.013
2	9.18	0.163	16.83	0.234	1.69	0.038	1.02	0.017	1.21	0.014

combustibility and thermochemical properties. 1-Butanol is also a valuable platform chemical used in the chemical, pharmaceutical, and food industries. $^{5-7}$ 

Moreover, 1-butanol is a common solvent used for the preparation of active pharmaceutical ingredients (API) in the pharmaceutical industry. Even though it is usually categorized as a green solvent<sup>8,9</sup> a GSK study on the cradle-to-gate life cycle of API environmental impacts showed that 1-butanol contributes to 75% of energy consumption and 50% of greenhouse gas emissions from the pharmaceutical industry.<sup>10</sup> Therefore, applications of recycled butanol from waste streams in the form of technical grade butanol could significantly reduce energy related costs and environmental risks.

An overview of various separation methods applied in downstream processing in a biorefinery has been reported in the literature.<sup>3,11</sup> Separation methods have been studied specifically for biobutanol recovery from fermentation broths based on flash fermentation,<sup>12</sup> distillation,<sup>13,14</sup> gas stripping,<sup>15</sup> membrane separation, extraction, and adsorption.<sup>16</sup> Previous research on various membrane-based separation methods for 1-butanol recovery such as pervaporation,<sup>17,18</sup> membrane separation with gas stripping,<sup>19</sup> and perstraction<sup>20</sup> has led to the development of better membrane performance with reduced toxicity and energy consumption.

However, some of the main challenges in separation that still need to be overcome are the high costs of extractants, low selectivity of adsorption, membrane fouling, and the need for better optimization of gas stripping operating parameters.<sup>21</sup>

Although freeze crystallization has been proposed<sup>16</sup> as a potential separation method for 1-butanol from aqueous streams, it has not previously been investigated. However, the present research is focused on 1-butanol recovery from acetone-butanol-ethanol (ABE) solutions based on freeze crystallization.

Freeze crystallization is a low-energy and environmentally safe separation technology, defined as ice formation in the form of an ice layer or in the form of suspended ice crystals from an aqueous solution.<sup>22</sup> In the case of water removal in the form of ice from aqueous solutions with freeze crystallization, seven times less energy is consumed in comparison with evaporation because of the lower latent heat of freezing than that of evaporation. Freeze crystallization has been mostly investigated and applied as a concentration and purification method in food processing<sup>23–25</sup> and wastewater treatment.<sup>26–28</sup>

In this study, suspension freeze crystallization was used as a concentration method for aqueous 1-butanol solutions, synthetic ABE solutions, and ABE fermentation broth. The studied synthetic ABE solutions consisted of three organic solvents and water, whereas real ABE fermentation broths also contained ionic substances and other constituents, making the solution matrix more complex. 1-Butanol is partially soluble in water, with a solubility of up to 9.68 wt %.<sup>29</sup> The main objective was to recover the 1-butanol as a butanol-enriched phase formed from concentrated solution, i.e., mother liquor,

as its solubility decreases with water removal after freeze crystallization and ice separation.

#### 2. MATERIALS AND METHODS

In the following sections, the principles of ABE fermentation and suspension freeze crystallization are presented.

2.1. ABE Fermentation. The ABE fermentation process generates a blend of ABE solvents upon the consumption of glucose by solventogenic Clostridia strains. The most prevalent volume ratio for acetone, 1-butanol, and ethanol (ABE) solvents in ABE fermentation is 3:6:1.<sup>30</sup> The Clostridium acetobutylicum strain NRRL B-527 culture was donated for research work by the Agricultural Research Services (ARS) Culture Collection, USA. The culture was germinated by inoculating it in reinforced Clostridium medium (RCM), and the pH was adjusted to  $6.8 \pm 0.2$  with 5 M potassium hydroxide. When the preculture OD 600 reached 1.5 (20-24 h), 5% v/v of the preculture was inoculated in 1000 mL of production (P2) medium to start the ABE fermentation fed-batch in a 3 L bioreactor (BIOSTAT B plus, Sartorius, Germany). The P2 medium was composed as follows (g/ L): glucose (60), ammonium acetate (2.2), potassium dihydrogen phosphate (0.5), dipotassium hydrogen phosphate (0.5), magnesium sulfate (0.2), p-aminobenzoic acid (0.1), thiamin (0.1), sodium chloride (0.01), manganese sulfate (0.01), ferrous sulfate (0.01), and biotin (0.01); the pH was adjusted to 6.5 with 5 M potassium hydroxide and bubbled with nitrogen for 10 min before autoclaving at 120 °C for 20 min. The pH breakpoint is linked to the shift from acidogenesis to solventogenesis. Hence, pH control was not used.<sup>31</sup> L-Cysteine was added as a reductant at 12.5 h after the onset of fermentation. When the residual glucose in the bioreactor decreased below 40 g/L, glucose feeding was initiated. The required volume of each feed pulse was determined on the basis of the amount of glucose necessary to replace the glucose utilized in the bioreactor. The fermentation was terminated after 312 h, and a total of 5 feedings were made at 30, 48, 72, 96, and 120 h of fermentation.<sup>32</sup> ABE solvents (acetone, 1-butanol, and ethanol), organic acids (acetic and butyric acids), and glucose were quantified by high-performance liquid chromatography (HPLC) using a Waters Alliance 2695 equipped with a Rezex H (7.8  $\times$  300 mm) column and Security Guard H+ precolumn. The temperature of the refractive index detector was 30 °C, and 14 mM sulfuric acid was used as an eluent in isocratic mode with a 0.6 mL/min flow rate.<sup>32</sup> Two types of ABE fermentation broth with slightly different concentrations were produced (Table 1).

**2.2.** Suspension Freeze Crystallization. The solvents used for preparing synthetic solutions were purchased from Aldrich Merck (acetone ( $\geq$ 99. 9%) and 1-butanol ( $\geq$ 99.9%)) and Altia Oyj (ethanol ( $\geq$ 99.5%)).

The synthetic solutions were prepared so as to have an approximately ten times higher concentration of acetone, 1-butanol, and ethanol than their concentrations in the produced ABE fermentation broths described in a previous study<sup>32</sup> and presented in Table 1, because the concentrations were so low that 1-butanol solubility could not be decreased sufficiently by water removal through freeze crystallization to form a 1-butanol-enriched phase.

In order to minimize the solvent evaporation, aqueous 8 wt % 1butanol, 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW (wt %) solutions were prepared inside a glass spinner flask (250 mL, Wheaton Celstir) that could be tightly closed on both side arms and was equipped with a paddle blade impeller. The solutions were

sample	mass percent, wt %				molality, mol/kg <sub>(water)</sub>		
ABEW	acetone	1-butanol	ethanol	water	acetone	1-butanol	ethanol
3:8:1:88	3	8	1	88	0.587	1.226	0.246
6:16:2:76	6	16	2	76	1.359	2.84	0.571
10:17:2:71	10	17	2	71	2.425	3.23	0.611

additionally stirred for 60 min with a magnetic stirrer. The solvent concentrations of the synthetic ABE solutions are listed in Table 2.

1-Butanol is partially soluble in the case of the 6:16:2:76 ABEW solution at room temperature, as the two liquid phases were present upon mixing (Figure A1). The percentage of undissolved 1-butanol in relation to the total 1-butanol added to prepare the 6:16:2:76 ABEW solution was determined with triplicate tests. In the tests, the total mass of the sample prepared by mixing ABE solvents and water was 50 g. After mixing and being left in a separatory funnel for 24 h, the undissolved 1-butanol was collected and quantified.

The ideality of aqueous ABE solutions (containing the same molality of acetone, ethanol, and 1-butanol) in the range of total molality from 0.64 to 5.05 mol/kg<sub>(water)</sub> was determined based on the basis of freezing point depression data obtained by suspension freeze crystallization.

The suspension melt crystallization setup is explained in our previous work.<sup>33</sup> The 250 mL dosage of the aqueous solution was fed into a glass jacketed crystallizer and stirred with a rotating scraper at 18 rpm. The temperature of the coolant (mixture of water and ethylene glycol) circulating through the jacket of the crystallizer was controlled with a Lauda ECO 1050 internal controller cooling thermostat. The solution temperature was measured by using a Lauda PT 100 thermosensor. Data on the coolant temperature inside the thermostat bath and measured solution temperature were collected by using a Wintherm software interface. The temperature data were presented in the form of a cooling curve that enabled a visual representation of the cooling process, seeding, and crystallization.

One-stage suspension freeze crystallization was performed as a concentration method for aqueous 8 wt % 1-butanol solutions, 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW solutions in the range of subcooling degrees from 0.24 to 1.15 °C and for a freezing time of 80 min (Figure A2). In contrast, the ABE fermentation broth was concentrated with two-stage suspension freeze crystallization, with a freezing time of 80 min per stage of freezing and in a subcooling range of 0.52 to 1.79 °C. The subcooling degree,  $\Delta T$ , represents the difference between the freezing point and the temperature of the solution prior to seeding.

**2.3. Separation and Characterization of Mother Liquor and Ice Samples.** After the freeze crystallization experiment, the mother liquor that was obtained was separated from the ice formed on the sieve. A sample of approximately 20 g of ice was washed with zero-degree water, and melted samples were analyzed with total organic carbon (TOC) measurements on a Shimadzu TOC-VCPH with analytically aided combustion oxidation/nondispersive infrared detection with a detection limit of 4  $\mu$ g/L and measurement range of 0–30 000 mg/L.

The mother liquor was collected and kept in a separatory funnel overnight. The main approach was to keep the separatory funnel closed to prevent the evaporation of solvents from the mother liquor. A few tests were performed where the mother liquor was kept in an open separatory funnel to determine the influence of solvent evaporation on the 1-butanol phase extraction. It was observed that two liquid phases, i.e., the 1-butanol-enriched phase and the waterenriched phase, were formed in the case of aqueous 8 wt % 1-butanol solutions and synthetic 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW solutions, but not for ABE fermentation broth, due to the low initial concentration of solvents. Hence, the freeze concentration of the aqueous 1-butanol and synthetic ABE solutions facilitated 1-butanol separation from the solutions, whereas freeze crystallization of the ABE fermentation broth samples resulted in water removal and concentration of the initial ABE fermentation broth. No separate 1-butanol enriched liquid fraction could be observed in fermentation broth experiments (Figure A3).

The acetone, 1-butanol, and ethanol concentrations in the 1-butanol-enriched and water-enriched phases were analyzed by gas chromatography (GC-2010 Plus, Shimadzu). The type of GC column used was a DB-WAXetr capillary column with a length of 30 m, an inner diameter of 0.3 mm, and a film thickness of 1  $\mu$ m. Two different types of standards were prepared for the 1-butanol-enriched phase samples and the water-enriched phase samples. The 1-butanol standard line constructed as a function of 1-butanol concentration in standard solutions (15 wt %, 20 wt %, and 99.9 wt %) and the corresponding relative area were used for the quantification of 1-butanol concentration in the 1-butanol phase samples.

Standards used in solvent quantification for the water-enriched phase samples had concentrations of 3:8:1:88, 6:16:2:76, and 10:17:2:71 ABEW solvents, which were the same as those of synthetic ABE solutions. The solvent concentration in the waterenriched phase samples was obtained by a comparison between the relative areas of standard solutions with known concentrations and the relative area of the water-enriched samples.

#### 3. RESULTS AND DISCUSSION

A solution cooling curve is obtained based on the basis of measuring the temperature data of the solution during periods of cooling, ice seeding, and crystallization. A typical cooling curve is shown in Figure 1.



Figure 1. Solution and coolant temperatures as functions of time.

After the solution is cooled to a certain temperature level, the ice seed is added, and the temperature of the solution rises as the latent heat is released when crystallization occurs. This temperature is considered the freezing point of the solution, and it has a constant value for a certain time, which depends on subcooling. As crystallization progresses further and the solution becomes more concentrated, the solution temperature starts to decrease.

The ideality of ABE solutions is determined based on the freezing point depressions of equimolar ABE solutions in the range of total molality of 0-5.05 mol/kg. Experimentally determined freezing points were correlated to freezing points modeled by Van't Hoff equations.

The freezing points as a function of the molality of the ABE solutions are shown in Figure 2.



Figure 2. Freezing point depressions of (a) ABE solutions in a total molality range of 0-5.05 mol/kg (molality of each organic compound is 1/3 of total molality) and (b) synthetic ABE solutions (3:8:1:88 ABEW, 6:16:2:76 ABEW, 10:17:2:71 ABEW).

It is apparent that the ABE solutions are ideal, as the water activity coefficient is unity ( $\gamma = 1$ ), which indicates that there is no clear interaction between water molecules and present solvent molecules in the studied molality range.

The freezing point depressions of 6:16:2:76 ABEW and 10:17:2:71 ABEW deviate from the ideal trend because the 1-butanol phases from these solutions started to form before actual ice crystallization occurred. At room temperature, around 65% of the initial 1-butanol in the 6:16:2:76 ABEW formed the 1-butanol phase according to the triplicate set of tests (Figure A1). As for the 10:17:2:71 ABEW solutions, the 1-butanol fraction started forming inside the crystallizer when the temperature of the solutions dropped to 9.5 °C (Figure A4).

The freezing points of the ABE synthetic solutions and ABE fermentation broth as a function of the water concentration are shown in Figure 3.

The ABE synthetic solutions exhibit a clearly different trend from the ABE fermentation broth, which is a result of the presence of other compounds besides the main solvents in the fermentation broth.

The ice yield, defined as the percentage of the mass of ice per mass of water in the feed solution, is shown in Figure 4.



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Figure 3. Freezing point of ABE solutions and the ABE fermentation broth.



Figure 4. Ice yield ( $[100 \cdot m_{ice}/m_{water, feed}]$ ) as a function of subcooling degree for 80 min of freezing (\* based on measured ice mass).

The ice yield for the 8 wt % 1-butanol, and 3:8:1:88 ABEW solutions were calculated based on water concentration, which is correlated with the final solution temperature reached during crystallization. In contrast, the ice yields for the 6:16:2:76 ABEW and 10:17:2:71 ABEW solutions were calculated based on measuring the ice mass because two liquid phases were present before freeze crystallization.

Ice yield, Y, is presented as a function of the subcooling degree,  $\Delta T_{inv}$  defined as the temperature difference between the solution freezing point and the internal coolant temperature. There is an expected correlation between ice yield and subcooling degree: the ice yield increases when a higher subcooling degree is applied during freeze crystallization. In Figure 4, it is apparent that the ice yield value is dependent on the initial water amount in the feed solution. Hence, ice yields gradually increase from a solution with 71 wt % of water (10:17:2:71 ABEW solution) to a solution with 92 wt % of water (aqueous 8 wt % 1-butanol solution).

In Figure 5, the ice yields obtained from fermentation broth in two-stage freeze crystallization are shown.

The maximum ice yield obtained from the fermentation broths in two-stage freeze crystallization experiments was approximately 86.7% for a maximum subcooling degree of 1.07  $^{\circ}$ C in the first stage of crystallization. Consequently, after the

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Figure 5. Ice yields obtained from fermentation broths in two-stage freeze crystallization for freezing of 80 min per stage.

two-stage freeze crystallization, the water removed from the feed fermentation broth with an initial 97 wt % of water resulted in the most concentrated mother liquor with a water content of 68 wt %. In an average range of subcooling degrees, the two-stage freeze crystallization of fermentation broths led to a relative reduction in the water content of 25%.

In Figure 6, butanol yields obtained from synthetic ABEW solutions are presented.



**Figure 6.** 1-Butanol yield ( $[100 \cdot m_{1-butanol, fraction}/m_{1-butanol, feed}]$ ) as a function of subcooling degree for 80 min of freezing.

The 1-butanol percentage is obtained on the basis of the cumulative amount of 1-butanol fraction formed during the cooling of solutions prior to ice seeding, which occurred in the case of the 6:16:2 and 10:17:2:71 ABEW solutions, and the amount of 1-butanol separated from the mother liquor after freeze crystallization.

The average 1-butanol yields of 9.85%, 59.46%, 22.46% with corresponding 1-butanol purities of 94.9%, 88.4%, and 85.1% were obtained from synthetic 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW solutions, respectively. 1-Butanol fractions obtained from synthetic ABE solutions contained water as an impurity between 5–15% depending on

studied synthetic solution and less than 0.35 wt-% of acetone and ethanol in total.

The cumulative 1-butanol yields in the case of 6:16:2:76 ABEW were higher than in the case of 10:17:2:71 ABEW, because its acetone concentration was lower compared to that in the former solution, and lower acetone concentration caused the solubility of 1-butanol in the water phase to decrease.

1-Butanol separation from synthetic ABE solutions promoted by freeze concentration depends on solvent evaporation from the mother liquor during two-liquid phase formation. In Figure 6, it is apparent that, for the 10:17:2:71 ABEW solutions, the yield of 1-butanol separated from the mother liquor that is formed by freeze crystallization at a subcooling degree of 0.78 °C is twice as much as the 1-butanol yield obtained with a subcooling degree of 0.7 °C. The reason was that the mother liquor obtained by freeze crystallization at a subcooling degree of 0.78 °C was kept in an open separatory funnel during two-liquid phase separation, which enabled the evaporation of acetone and a decrease of 1-butanol solubility in the water phase.

#### 4. CONCLUSIONS

In this work, suspension freeze crystallization was used as a concentration method for aqueous 1-butanol, synthetic ABE solutions, and fermentation broths. Water removal in the form of ice enabled the concentration of synthetic ABE solutions so that the 1-butanol solubility decreased in the mother liquor, and the 1-butanol was separated from the mother liquor in the butanol-enriched. To attain a sufficiently high concentration of 1-butanol in ABE fermentation broth could be a topic for future studies to approach the concentration of studied synthetic ABE solutions. Beside freezing point differences, the liquid—liquid equilibrium of synthetic ABE solution and fermentation broth can differ greatly, which could be investigated more comprehensively.

The main outcomes of the present study are as follows:

- Based on the freezing point depression study, aqueous acetone-1-butanol-ethanol solutions with an equal number of moles of each solvent are ideal solutions.
- Ice yields from aqueous 8 wt.% 1-butanol and synthetic ABE solutions tended to increase for higher subcooling

degrees and higher initial water concentration of the feed solution.

- Purities of 1-butanol present in 1-butanol-enriched phases that were formed from mother liquors of synthetic 3:8:1:88 ABEW, 6:16:2:76 ABEW, and 10:17:2:71 ABEW solutions decreased as the concentration of 1-butanol increased in the feed ABE solution.
- Cumulative 1-butanol yields were in the range from 9.85% to 59.46%.
- Two-stage freeze crystallization enables the concentration of fermentation broths, from an initial water content of 97 wt % to a minimum water content of 68 wt % with the freezing time of 80 min per step. Concentrated mother liquor should be further processed with a different separation method to separate different solvents.

#### ASSOCIATED CONTENT

#### **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.2c01546.

Figure A1. 6:16:2:76 ABEW solution with 1-butanol phase after mixing at 22 °C; Figure A2. Two-liquid phase and ice system formation during freeze crystallization of 6:16:2:76 ABEW; Figure A3. Freeze crystallization of ABE fermentation broth; Figure A4. 10:17:2:71 ABEW solution upon cooling: (a) 1-butanol phase started forming at a temperature of 9.5 °C and (b) formed 1-butanol phase at -7.9 °C prior to ice seeding (PDF)

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#### Notes

The authors declare no competing financial interest.

#### DEDICATION

Dedicated to the life and research works of Professor John N. Sherwood.

#### REFERENCES

(1) A new Circular Economy Action Plan For a Cleaner and More Competitive Europe; European Commission: Brussels, Belgium, 2020. (2) Bergeron, C.; Carrier, D. J.; Ramaswamy, S. Biorefinery Co-Products: Phytochemicals, Primary Metabolites and Value-Added Biomass Processing, 1st ed.; Wiley, 2012. DOI: 10.1002/9780470976692.

(3) Ramaswamy, S. Separation and Purification Technologies in Biorefineries; John Wiley & Sons Inc.: Chichester, West Sussex, United Kingdom, 2013.

(4) Dechow, F. J. Separation and Purification Techniques in Biotechnology; Noyes Publications: Park Ridge, N.J., U.S.A, 1989.

(5) Bankar, S. B.; Survase, S. A.; Ojamo, H.; Granström, T. Biobutanol: The Outlook of an Academic and Industrialist. *RSC Adv.* **2013**, 3 (47), 24734.

(6) Bioelectrosynthesis: Principles and Technologies for Value-Added Products; Wang, A., Liu, W., Zhang, B., Cai, W., Eds.; Wiley-VCH: Weinheim, 2020.

(7) Du, G.; Zhu, C.; Xu, M.; Wang, L.; Yang, S.-T.; Xue, C. Energy-Efficient Butanol Production by Clostridium Acetobutylicum with Histidine Kinase Knockouts to Improve Strain Tolerance and Process Robustness. *Green Chem.* **2021**, *23* (5), 2155–2168.

(8) Tobiszewski, M.; Namieśnik, J.; Pena-Pereira, F. Environmental Risk-Based Ranking of Solvents Using the Combination of a Multimedia Model and Multi-Criteria Decision Analysis. *Green Chem.* **2017**, *19* (4), 1034–1042.

(9) Cue, B. W.; Zhang, J. Green Process Chemistry in the Pharmaceutical Industry. *Green Chemistry Letters and Reviews* 2009, 2 (4), 193–211.

(10) Jiménez-González, C.; Curzons, A. D.; Constable, D. J. C.; Cunningham, V. L. Cradle-to-Gate Life Cycle Inventory and Assessment of Pharmaceutical Compounds. *Int. J. LCA* **2004**, *9* (2), 114–121.

(11) Doran, P. M. Unit Operations. In *Bioprocess Engineering Principles*; Elsevier, 2013; pp 445–595. DOI: 10.1016/B978-0-12-220851-5.00011-3.

(12) Grisales Díaz, V. H.; von Stosch, M.; Willis, M. J. Butanol Production via Vacuum Fermentation: An Economic Evaluation of Operating Strategies. *Chem. Eng. Sci.* **2019**, *195*, 707–719.

(13) Errico, M.; Sanchez-Ramirez, E.; Quiroz-Ramirez, J. J.; Segovia-Hernandez, J. G.; Rong, B.-G. Synthesis and Design of New Hybrid Configurations for Biobutanol Purification. *Comput. Chem. Eng.* **2016**, *84*, 482–492.

(14) Chen, H.; Cai, D.; Chen, C.; Wang, J.; Qin, P.; Tan, T. Novel Distillation Process for Effective and Stable Separation of High-Concentration Acetone–Butanol–Ethanol Mixture from Fermentation–Pervaporation Integration Process. *Biotechnol Biofuels* **2018**, *11* (1), 286.

(15) Kongjan, P.; Tohlang, N.; Khaonuan, S.; Cheirsilp, B.; Jariyaboon, R. Characterization of the Integrated Gas Stripping-Condensation Process for Organic Solvent Removal from Model Acetone-Butanol-Ethanol Aqueous Solution. *Biochemical Engineering Journal* 2022, *182*, 108437.

(16) Oudshoorn, A.; van der Wielen, L. A. M.; Straathof, A. J. J. Assessment of Options for Selective 1-Butanol Recovery from Aqueous Solution. *Ind. Eng. Chem. Res.* **2009**, *48*, 7325–7336, DOI: 10.1021/ie900537w.

(17) Tang, T.; Ling, T.; Xu, M.; Wang, W.; Zheng, Z.; Qiu, Z.; Fan, W.; Li, L.; Wu, Y. Selective Recovery of n -Butanol from Aqueous Solutions with Functionalized Poly(Epoxide Ionic Liquid)-Based Polyurethane Membranes by Pervaporation. *ACS Omega* **2018**, 3 (11), 16175–16183.

(18) Xue, C.; Yang, D.; Du, G.; Chen, L.; Ren, J.; Bai, F. Evaluation of Hydrophobic Micro-Zeolite-Mixed Matrix Membrane and Integrated with Acetone–Butanol–Ethanol Fermentation for Enhanced Butanol Production. *Biotechnol Biofuels* **2015**, *8* (1), 105.

(19) Zhu, C.; Chen, L.; Xue, C.; Bai, F. A Novel Close-Circulating Vapor Stripping-Vapor Permeation Technique for Boosting Biobutanol Production and Recovery. *Biotechnol Biofuels* **2018**, *11* (1), 128.

(20) Kim, J. H.; Cook, M.; Peeva, L.; Yeo, J.; Bolton, L. W.; Lee, Y. M.; Livingston, A. G. Low Energy Intensity Production of Fuel-Grade

Bio-Butanol Enabled by Membrane-Based Extraction. *Energy Environ.* Sci. 2020, 13 (12), 4862–4871.

(21) Huang, H.-J.; Ramaswamy, S.; Liu, Y. Separation and Purification of Biobutanol during Bioconversion of Biomass. *Sep. Purif. Technol.* **2014**, *132*, 513–540.

(22) Mersmann, A.; Kind, M.; Stichlmair, J. *Thermal Separation Technology*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011. DOI: 10.1007/978-3-642-12525-6.

(23) Qin, F. G. F.; Ding, Z.; Peng, K.; Yuan, J.; Huang, S.; Jiang, R.; Shao, Y. Freeze Concentration of Apple Juice Followed by Centrifugation of Ice Packed Bed. *Journal of Food Engineering* **2021**, 291, No. 110270.

(24) Orellana-Palma, P.; Guerra-Valle, M.; Gianelli, M. P.; Petzold, G. Evaluation of Freeze Crystallization on Pomegranate Juice Quality in Comparison with Conventional Thermal Processing. *Food Bioscience* **2021**, *41*, No. 101106.

(25) Moreno, F. L.; Hernández, E.; Raventós, M.; Robles, C.; Ruiz, Y. A Process to Concentrate Coffee Extract by the Integration of Falling Film and Block Freeze-Concentration. *Journal of Food Engineering* **2014**, *128*, 88–95.

(26) Xu, C.; Kolliopoulos, G.; Papangelakis, V. G. Industrial Water Recovery via Layer Freeze Concentration. *Sep. Purif. Technol.* **2022**, 292, 121029.

(27) Tongshuai, L.; Yan, Z.; Yuanqing, T.; Xiaozhuang, W.; Chen, Z.; Nan, W.; Yucan, L. Application of Progressive Freeze Concentration in the Removal of Ca2+ from Wastewater. *Journal of Water Process Engineering* **2022**, *46*, No. 102619.

(28) Yang, Y.; Lu, Y.; Guo, J.; Zhang, X. Application of Freeze Concentration for Fluoride Removal from Water Solution. *Journal of Water Process Engineering* **2017**, *19*, 260–266.

(29) Knight, W. S. Thermodynamics of Aqueous Solutions of Alcohols and p-Dioxane. Thesis. 1962. http://www.ddbst.com.

(30) Tang, Q.; Jiang, P.; Peng, C.; Duan, X.; Zhao, Z. Impact of Acetone–Butanol–Ethanol (ABE) and Gasoline Blends on the Energy Balance of a High-Speed Spark-Ignition Engine. *Applied Thermal Engineering* **2021**, *184*, No. 116267.

(31) Ezeji, T. C.; Qureshi, N.; Blaschek, H. P. Acetone Butanol Ethanol (ABE) Production from Concentrated Substrate: Reduction in Substrate Inhibition by Fed-Batch Technique and Product Inhibition by Gas Stripping. *Appl. Microbiol. Biotechnol.* **2004**, 63 (6), 653–658.

(32) Chandgude, V.; Välisalmi, T.; Linnekoski, J.; Granström, T.; Pratto, B.; Eerikäinen, T.; Jurgens, G.; Bankar, S. Reducing Agents Assisted Fed-Batch Fermentation to Enhance ABE Yields. *Energy Conversion and Management* **2021**, 227, No. 113627.

(33) Osmanbegovic, N.; Yuan, L.; Lorenz, H.; Louhi-Kultanen, M. Freeze Concentration of Aqueous [DBNH][OAc] Ionic Liquid Solution. *Crystals* **2020**, *10* (3), 147.

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