Module-Based Synthesis and Intensification for the Acetone-Butanol-Ethanol (ABE) Mixture Separation

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Abstract. This work proposed a synthesis problem separating the Acetone-Butanol-Ethanol (ABE) mixture obtained after biomass fermentation. The synthesis problem was represented by a module-based superstructure and reformulated as a linear programming (LP) problem. The proposed framework combined process synthesis and process intensification of distillation processes with optimal structures. This framework discretized the liquid composition space of the ethanol-butanol-water ternary mixture into subspaces in which either vapor-liquid equilibrium or vapor-liquid-liquid equilibrium take place. These subspaces were assigned to distillation modules and decanter modules, respectively. The combinations between modules were represented by a superstructure, which was reformulated as a linear programming problem. The optimization solution shows the liquid and vapor flow paths with a minimum utility cost. Thus, the optimal connection between modules is known. Therefore, the optimization solution was interpreted into an intensified process by following several guidelines. The interpreted process was validated through process simulation. The results showed utility cost saving of around 34.5% compared to a base case process.

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Keywords: Azeotropic Distillation, Process Synthesis, Process Intensification, Optimization

Introduction

Biobutanol and Bioethanol are fuels that can be obtained from the separation and purification of the Acetone-Butanol-Ethanol (ABE) mixture, which is obtained after pretreatment, saccharification, and fermentation of biomass. The separation of the ABE mixture after the fermentation step is challenging because this effluent contains more than 75 w% water. The mixture forms an ethanol-water homogeneous azeotrope and a butanol-water heterogeneous azeotrope. Therefore, the ABE mixture has been typically separated either using liquid-liquid extraction (LLE) or azeotropic distillation (AZD). LLE uses an entrainer to remove water firstly and secondly acetone, ethanol, and butanol [1]. In AZD, a preconcentration column removes more than 90 wt% of water. Then acetone can be separated next, in the second column [2,3], or in the last column [4]. In AZD, a decanter separates butanol (i.e., organic phase) and water (i.e., aqueous phase).

The previous works aim to reduce the Total Annual Cost (TAC) of an existing ABE separation process by using more energy-efficient distillation, heat integration, or membranes. Starting from a pre-established process inherently limits design space. Thus, this research proposes a process synthesis and intensification (*PS+I*) framework for separating the ABE mixture without the need for any pre-established process structure. The proposed framework uses a module-based superstructure in which cooling, heating, mixing, splitting, and phase equilibrium are the phenomena embedded in the superstructure [5,6]. The proposed *PS+I* framework consists of the following steps: 1) database generation, 2) optimization, 3) solution interpretation, and 4) solution validation.

Problem statement

The synthesis problem for separating the ABE mixture was solved under the following assumptions: 1) The feed conditions (flow rate, composition, temperature, and enthalpy) are given in advance, 2) All products are fed and withdrawn as saturated liquids, 3) The specification of each product is assigned as the lower bound of the concentration of its key component, 4) Vapor-liquid equilibrium (VLE) is reached in each distillation module, 5) Vapor-liquid-liquid equilibrium (VLLE) is reached in each decanter module, 6) The operating pressure of distillation modules is given in advance, and the pressure drop is negligible, 7) Heat exchange among distillation modules and decanter modules is not considered, 8) The operating pressure and temperature in decanter modules are given in advance, 9) Utility costs per unit amount of heating and cooling are given in advance, 10) The optimization criterion is based only on the utility costs, 11) The process is at steady state.

Figure 1 explains the steps in the proposed *PS+I* framework. The first step consists of making a database with the molar composition and molar enthalpy of each phase for each subsystem in the ethanol-water-butanol ternary diagram. For each subspace, the simulation of a Flash drum was executed in Aspen Plus to obtain the parameters. These calculations were automatized by implementing a VBA macro in Microsoft Excel. It is worth mentioning that any commercial software or numerical calculation can be used as long as the thermodynamic model is known. It is important to formulate the optimization problem before the second step. Therefore, the concepts of modules are defined and incorporated into a superstructure. In the second step, the optimization problem is solved. In the third step, the optimization solution is interpreted as a process that considers only meaningful flows. Finally, the interpreted process is validated through simulation in the fourth step. More details about the proposed framework are explained in the following sections.

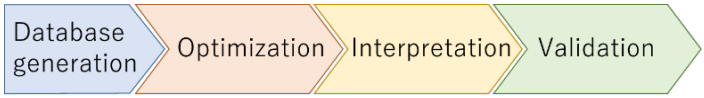


Fig. 1 Steps in the *PS+I* framework.

Superstructure formulation

In this research, the entire liquid composition space in the ternary diagram is discretized into a sufficient number of subspaces *N*. A representative composition is chosen at each subspace and is assigned to a distillation module. Also, in the vapor-liquid-liquid (VLL) region, the endpoints of each tie line are assigned to a decanter module *M*. Figure 2 shows the conceptual representation of distillation modules, decanter modules, and their connections in the proposed superstructure. The white squares numbered from 1 to *N* denote distillation modules, and black squares from 1 to *M* denote decanter modules. Moreover, each module is divided into two parts: the output and input parts. Thus, two squares of the same number correspond to the same module. The distillation modules have liquid, vapor, and heat inlets and outlets, while the decanter modules have liquid, vapor, and heat inlets but two liquids and heat outlets. The blue, green, and red lines among the modules are the liquid, vapor, and heat connections. Moreover, distillation-distillation, decanter-decanter, distillation-decanter, and decanter-distillation module connections can derive the optimal process structure without assuming any pre-established distillation sequence.

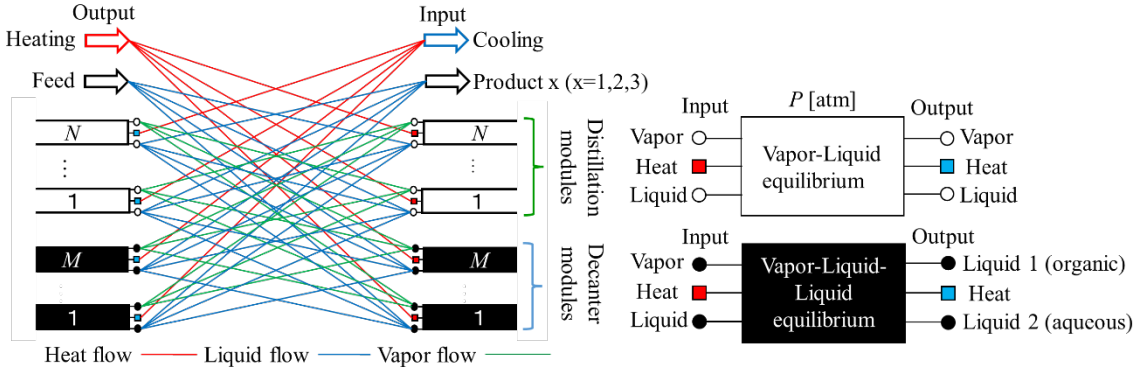


Fig. 2 Conceptual representations: superstructure (left), distillation module (top right), decanter module (bottom right).

The proposed superstructure can also consider liquid-liquid extraction by adding extraction modules in which the Liquid-Liquid equilibrium is reached. However, it is out of the scope of this research.

Mathematical formulation

The superstructure is reformulated as a mathematical programming problem. The objective function is the utility cost minimization (UC) shown in Equation (1).

$$UC = \sum_{i \in S_M} \left(C_H Q_i^H + C_C Q_i^C \right) + \sum_{j \in S_D} \left(C_H Q_j^H + C_C Q_j^C \right) \quad (1)$$

Equation (2) shows the feed material balance of the feed. Equation (3) shows the molar purity specification of products. Equations (4) and (5) show the heat balance in distillation and decanter modules. Equations (6) and (7)

show the material balance of each component in distillation and decanter modules. Equations (8) and (9) show the material balance in distillation and decanter modules, respectively.

$$\sum_{i\in S_{\mathrm{M}}}(L_{\mathrm{F}i})+\sum_{j\in S_{\mathrm{D}}}(L_{\mathrm{F}j})+L^{\mathrm{F}}=0 \tag{2}$$

$$x_k^{\mathrm{P}}\sum_{j\in S_{\mathrm{M}}}(L_{jk}^{\mathrm{P}})+x_k^{\mathrm{P}}\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmk}^{\mathrm{D}})-\sum_{j\in S_{\mathrm{M}}}(L_{jk}^{P}x_{jk})-\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmk}^{\mathrm{P}}x_{jmk}^{\mathrm{D}})\le 0\quad(k\in S_{\mathrm{p}}) \tag{3}$$

$$\begin{aligned}&\sum_{j\in S_{\mathrm{M}}}(L_{ji}h_j^{\mathrm{L}}+V_{ji}h_j^{\mathrm{V}})+L_{\mathrm{F}i}h^{\mathrm{F}}+Q_i^{\mathrm{H}}+\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}}h_{jm}^{\mathrm{D}})-h_i^{\mathrm{L}}\sum_{j\in S_{\mathrm{D}}}(L_{ij})-\\&\sum_{j\in S_{\mathrm{M}}}(L_{ij}h_i^{\mathrm{L}}+V_{ij}h_i^{\mathrm{V}})-h_i^{\mathrm{L}}\sum_{p\in S_{\mathrm{p}}}(L_{ip}^{\mathrm{P}})-h_i^{\mathrm{V}}\sum_{j\in S_{\mathrm{D}}}(V_{ij})-Q_i^{\mathrm{C}}=0\quad(i\in S_{\mathrm{M}})\end{aligned} \tag{4}$$

$$\begin{aligned}&\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}}h_{jm}^{\mathrm{D}}+V_{jmi}^{\mathrm{D}}h_{jm}^{\mathrm{D}})-\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{imj}^{\mathrm{D}}h_{im}^{\mathrm{D}}+V_{imj}^{\mathrm{D}}h_{im}^{\mathrm{D}})+L_{\mathrm{F}i}h^{\mathrm{F}}+Q_i^{\mathrm{H}}+\\&\sum_{j\in S_{\mathrm{M}}}(L_{ji}h_j^{\mathrm{L}}+V_{ji}h_j^{\mathrm{V}})-\sum_{m=1,2}\sum_{j\in S_{\mathrm{M}}}(L_{imj}^{\mathrm{D}}h_{im}^{\mathrm{D}})-\sum_{m=1,2}\sum_{p\in S_{\mathrm{p}}}(L_{imp}^{\mathrm{P}}h_{im}^{\mathrm{D}})-Q_i^{\mathrm{C}}=0\quad(i\in S_{\mathrm{D}})\end{aligned} \tag{5}$$

$$\sum_{j\in S_{\mathrm{M}}}(L_{ji}+V_{ji})+L_{\mathrm{F}i}+\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}})-\sum_{j\in S_{\mathrm{M}}}(L_{ij}+V_{ij})-\sum_{p\in S_{\mathrm{p}}}(L_{ip}^{\mathrm{P}})-\sum_{j\in S_{\mathrm{D}}}(L_{ij}+V_{ij})=0\quad(i\in S_{\mathrm{M}}) \tag{6}$$

$$\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}})+\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{imj}^{\mathrm{D}})+L_{\mathrm{F}i}\sum_{j\in S_{\mathrm{M}}}(L_{ji}+V_{ji})-\sum_{m=1,2}\sum_{j\in S_{\mathrm{M}}}(L_{imj}^{\mathrm{D}})-\sum_{m=1,2}\sum_{p\in S_{\mathrm{p}}}(L_{imp}^{\mathrm{P}})=0\quad(i\in S_{\mathrm{D}}) \tag{7}$$

$$\begin{aligned}&\sum_{j\in S_{\mathrm{M}}}(L_{ji}x_{jk}+V_{ji}y_{jk})+L_{\mathrm{F}i}x_k^{\mathrm{F}}+\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}}x_{jmk}^{\mathrm{D}})-x_{ik}\sum_{j\in S_{\mathrm{D}}}(L_{ij})-\\&\sum_{j\in S_{\mathrm{M}}}(L_{ij}x_{ik}+V_{ij}y_{ik})-x_{ik}\sum_{p\in S_{\mathrm{p}}}(L_{ip}^{\mathrm{P}})-y_{ik}\sum_{j\in S_{\mathrm{D}}}(V_{ij})=0\quad(i\in S_{\mathrm{M}},k\in S_{\mathrm{p}})\end{aligned} \tag{8}$$

$$\begin{aligned}&\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmi}^{\mathrm{D}}x_{jmk}^{\mathrm{D}})-\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{imj}^{\mathrm{D}}x_{imk}^{\mathrm{D}})+\sum_{j\in S_{\mathrm{M}}}(L_{ji}x_{jk}+V_{ji}y_{jk})+\\&L_{\mathrm{F}i}x_k^{\mathrm{F}}-\sum_{m=1,2}\sum_{j\in S_{\mathrm{M}}}(L_{imj}^{\mathrm{D}}x_{imk}^{\mathrm{D}})-\sum_{m=1,2}\sum_{p\in S_{\mathrm{p}}}(L_{imp}^{\mathrm{P}}x_{imk}^{\mathrm{D}})=0\quad(i\in S_D,k\in S_{\mathrm{p}})\end{aligned} \tag{9}$$

where S_{M}, S_{D}, and S_{p} are the sets of the distillation modules, decanter modules, and products, respectively. The parameters in the optimization problem are: the cost per unit amount of heating and cooling (c_{H} and c_{C}), the composition, molar enthalpy, and inlet flow of the feed (x_k^{F} ,h^{F}, and L^{F}), the lower bound of the composition of each product (x_k^{P}), the phase compositions in equilibrium (i.e., x_{ik}, x_{jmk}^{D}, y_{jk}) and their molar enthalpy (i.e., h_i^{L}, h_i^{V}, h_{jm}^{D}). The optimization variables are: heating and cooling (Q_i^{H} and Q_i^{C}), liquid and vapor flow rates (L_{ij} and V_{ij}), feed flow rate ($L_{\mathrm{F}i}$), the liquid flow rate from distillation modules to products (L_{jk}^{P}), the liquid flow rates from decanter modules to products (L_{jmk}^{P}), and liquid flow rates into decanters (L_{jmi}^{D}) for each module. Equations (1) to (9) are expressed as linear relationships of optimization variables. Thus, the optimization problem can be solved as a linear programming (LP) problem. In addition, all optimization variables are non-negative.

Solution Procedure

The solution of the *PS+I* framework is solved as follows:

1. The parameters for each distillation and decanter module are calculated in advance in the process simulation software Aspen Plus V.11®. Then, these values are used for solving the optimization problem.
2. The LP problem is solved in the optimization software CPLEX Optimization Studio 12.7. The exact minimum solution can be obtained if the optimization problem has an infinite number of modules. However, this situation is not realistic. Therefore, the problem is solved for a finite number of modules N and M. Here, the equality constraints $h(x)=0$ are relaxed as $-\varepsilon\le h(x)\le\varepsilon$ in order to obtain a solution.
3. The value of ε is reduced (e.g., 0.01) until the component material is within a tolerance of 1% (e.g., $\tau=0.01$).

$$\sum_{i\in S_{\mathrm{M}}}(L_{\mathrm{F}i})+\sum_{j\in S_{\mathrm{D}}}(L_{\mathrm{F}j})-\sum_{k\in S_{\mathrm{M}}}x_k^{\mathrm{P}}\sum_{i\in S_{\mathrm{M}}}(L_{jk}^{\mathrm{P}})+\sum_{k\in S_{\mathrm{D}}}x_k^{\mathrm{P}}\sum_{m=1,2}\sum_{j\in S_{\mathrm{D}}}(L_{jmk}^{\mathrm{D}})\le\tau \tag{10}$$

4. The solution is plot in a ternary diagram. Since some flows have values, only flows with significant flow rates are plotted (i.e., L_{ij}, and V_{ij} more than 10 kmol/h).
5. The plotted solution is interpreted and translated into an intensified process with an optimal distillation structure.
6. The interpreted process is validated in Aspen Plus V.11®.

Figure 3 shows the software utilization/integration in the solution procedure. A VBA macro is linked to Aspen Plus, and it runs automatically until the parameters for all modules are generated. Then, the optimization software reads the parameters from the Excel file, runs the optimization, and writes the solution back Excel file. Using a macro, only the meaningful flows in the optimal solution are plotted for interpretation. Finally, the interpreted process is simulated in Aspen plus V11.0. The process interpretation and validation are made by the end-user. However, this work provides several guidelines to assist end-users in the interpretation step.



Fig. 3 Solution procedure.

Case study

The reference ABE separation process is shown in Figure 4 [2]. In the process, Column 1 removes 98.7% of the water in the feed, Column 2 purifies acetone, Column 3 separates ethanol at a composition near its azeotrope. Columns 4 and 5 separate butanol and water through a decanter. In addition, there are two recycle streams to the decanter.

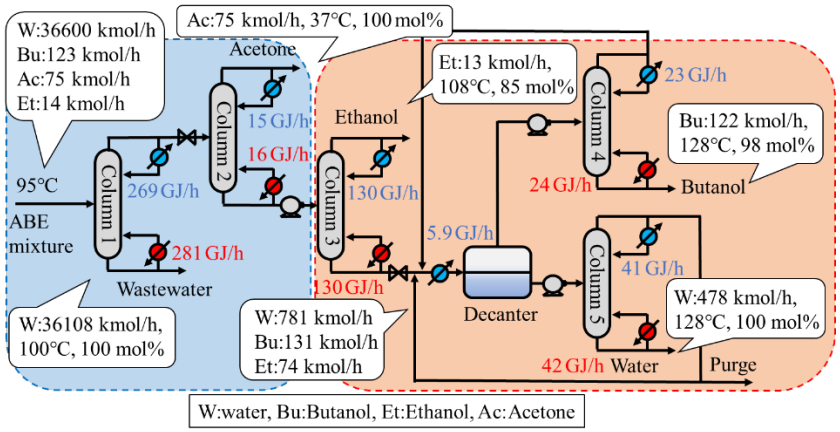


Fig. 4 Reference case for the ABE separation process.

The process in Figure 4 was simulated in Aspen Plus V.11®. The utility cost was 5,172 \$/h, and that of the red region accounted for 39.8% (2,060 \$/h). In this research, it is assumed that c_H =10 \$/GJ and c_C =0.5 \$/GJ. This process has three problems: 1) Column 3 is the second largest energy consumer (130 GJ/h), making ethanol separation energy-intensive, 2) the total recycle flow is over 1000 kmol/h, 3) ethanol accumulates in Column 4.

Results and discussion

In this work, the operating pressure is 1 atm, and the decanter temperature is 90 °C. The liquid composition in the ternary diagram is discretized in intervals of 0.02 ($N = 1330$), and six tie lines are considered ($M = 6$). The acetone, water, and butanol purity is over 98 mol%, while ethanol is 85 mol%. The NRTL thermodynamic model in Aspen Plus V.11® was used to calculate the modules' parameters.

Figure 5 shows the liquid and vapor flows between modules plotted in a ternary diagram. The utility cost of the optimization problem is 29.9 \$/h. Only meaningful modules with flows over 10 kmol/h were plot. Black squares represent the chosen distillation, while solid lines connecting modules represent the selected liquid or vapor flow paths. Solid red and blue squares represent modules where heating or cooling occurs. The guidelines for process

interpretation are: 1) identify cooling and heating modules, 2) flows in the VLL region, and 3) flows in the ternary diagram.

Heating takes place at water and butanol high concentrations. Therefore, they exit at the bottom reboilers. Cooling occurs near the Ethanol/Water azeotrope, and therefore, it exits at a top condenser. A decanter separates aqueous and organic phases, but also a decanter separates the water product. On the right side of the distillation boundary, ethanol is gradually concentrated. On the left side of the distillation boundary, butanol product and ethanol/water/butanol streams split. Based on these interpretations, the proposed optimal process is shown in Figure 6.

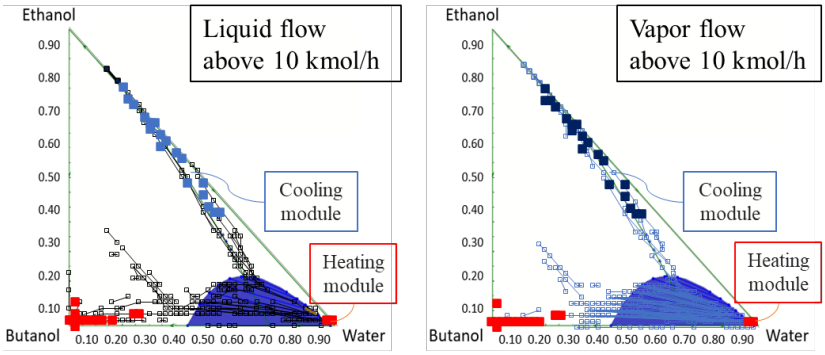


Fig. 5 Optimal solution: liquid flows (left), vapor flows (right).

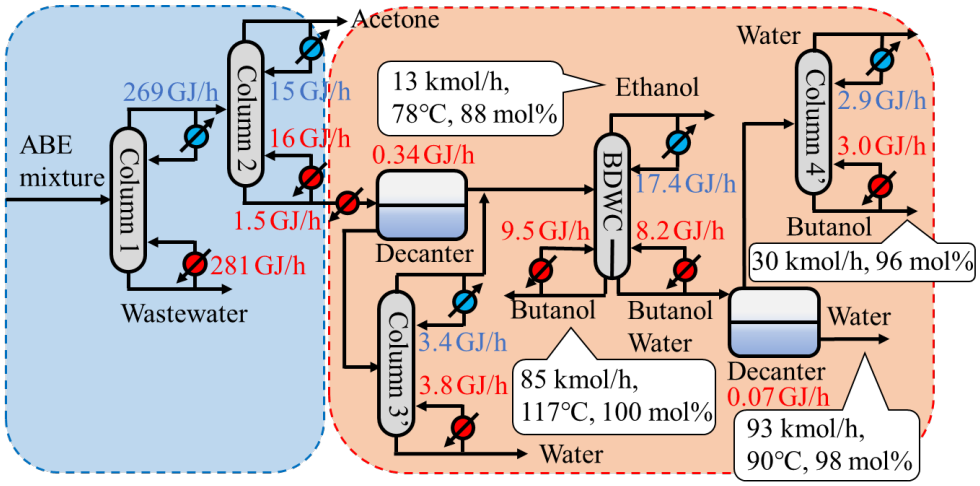


Fig. 6 Proposed optimal ABE separation process.

The utility cost of the interpreted process is 3,387 $/h, which is 34.5 % less than that of the reference case. Also, the utility cost of the proposed process in the red region is 275 $/h, which is 86.6 % less than that of the reference case in the red region. In Column 3', the water product leaves at the bottom. In the Bottom Divided Wall Column (BDWC), the ethanol product leaves at the top, and the butanol product and an ethanol/water/butanol stream leave at the bottom. In Column 4', the butanol product leaves at the bottom. A bottom decanter separates the water product from the organic phase entering Column 4'. Butanol is obtained from two product streams, while water is obtained from three product streams. For butanol, the product stream of BDWC has a nearly 100 mol% purity while the product stream of Column 4' has a 96 mol% purity. The specified purity (98 mol%) is obtained by mixing these streams. A similar analysis with water can be done. The proposed optimal process has the following features: 1) BDWC is less energy-intensive (17.7 GJ/h) than Column 3, 2) recycling to decanters is not necessary, and 3) a second decanter is used to separate water as a product in the aqueous phase stream. The typical two-column butanol water separation is not the best choice because it will generate recycle flows to the decanter and increase the heating utility [7].

The BDWC cannot be simulated directly in Aspen Plus. However, an equivalent structure of three distillation columns with liquid and vapor flow interconnections was simulated. It is the typical approach to simulating Divided Wall Columns [8].

Conclusions

This research presented a process synthesis and intensification framework for separating the Acetone-Butanol-Ethanol (ABE) mixture, which is important for obtaining biofuels. Acetone was separated first, and then a mixture of ethanol, butanol, and water was separated later. The later ternary mixture forms a homogeneous azeotrope and a region with two liquids. Therefore, its separation cannot be done with conventional distillation columns. The proposed framework used a module-based superstructure in which distillation and decanter modules can connect to generate optimal liquid and vapor flow paths to derive optimal structures. The superstructure was reformulated as a linear programming problem to minimize the utility cost. Once the optimal solution was obtained, the proposed process was derived after following several interpretation guidelines. The proposed intensified process was validated through rigorous simulation. The simulation results showed that the utility cost attained savings of 34.5% compared to the base case taken.

The main contribution of this work is to derive the optimal process structure without the need for any pre-established structure. Then, an optimization technique can be used to refine its design by considering other objective functions such as cost, control, environmental impact, and safety. This proposed synthesis problem can be applied to any process that uses decanters.

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