Separation Process Synthesis for High-GWP Refrigerant Mixtures: Extractive Distillation using Ionic Liquids

Mohammed Sadaf Monjur, Ashfaq Iftakher, and M. M. Faruque Hasan*

Artie McFerrin Department of Chemical Engineering, Texas A&M University

College Station, TX 77843-3122, USA.

Abstract

Due to their high global warming potential (GWP), the separation and recovery of hydrofluorocarbons (HFCs) from different refrigerant mixtures is an important issue. HFC mixtures are azeotropic in nature, thereby rendering the conventional distillation based separation difficult and energy intensive. Extractive distillation (ED) with ionic liquid (IL) as solvent provides an attractive strategy for selective separation of HFC mixtures. However, systematic design and optimization of ED-based separation processes is nontrivial. In this work, we present SPICE_ED which is a software framework for the detailed design, synthesis and techno-economic analysis of ED-based separation processes. The framework employs a building block representation followed by superstructure optimization that is able to automatically generate numerous design solutions and screen the best without requiring prior expert knowledge of candidate configurations. For a given IL as solvent and a set of design specifications, one can automatically determine the feasibility of the solvent and obtain the optimal process flowsheets that correspond to minimum energy consumption, minimum separation cost, or minimum emission/waste. We demonstrate the capability of SPICE_ED for the separation of R-410A (50 wt% R-32 and 50 wt% R-125) using [bmim][PF₆], a commonly used IL. Our optimized design only requires an equivalent work of 338.2 kJ/kg R-410A, which is about 48% less than the previously reported value of 656 kJ/kg. The newly identified design also achieves more than 47%and 27% reduction in emission (sustainability) and cost, respectively. Through multiobjective optimization, we further identify an operating regime to separate R-410A at near-minimum cost without significantly increasing the energy consumption and CO_2 -eqv emission. The processes obtained from SPICE_ED show excellent agreement with the key performance metrics when simulated in Aspen Plus, thereby establishing confidence in our designs as realistic and implementable.

Keywords: Sustainable Process Design, Process Intensification, Extractive Distillation, Ionic Liquids, Refrigerant Separation.

^{*}Correspondence should be addressed to M.M. Faruque Hasan at hasan@tamu.edu, Phone: (979) 862-1449.

1 Introduction

Hydrofluorocarbons (HFCs) are 3^{rd} generation of fluorinated gases which are commonly used in refrigeration cycles. Despite their thermodynamic stability, negligible toxicity and predominant use,¹ HFCs are not sustainable refrigerants. They have high global warming potential (GWP). About 2–3% of the total global greenhouse gas (GHG) emission is due to the millions of tons of HFC emission worldwide.² There is a significant interest to replace HFCs by 4th generation of fluorinated gases commonly known as hydrofluoroolefins (HFOs), which possess zero ozone depletion potential and much lower GWP.³ To minimize the potential emissions of used HFCs, several international agreements and regulations are in place. Examples include the Kigali Amendment to the Montreal Protocol⁴ that recommends reducing the global HFC emissions by 80–85% by 2047, the European Regulation on fluorinated gases,^{5,6} and the 2020 American Innovation and Manufacturing (AIM) Act⁷. Incineration of the HFCs is not a practical option, since it would result in the release of a large amount of CO₂ into the atmosphere. Recycled HFCs, on the other hand, would potentially have a market value of more than a billion dollars in the United States alone, while preventing their release into the atmosphere. Furthermore, recycled HFCs can be blended with HFOs to significantly reduce the overall GWP.⁴

HFC recycling is essentially a separation problem that is nontrivial and poses several challenges. These refrigerant mixtures often form azeotropes that behave as a single fluid. Conventional separation techniques (e.g., cryogenic distillation) for HFC separation are highly energy-intensive and costly. They also involve complex process operations and safety hazards.⁴ In an effort to transition to low-carbon economy, it is highly desirable to expedite the development and implementation of innovative technologies to ensure increased recovery, reuse, and recycling of HFCs. Process intensification is such an enabling technology.^{8–11}

Intensified process units such as, extractive distillation (ED) can help attain high-purity products from azeotropic mixtures. The working principle of ED critically depends on the use of a suitable solvent that selectively absorbs one of the refrigerants, thereby operating at conditions that prevent any potential azeotrope formation. The high selectivity and affinity of the solvent towards a particular component of the mixture also improves the separation performance to achieve high purity and high recovery. Among the many chemicals that can be used as solvents, ionic liquids (ILs) show promise due to their high thermal and chemical stability and highly selective gas solubility. An IL is composed of a large organic cation and an inorganic anion with a melting point typically below 100°C.¹² As a result, ILs generally remain liquid at room temperature. Unlike most organic solvents, ILs have extremely low vapor pressure. Hence, the amount of IL going to the distillate is negligible, thereby ensuring minimum contamination of the refrigerant gas with solvent.¹³ The low vapor pressure also allows efficient regeneration. ILs are often called 'designer solvents' as their properties such as density, viscosity and gas solubility can be tuned as required. All these make ILs ideal candidates as entrainers for ED. The solubility of different HFCs in ILs has been extensively studied both experimentally and computationally in the past.^{5,13–28} However, effective process design of IL-based extractive distillation requires equilibrium and kinetic data which may not be always available at all conditions. This requires predictive modeling of gas solubility and other properties. In that regard, several thermodynamic approaches (e.g., Gamma-Phi²⁴ method embedding NRTL or Margules activity coefficient models and cubic equation of states (EoS) such as the Van der Waals, Redlich–Kwong and Peng Robinson models) are available.^{27,29}

Apart from the gas solubility and the selectivity, the regeneration of ILs is extremely important, especially from the standpoint of energy requirement and cost. An IL-based extractive separation process can be designed and configured in several ways depending on the modes of IL regeneration. One can regenerate the rich solvent using a single flash (Figure 1a), using multiple flash in series (Figure 1b), using conventional distillation (CD) columns (Figure 1c), or using stripping columns (SC) (Figure 1d). It is not trivial to know which alternative is the best, as the choice depends on the feed mixed-refrigerant composition, solvent selection, operating conditions, and so on. The selection of optimal process pathways further involves discrete decisions that result in a combinatorial (mixed-integer) optimization problem. Evidently, Figures 1a-d exhibit only a subset of all possible process configuration choices. Therefore, a need arises for a systematic platform that can consider all combinatorial choices (e.g., using a process superstructure as shown in Figure 1e) and perform rigorous optimization of the process superstructure to automatically identify optimal process designs and configurations.

Although many works have addressed the separation of azeotropic mixtures using ILs as entrainers for ED in the past $^{24,30-48}$, process synthesis for the determination of optimal process configurations and optimal operating conditions remains a challenge. An ED column consists of many stages where each stage has both liquid and vapor flows that are determined by gas absorption and phase equilibria. Rigorous optimization considering these complex phenomena is difficult. Furthermore, the overall separation process includes additional desorption or flash columns, pumps, condensers, reboilers, and economizers. All these lead to the existence of a large number of degrees of freedom (e.g., solvent flow rate, number of stages, feed stage, solvent trays, column pressure, temperature, reflux ratio, etc). The selection of a suitable solvent also plays a role in ensuring the desired purity and recovery.^{13,29} In this regard, model-based optimization approaches offer promising solutions. Several works have been reported in the literature. For example, Valencia-Marqueze et al.⁴⁹ used disjunctive mixed-integer nonlinear programming (MINLP) for the simultaneous design of IL solvent and ED column for ethanol–water separation. Zhou et al. 50 performed multiobjective optimization using a hierarchical framework for solvent design for ED processes. Waltermann et al.⁵¹ used MINLP for hierarchical solvent selection and process design with energy integration for azeotropic distillation. Tian and Pistikopoulos⁵² proposed a phenomena based systematic approach for solvent selection and process intensification using the generalized modular representation framework (GMF). However, none of these works perform design at the



Figure 1: Alternative process configurations for extractive distillation (ED)-based separation: (a) ED followed by a single flash separator, (b) ED followed by a series of flash separators, (c) ED followed by a conventional distillation column, (d) ED followed by a stripping column, and (e) a full-connectivity process network or superstructure that includes all alternative configurations. A structural optimization of the superstructure would lead to an optimal subnetwork representing the best design alternative.

phenomena, task and unit operation levels simultaneously, and therefore, are unable to consider all design alternatives at the same time.

There are recent works addressing the separation problem of R-410A using IL. For example, Asensio-Delgado et al.⁴⁷ simulated a R-410A separation process that utilizes $[\text{emim}][\text{Tf}_2\text{N}]$ as solvent and reported 99.5 wt% and 84.0 wt% purity of R-125 and R-32 rich product, respectively. Finberg and Shiflett⁴⁸ considered $[\text{bmim}][\text{PF}_6]$ for an ED-based separation process and reported simulation results of 99.5 wt% purity for both R-125 and R-32 rich products. However, to the best of our knowledge, there has not been any published work that optimizes ED-based separation process for refrigerant mixtures either taking into account the energy minimization, sustainability, and process economics as design objectives or the multiobjective design based on economics and energy aspects. In this work, we aim to address this gap by employing SPICE_ED (Synthesis and Process Intensification of Chemical Enterprises Involving Extractive Distillation), which is a software framework for the detailed design, synthesis and techno-economic analysis of ED-based separation processes. Our framework employs a building block representation⁵³ in a superstructure optimization setting that can generate a set of process configurations and identify the best design solution without requiring prior knowledge of candidate configurations. For a particular IL as solvent and a set of design specifications, SPICE_ED can automatically determine the feasibility of the selected solvent and identify the optimal process configuration satisfying the minimum energy consumption, minimum separation cost, or minimum emission/waste requirement. SPICE_ED employs a bottom up approach that provides a seamless transition between the phenomena, tasks, unit operations and flowsheet level designs. This enables to consider all plausible combinatorial choices. We demonstrate the applicability of SPICE_ED for the separation of R-410A (50 wt% R-32 and 50 wt% R-125) using $[\text{bmim}][\text{PF}_6]$, a commonly used IL. We further *in-silico* validate the designs using commercial process simulator (Aspen Plus v10) and observe that all the main design variables attain great similarity with the values obtained through SPICE_ED.

The remainder of the article is organized as follows: In Section 2, we present a brief description of the representation and modeling techniques used in SPICE_ED. In Section 3, we describe the improvement obtained using our framework for a base-case design and its validation to establish the confidence on our design solutions. In Section 4, we present our process synthesis results for different economic, environmental, and sustainability objectives. In Section 5, we summarize the key findings and provide some concluding remarks.

2 SPICE_ED Framework

Existing process synthesis methods mostly focus on screening the best design configuration, given that all plausible design configurations and the potential unit operations are known beforehand. However, process intensification sometimes requires innovative designs to make drastic improvement. Therefore, the following question remains: How can we systematically identify and

generate all plausible intensification opportunities at the equipment and flowsheet levels? How can we systematically intensify a process, and incorporate process intensification in flowsheet synthesis and optimization? SPICE_ED fills this critical gap in the space of extractive distillation-based separation process synthesis. While SPICE_ED serves as a computational platform for specialized design and intensification of ED processes, it is being developed in such a way that it can be readily integrated with SPICE^{53–56}, which is a MINLP-based broader framework for the synthesis and process intensification of chemical enterprises in general. While SPICE_ED inherits a library of general mass and energy conservation models, operational constraints and objective functions from SPICE, it further includes rigorous phenomena and thermodynamic property models specifically suitable for extractive distillation. SPICE_ED can be deployed for different purposes, as shown in Figure 2. A user can perform process design activities by providing the specifications on the feed mixtures, products and utilities. Additionally, user can define the solvent properties, cost functions, and economic and emission parameters. At the conceptual design stage, one can use SPICE_ED to determine whether an ED-based partial or full-scale process intensification is useful for a given design problem. If ED shows promise, then SPICE_ED can be further employed to perform detailed design of ED configuration. Decision variables, such as the number of theoretical stages, reflux ratios, feed stages of the solvent, amount of makeup solvent, etc., are optimized to achieve the desired separation for select design targets (e.g., minimization of energy consumption, minimization of CO_2 -eqv emissions, or minimization of the total cost of separation). Additionally, multiobjective optimization can be performed to generate Pareto solutions considering the impact of multiple conflicting objectives. One can also perform rigorous simulation for fixed input parameters and fixed design configurations. SPICE_ED can be further used to perform various analyses, e.g., sensitivity analysis, techno-economic analysis (TEA) and life-cycle analysis (LCA). The functionality of SPICE_ED not only allows to generate the most optimal designs, the underlying model can be solved repeatedly to generate rank-ordered lists of design configurations and top solvents. As a consequence, theoretical bounds on process design opportunities and maximum achievable intensification targets can be obtained. Finally, SPICE_ED can be used to perform material-property-performance mapping to guide the development of novel and improved solvents with superior performance.

2.1 Building Block-based Representation

At the core of the SPICE_ED framework, we have the building block-based process representation. In this representation, we use building blocks and their boundaries to represent all the physicochemical process phenomena. Using this representation, process synthesis and intensification can be performed from the phenomena scale. This is a unique capability for coming up with innovative designs without any pre-postulation of candidate designs. A general description of the use of building block representation can be found elsewhere. $^{56-61}$

Each block in this representation consists of two main elements: block interior and block



Figure 2: SPICE_ED framework. The framework is developed based on building block-based process representation. User can use SPICE_ED to perform several tasks such as targeting/benchmarking, conceptual design, process simulation and analysis, process synthesis, optimization, and material-property-performance mapping of solvent-based extractive distillation processes.

boundary (Figure 3a). The same block interior can represent either a reactor (if filled with catalyst), or an adsorber (if filled with adsorbent materials). A block interior can also be empty. A block allows streams to enter or exit from adjacent blocks. Similarly, fresh feed and products can be introduced or withdrawn from each block. Additionally, hot and cold utilities are allowed to provide heat or take heat energy from each block. To represent the interaction between adjacent blocks, we define three distinct types of block boundaries : unrestricted boundary, semi-restricted boundary, and completely restricted boundary. We allow material and energy to pass through unrestricted boundaries. Stream compositions remain the same upon passing through such a boundary. Apart from stream flows, unrestricted boundaries also facilitate pressure manipulators (e.g., pump, compressor, value or expander) to allow pressure changes in streams. We use semi-restricted boundary to represent separation phenomena. The presence of a semi-restricted boundary between two blocks indicates that there exists a mass transfer interceptor that selectively allows transfer of mass. Unlike unrestricted boundaries, streams passing through these boundaries experience changes in composition. The change of composition is determined by equilibrium or rate-based separation models. Membrane is a good example of rate-based separation. Fick's law or Darcy's law can be used to model such a rate based mass transfer. On the other hand, equilibrium based separation depends upon phase equilibria. The type of separation (rate-based or equilibrium-based) and the corresponding phenomena models determine change in compositions in different phases. The third type of boundary is the completely restricted boundary. Such a boundary does not allow any material and energy flow, and can be used to represent the boundary of any equipment. In the context of extractive distillation, completely restricted boundary could represent the column wall of an ED unit, or the internal walls of a dividing-wall distillation column.

By using single or multiple blocks, all fundamental phenomena can be represented by the building block-based representation. In the case of ED process, the set of all basic phenomena is depicted in Figure 3b. We observe that a single block is sufficient to represent mixing (Figure 3b(i)), splitting (Figure 3b(ii)), and heating/cooling (Figure 3b(iii)). On the other hand, pressure change (Figure 3b(iv)) and phase change (Figure 3b(v)) require two adjacent blocks with a common unrestricted boundary. Each equilibrium tray of a distillation or ED column represented using a pair of adjacent blocks (one with liquid phase and the other with vapor phase) and a common boundary with vapor-liquid equilibrium (VLE) as the assigned phenomena. Phase change also occurs in the total condenser, where vapor condenses to liquid. We employ a semi-restricted boundary to depict the contact between two different phases (the green vertical line in Figure 3b(vi)). VLE is of particular importance, since it is the key thermodynamic phenomena that occurs inside an ED column. SPICE_ED allows VLE modeling through several types of thermodynamic models, such as the Gamma-Phi method or cubic EoS models.

After representing the basic operations and the thermodynamic, kinetic and transport phenomena, we proceed to represent the unit operations using a set of blocks. Figure 3c depicts the two most common units that are required for an ED process. A flash separator consists of a single VLE stage, thus only two blocks are sufficient for its representation (Figure 3c(i)). A distillation column (conventional or intensified ED) has several equilibrium stages. Such a unit operation requires two sets of adjacent blocks in series (Figure 3c(ii)).

At the unit operation level, building block-based representation allows automatic flowsheet generation. To screen the best of configurations, we further construct a superstructure by arranging sets of blocks in a two dimensional grid. We denote the position of each block in a superstructure by $B_{i,j}$, where *i* is the row number and *j* is the column number. A superstructure is a large flowsheet with many plausible designs. An example of such a superstructure is shown in Figure 3d(i), which includes many possible choices of process configurations. For example, while considering IL regeneration, SPICE_ED can suggest designs with a single flash separator operating at vacuum condition, or with two flash separators where one operates at atmospheric pressure and the other operates at vacuum condition. Alternatively, it can suggest a stripping column or a conventional distillation column. While considering energy intensive units like distillation and stripping columns, SPICE_ED can further suggest heat integration between the hot and cold process streams so that the overall energy consumption for the whole flowsheet can be improved. Figure 3d(ii) depicts the building block equivalent representation of the classical unit operation-based superstructure (Figure 3d(i)) with a 52 × 6 grid dimension. Detail description of this is discussed in Section S3 of the Supporting Information.

Physical attributes such as temperature, pressure and component composition of a block $B_{i,j}$



(a) Building block and (b) Phenomena representation boundaries

(c) Equipment representation

Figure 3: Building block-based representation of extractive separation process. (a) Each building block is a fundamental design element that can accommodate common physicochemical phenomena by using it's two unique features: block interior and block boundaries; (b) single or multiple number of blocks are required to represent fundamental physicochemical phenomena in extractive distillation; (c) When several phenomena representing blocks are arranged, different types of unit operations can be presented; and (d) a general representation of the entire superstructure can be obtained using building blocks, thereby enabling a single model formulation for ED process synthesis.

are denoted as: $T_{i,j}$, $P_{i,j}$, and $y_{i,j,k}$, respectively, where, k represents a chemical species. We utilize several sets to formulate the optimization model: sets of row and column numbers are $i \in \mathcal{I} = \{1, ..., |\mathcal{I}|\}$ and $j \in \mathcal{J} = \{1, ..., |\mathcal{J}|\}$, set of components $\mathcal{K} = \{k|k = 1, ..., |\mathcal{K}|\}$ which includes both the refrigerants and ILs, set of fresh feeds $\mathcal{F} = \{f|f = 1, ..., |\mathcal{F}|\}$, set of products $\mathcal{P} = \{p|p = 1, ..., |\mathcal{P}|\}$, set of separation phenomena $\mathcal{S} = \{s|s = 1, ..., |\mathcal{S}|\}$, and the set of enabling materials $\mathcal{M} = \{m|m = 1, ..., |\mathcal{M}|\}$.

2.2 Mass and Energy Balances

Mass and energy balances provide a set of rigorous constraints to ensure the feasibility of a design. These balances for each block $B_{i,j}$ are summarized as follows:

$$F_{i,j-1,k} + R_{i-1,j,k} - F_{i,j,k} - R_{i,j,k} + \sum_{f \in \mathcal{F}} M_{i,j,k,f} - \sum_{p \in \mathcal{P}} N_{i,j,k,p} + \sum_{(i',j') \in Link} J_{i',j',i,j,k} - \sum_{(i',j') \in Link} J_{i,j,i',j',k} = 0, \quad (i,j) \in OB, k \in \mathcal{K},$$
(1)

$$F_{i,j-1,k} + R_{i-1,j,k} + R_{i-1,j+1,k} - F_{i,j+1,k} - R_{i,j,k} - R_{i,j+1,k} + \sum_{f \in \mathcal{F}} M_{i,j,k,f} - \sum_{p \in \mathcal{P}} N_{i,j,k,p} + \sum_{f \in \mathcal{F}} M_{i,j+1,k,f} - \sum_{p \in \mathcal{P}} N_{i,j+1,k,p} + \sum_{(i',j') \in Link} J_{i',j',i,j,k} - \sum_{(i',j') \in Link} J_{i,j,i',j',k} = 0, \quad (i,j) \in TB, k \in \mathcal{K},$$

$$(2)$$

$$F_{i,j,k} = FP_{i,j,k} - FN_{i,j,k}, \quad i, j \in ActF, k \in \mathcal{K},$$

$$R_{i,j,k} = RP_{i,j,k} - RN_{i,j,k}, \quad (i,j) \in ActR, k \in \mathcal{K},$$
(3)

$$FP_{i,j,k} = y_{i,j,k} \sum_{k' \in \mathcal{K}} FP_{i,j,k'}, \quad (i,j) \in UnFP, k \in \mathcal{K},$$

$$FN_{i,j,k} = y_{i,j+1,k} \sum_{k' \in \mathcal{K}} FN_{i,j,k'}, \quad (i,j) \in UnFN, k \in \mathcal{K},$$

$$RP_{i,j,k} = y_{i,j,k} \sum_{k' \in \mathcal{K}} RP_{i,j,k'}, \quad (i,j) \in UnRP, k \in \mathcal{K},$$

$$RN_{i,j,k} = y_{i-1,j,k} \sum_{k' \in \mathcal{K}} RN_{i,j,k'}, \quad (i,j) \in UnRN, k \in \mathcal{K},$$

(4)

$$N_{i,j,k,p} = y_{i,j,k} \sum_{k' \in \mathcal{K}} N_{i,j,k',p}, \quad (i,j,p) \in ProdB, k \in \mathcal{K},$$
(5)

$$J_{i,j,i',j',k} = y_{i,j,k} \sum_{k' \in \mathcal{K}} J_{i,j,i',j',k'}, \quad (i,j,i',j') \in Link, k \in \mathcal{K},$$

$$(6)$$

$$y_{k,p}^{\min,prod} \sum_{i,j,k,p} N_{i,j,k,p} \le \sum_{i,j,p} N_{i,j,k,p}, \quad (i,j,p) \in ProdB, (k,p) \in KP,$$

$$\tag{7}$$

$$\sum_{k \in \mathcal{K}} y_{i,j,k} = 1, \quad (i,j) \in ActB,$$
(8)

$$y_{i,j,k=IL} = 0, \ (i,j) \in VB \tag{9}$$

$$EF_{i,j-1} + ER_{i-1,j} - EF_{i,j} - ER_{i,j} + EJ_{i,j}^{f} - EJ_{i,j}^{p} + EM_{i,j} - EN_{i,j} + W_{i,j}^{comp} - W_{i,j}^{exp} + W_{i,j}^{pump} - W_{i,j}^{val} + Q_{i,j}^{h} - Q_{i,j}^{c} = 0, \quad (i,j) \in OB,$$
(10)

$$EF_{i,j-1} + ER_{i-1,j} - EF_{i,j+1} + ER_{i-1,j+1} - ER_{i,j+1} - ER_{i+1,j+1} + EJ_{i,j}^{f}$$

- $EJ_{i,j}^{p} + EJ_{i,j+1}^{f} - EJ_{i,j+1}^{p} + EM_{i,j} - EN_{i,j} + EM_{i,j+1}$
- $EN_{i,j+1} + Q_{i,j}^{h} - Q_{i,j}^{c} + Q_{i,j+1}^{h} - Q_{i,j+1}^{c} = 0, \quad (i,j) \in TB,$
(11)

$$Q_{i,j}^{h} = \sum_{(i',j')\in Hx} q_{i'j',i,j}^{hex}, \quad (i,j)\in CB, \quad Q_{i,j}^{c} = \sum_{(i',j')\in Hx} q_{i,j,i',j'}^{hex}, \quad (i,j)\in HB,$$
(12)

To reduce the model complexity, depending on the number of blocks, we dissect the overall The motivation arises from the fact that, all the associated material balance in two parts. phenomena in extractive distillation representation require either one or two blocks. Here, Eq. 1 denotes material balance constraints for a single block whereas, Eq. 2 denotes material balance constraints for two blocks. Set, OB and TB defines all (i, j) positions of one block and two blocks, respectively. In other words, TB constitutes all blocks where the VLE relationship holds in the distillation column. In the material balances, intra-block streams are denoted by $F_{i,j,k}$ and $R_{i,j,k}$. where $F_{i,j,k}$ = flow between horizontal block pairs, and $R_{i,j,k}$ = flow between vertical block pairs. Introduction of fresh feed and withdrawal of product from each block are denoted as $M_{i,j,k,f}$ and $N_{i,j,k,p}$, respectively. Additionally, to increase the connectivity between the non-adjacent blocks we allow "jump stream" which is denoted by $J_{i,j,i',j',k}$. Here, set $Link_{i,j,i',j',k}$ connects block $B_{i,j}$ and $B_{i',j'}$ and thus allows flow from block $B_{i,j}$ to block $B_{i',j'}$. Note that we allow jump connection between selected block pairs to reduce the model size. Eq. 3 calculates the horizontal $(F_{i,i,k})$ and vertical $(R_{i,j,k})$ intra-block flow rates. The blocks where these equations are active are defined by sets ActF and ActR, respectively. Here, $FP_{i,j,k}$ $(RP_{i,j,k})$ defines the flow rate from left (top) block, $B_{i,j}$ ($B_{i,j}$) to right (bottom) block $B_{i,j+1}$ ($B_{i+1,j}$). Conversely, $FN_{i,j,k}$ ($RN_{i,j,k}$) defines the flow rate from right (bottom) block, $B_{i,j+1}$ ($B_{i+1,j}$) to left (top) block $B_{i,j}$ ($B_{i,j}$). As mentioned before, when a stream passes through a unrestricted boundary, it does not experience any change in composition. This is ensured by Eq. 4, where, sets UnFP, UnFN, UnRP, and UnRN define the blocks where the flow variables $FP_{i,j,k}$, $FN_{i,j,k}$, $RP_{i,j,k}$, and $RN_{i,j,k}$ are allowed, respectively. Similar to unrestricted flow, product streams and jump streams also have the same composition of the source block. Therefore, for these two streams we write Eqs. 5 and 6, respectively. Here,

set ProdB = the set that connects product stream p to block (i, j) from where it leaves the superstructure. Eq. 7 ensures the minimum purity for each product stream, where $y_{k,p}^{min,prod}$ = parameter that defines the minimum purity requirement for component k in product stream p and KP = set that connects component k to product stream p. The summation of all the associated component mole fractions has to be equal to one in all the active blocks. Eq. 8 ensures this constraint, whereas ActB denotes all the active blocks in the superstructure. The benefit of having the ActB is that it reduces the number of required blocks significantly. One important thing to be noted here is that, all other sets of blocks are subsets of ActB. Because of the negligible vapor pressure of IL, we assumed that no IL goes to the vapor phase (Eq. 9). Here, set VB denotes the vapor blocks.

Similar to mass balance constraint, energy balance is also written for one block (Eq. 10) and two blocks (Eq. 11). Here, $EF_{i,j}$ and $ER_{i,j}$ denote the enthalpies of horizontal and vertical streams, respectively. Enthalpies of the jump inlet, jump outlet, fresh feed, and product streams are denoted by $EJ_{i,j}^f$, $EJ_{i,j}^p$, $EM_{i,j}$, and $EN_{i,j}$, respectively. $W_{i,j}^{comp}$ and $W_{i,j}^{pump}$ denote the compression and pump work, respectively, wheres $W_{i,j}^{exp}$ and $W_{i,j}^{val}$ represent the expansion and valve work, respectively. Finally, external hot and cold utility requirement are denoted by $Q_{i,j}^h$ and $Q_{i,j}^c$, respectively. Eq. 12 represent the heat integration model where $q_{i,j,i',j'}^{hex}$ is the amount of heat energy that flows from a hot block $B_{i',j'}$ to a cold block $B_{i,j}$. Set $Hx_{i,j,i',j'}$ connects the hot (denoted by set HB) and cold (denoted by set CB) block pairs and allows heat flow.

2.3 Phenomena Models

As mentioned earlier, VLE is the predominant thermodynamic phenomena that occur in an ED unit. Hence, the phenomena model tab of SPICE_ED has detailed VLE model that gives reliable solubility prediction of refrigerants in IL. In this study we employ Gamma-Phi based model to predict the solubility. We also consider the VLE relationships between refrigerants. The overall model is summarized as follows:

$$y_{i,j,k}P_{i,j} = y_{i,j+1,k}P_{i,j,k}^{sat}, \quad (i,j) \in VLE^{ref}, k \in \mathcal{K}^{ref}, (s,m) \in Equil,$$

$$(13)$$

$$y_{i,j,k}\Phi_{i,j,k}P_{i,j} = y_{i,j+1,k}\gamma_{i,j+1,k}P_{i,j,k}^{sat}, \ (i,j) \in VLE^{IL}, k \in \mathcal{K}^{ref}, (s,m) \in Equil,$$
(14)

$$\Phi_{i,j,k} = \exp \frac{(B_{i,j,k} - (1 - \alpha_{k,k''})V_{i,j,k''})(P_{i,j} - P_{i,j,k}^{sat})}{RT_{i,j}},$$

$$(i,j) \in VLE^{IL}, k \in \mathcal{K}^{ref}, k'' \in \mathcal{K}^{IL},$$
(15)

$$\ln \gamma_{i,j+1,k} = (y_{i,j+1,k''})^2 \left[\tau_k^{21} \left(\frac{G_k^{21}}{y_{i,j+1,k} + y_{i,j+1,k''} G_k^{21}} \right)^2 + \frac{\tau_k^{12} G_k^{12}}{(y_{i,j+1,k''} + y_{i,j+1,k} G_k^{12})^2} \right],$$
(16)
$$(i,j) \in VLE^{IL}, k \in \mathcal{K}^{ref}, k'' \in \mathcal{K}^{IL},$$

$$P_{i,j} \ge P_{i,j}^{bub}, \quad (i,j) \in LB; \quad P_{i,j} \le P_{i,j}^{dew}, \quad (i,j) \in VB,$$

$$(17)$$

$$P_{i,j}^{bub} = \sum_{k \in \mathcal{K}} y_{i,j,k} P_{i,j,k}^{sat}, \quad (i,j) \in LB, \quad P_{i,j}^{dew} = \frac{1}{\sum_{k \in \mathcal{K}} \frac{y_{i,j,k}}{P_{i,j,k}^{sat}}}, \quad (i,j) \in VB$$
(18)

The VLE relationship between refrigerants are modeled by Eq. 13, where $P_{i,j,k}^{sat}$ = saturation pressure of component k, which is determined by Antoine equation. If, however, IL is present in the system, the solubility of refrigerant in IL is expressed through the Gamma-Phi equation (see Eq. 14). Here, fugacity coefficient, $\Phi_{i,j,k}$ accounts for the vapor phase nonideality, whereas activity coefficient, $\gamma_{i,j,k}$ accounts for the liquid phase nonideality in block (i, j) for component k, respectively. The sets VLE^{ref} and VLE^{IL} are the set that defines the vapor blocks of the VLE block pairs, where VLE separation are allowed. Set Equil relates separation phenomena $s = \{VLPC\}$ to enabling material $m = \{VLI\}$, where VLPC stands for vapor liquid phase contact and VLI stands for vapor liquid interface. Eq. 15 estimates the fugacity coefficient of the refrigerants, where, $B_{i,j,k}$ is the second virial coefficient of the refrigerants at the system temperature $T_{i,j}$, $V_{i,j,k''}$ is the molar liquid volume of the IL at the system temperature $T_{i,j}$, $\alpha_{k,k''}$ is an unique temperature depended constant for each binary system (refrigerant/IL), and R is universal gas constant. Sets \mathcal{K}^{ref} and \mathcal{K}^{IL} are the subsets of set k that defines refrigerants and ILs, respectively. Shiflett and Yokozeki²³ reported the $\alpha_{k,k''}$ value for several binary mixtures. For R-32/[bmim][PF₆] binary mixture $\alpha_{k,k''}$ is 0.756. For R-125/[bmim][PF₆] mixture it is 0.531. See the Supporting Information (Section S2) for the temperature dependent correlation of $V_{i,j,k''}$. We employ NRTL model to estimate the liquid phase activity coefficient by Eq. 16. Here, τ_k^{12} and τ_k^{21} are binary interaction parameters that dictate the solubility of refrigerants in the IL. Eq. 17 checks consistency in phases by enforcing the pressure of liquid and vapor blocks to lie above the bubble $(P_{i,j}^{bub})$ pressure, and below the bubble pressure, respectively. Here, set LB denotes the liquid phase blocks. Eq. 18 determines the bubble and dew pressures of the mixture.

2.4 Thermodynamic Property Models

Along with the fundamental mass and energy balance and phenomena models, thermodynamic properties of associated components also play a key role in ensuring a reliable design. Since, in this work, we focus on energy intensive distillation/ED operation, it is of utmost importance to employ a reliable thermodynamic model that can accurately capture the properties of the associated components. However, such models are in general, highly non-linear and non-convex. Therefore, employing such complex models in an optimization framework such as SPICE_ED, would significantly increase the model complexity. To circumvent this issue, we employ data driven surrogate models to estimate the properties with sufficient accuracy. As a result, the model complexity becomes tractable without hampering the prediction accuracy.

We estimate the saturation pressure $P_{i,j,k}^{sat}$ of the refrigerants based on Antoine equation as

follows:

$$P_{i,j,k}^{sat} = \exp\left(A_k^{ant} - \frac{B_k^{ant}}{T_{i,j} + C_k^{ant}}\right), \quad (i,j) \in ActB, k \in \mathcal{K}^{ref},\tag{19}$$

The second virial coefficient $(B_{i,j,k})$ of the refrigerants are obtained from Yokozeki et al.⁶² and then fitted to a polynomial function as follows:

$$B_{i,j,k} = B_k^a T_{i,j}^2 + B_k^b T_{i,j} + B_k^c, \quad (i,j) \in VLE^{IL}, k \in \mathcal{K}^{ref},$$
(20)

The specific enthalpies of the IL is estimated as a linear function of the system temperature by the following equation:

$$H_k = H_k^a T_{i,j} + H_k^b, \quad (i,j) \in LB, k \in \mathcal{K}^{IL},$$

$$\tag{21}$$

Specific enthalpy of refrigerants are estimated from Aspen Plus. For vapor phase, it is fitted to a polynomial function as follow:

$$H_{k}^{vap} = H_{k}^{a,vap} T_{i,j}^{2} + H_{k}^{b,vap} T_{i,j} + H_{k}^{c,vap}, \quad (i,j) \in VB, k \in \mathcal{K}^{ref},$$
(22)

However, predicting the liquid phase specific enthalpy of the refrigerants are challenging. The reason being, the functional form of enthalpy is non-smooth with respect to temperature. Hence, we employ piecewise approximation to have a reliable prediction of the liquid phase specific enthalpy. Figure 4 presents both the non-smooth behavior of the actual enthalpy values and the piecewise approximation that we employ in SPICE_ED. In the figure, red triangles represents the actual specific enthalpies obtained from Aspen Plus, wheres green, gray and blue lines are the piecewise approximation. Note that we dissect the whole temperature domain in three segments and have three different surrogate predictions of the enthalpy. Because of this, the prediction accuracy is satisfactory ($R^2 > 0.99$), which can also be seen from the Figure 4. We present the detailed formulation of the piecewise approximation in the Section S1 of the Supporting Information. Additionally, all the parameter values of Eqs. 19–22 are presented in the Supporting Information (Section S2).

2.5 Objective Functions

2.5.1 Energy Consumption

For any separation process, energy consumption is a major design decision that dictates the profitability of the process. Since distillation is well-known to be an energy intensive unit, it is important to consider energy minimization of ED process. The objective function for minimizing the equivalent work (W^{eqv}) consumption is expressed as follows:

$$\min W^{eqv} = \frac{1}{\eta_c} \sum_{(i,j)\in ActB} W^{comp}_{i,j} + \frac{1}{\eta_p} \sum_{(i,j)\in ActB} W^{pump}_{i,j} + \omega \bigg(\sum_{(i,j)\in ActB\setminus CB} Q^h_{i,j} + \sum_{(i,j)\in ActB\setminus HB} Q^c_{i,j} \bigg),$$
(23)



Figure 4: Liquid phase specific enthalpy of R-32 (a) and R-125 (b).

s.t. Eqs. 1-22 and S1-S13

Here, the first two terms estimate the work requirement in the compressor and the pump. η_c and η_p define the respective efficiency. The hot and cold utility consumption are estimated by the third and the fourth term, respectively. Lastly, ω converts the heat energy to equivalent work and is taken as 0.23 by considering a Carnot efficiency of 30% and turbine efficiency of 75%. Similar value of heat to work conversion factor is reported by Fernandez et al.⁶³ and Jung et al.⁶⁴ For compressor, we assume both isentropic and mechanical efficiency to be 80%, while for pump, the efficiencies of pump and motor are considered to be 50% and 90%, respectively. With regard to the constraints, the equation numbers starting with 'S' are reported in the Supporting Information.

2.5.2 Process Sustainability

For any process, along with energy consumption, the sustainability is also an important metric that determines the environmental footprint of the process. Thus, we aim to minimize the CO_2 -eqv emission of the extractive distillation process by the following objective function:

$$\min \beta^{elec} \left(\frac{1}{\eta_c} \sum_{(i,j)\in ActB} W_{i,j}^{comp} + \frac{1}{\eta_p} \sum_{(i,j)\in ActB} W_{i,j}^{pump} \right) + \beta^{hu} \sum_{(i,j)\in ActB\setminus CB} Q_{i,j}^h.$$
(24)

s.t. Eqs. 1-22 and S1-S13

Here, the first two terms estimate the indirect CO_2 -eqv emission that originate from the electricity consumption for operating compressors and pumps. The final term computes the indirect CO_2 -eqv emission for consuming hot utility. Here, β^{elec} is considered to be 116 kg CO_2 -eqv/GJ of electricity,⁶⁵ while β^{hu} is considered to be 38.8 kg CO_2 -eqv/GJ of hot utility.⁶⁶ For most cases, we anticipate a positive relationship between the indirect CO₂-eqv emission and the overall energy consumption. Still, indirect CO₂-eqv emission needs to be considered as a design objective separately, since the sustainable design can differ from the most energy efficient design depending on the relative values of the emission parameters (β^{elec} and β^{hu}).

2.5.3 Process Economics

The economic objective function involves the minimization of the total separation cost (SC) which is formulated as follows:

$$\min SC = \frac{UC^{IL}R_{i=5,j=3,k=IL}}{t^{opt}} + UC^{elec} \left(\frac{1}{\eta_c} \sum_{(i,j)\in ActB} W_{i,j}^{comp} + \frac{1}{\eta_p} \sum_{(i,j)\in ActB} W_{i,j}^{pump} \right) + UC^{hu} \sum_{(i,j)\in ActB\setminus CB} Q_{i,j}^h + UC^{cu} \sum_{(i,j)\in ActB\setminus HB} Q_{i,j}^c + UC^{ref} \sum_{(i,j)\in Cond} Q_{i,j}^c \qquad (25) + \frac{\sigma^{main} \times FCI}{t^{opt}} + \frac{CRF \times FCI}{t^{opt}} FCI = LF \times \left[\sum_{e\in\mathcal{E}} C_e \left(\frac{S_e}{S_e^{ref}} \right)^{n_e} \frac{I_{2020}}{I_e^{ref}} \right] \qquad (26)$$

s.t. Eqs. 1–22 and S1–S34

Here, the cost of the IL is estimated by the first term. IL is considered to be fully replaced every year and t^{opt} is the annual operating time in seconds considering 8000 hrs of annual operation. The second and third term estimate the cost due to the electricity consumption in the compressors and the pumps, respectively. The hot and cold utility costs are defined by the fourth and fifth term. The sixth term estimates the refrigeration cost in the condenser of the ED column. As the temperature of the condenser in the ED column is lower⁶⁷ than the ambient temperature, cooling water is not sufficient to supply the required cooling. Thus, we consider that the cooling requirement in the condenser is supplied by refrigerant. Set Cond is the set of blocks that denotes condenser. UC^{IL} , UC^{elec} , UC^{hu} , UC^{cu} , and UC^{ref} are the unit cost of IL, electricity, hot utility, cold utility, and refrigerant, respectively. We consider IL cost, electricity, hot utility, cold utility, and refrigerant cost to be $1000/kg^{68}$ $19.4/GJ^{57}$ $9.9/GJ^{57}$ $1.9/GJ^{61}$ and $18/GJ^{69}$ respectively. In the seventh term, the parameter σ^{main} is used to estimate the annual maintenance cost as a percentage of the fixed capital investment (FCI). In this study we consider σ^{main} to be 7.5%. In the eighth term, CRF stands for capital recovery factor and is used to estimate the annual contribution of the FCI. CRF is estimated by considering 10% interest rate and 10 years of plant life. The FCI is estimated by Eq. 26 from the total equipment purchase cost. To estimate the total installed cost of the process, lang factor (LF) is considered. In this study we consider LF to be 4.74. The purchase cost of equipment e is estimated from the followings: reference installation cost (C_e) , scaling parameter (S_e) , reference size (S_e^{ref}) , scaling factor (n_e) , Chemical Engineering Plant Cost Index (CEPCI) of year 2020 (I_{2020}), and reference year of the installation cost (I_e^{ref}). Here, I_{2020} is taken as 668⁷⁰ and I_e^{ref} is obtained from http://www.chemengonline.com/pci. The equipment set \mathcal{E} contains all the associated equipments, such as distillation column (conventional and extractive), stripping column, condenser, re-boiler, cooler, heater, heat exchanger, compressor, pump, vacuum pump, and flash separator. The detailed formulation of the equipment purchase cost function are provided in Section S4 in the Supporting Information, while the cost parameters are presented in Table 1.

Equipment	Reference purchase $\cot C_e$ (\$)	Scaling factor n_e	Reference size S_e^{ref}	Scaling parameter S_e
Distillation $column^{71}$	100000	0.81	20	Height \times diameter ^{1.5} (m ^{2.5})
Distillation trays 71	3000	0.80	2.13	Diameter (m)
Heater, cooler, condenser, re-boiler and heat exchanger 71	70000	0.71	100	Heat transfer area (m^2)
$\rm Compressor^{71}$	1350000	0.90	1000	Power requirement (kW)
Vacuum pump ⁷¹	27000	0.88	10	Power requirement (kW)
$Pump^{71}$	25000	0.59	5	Power requirement (kW)
Flash separator 72	2860	0.80	1	Feed flow rate (kg s ⁻¹)

 Table 1: Capital Cost Parameters and Scaling Factors.

2.5.4 Multiobjective Optimization

Energy minimization, emission reduction and cost minimization, when considered independently as design objectives, may lead to process designs that lie at extreme regions of the operability window. Hence, with a view to simultaneously capturing the effect of economics and cost aspects, we perform ϵ -constraint based multiobjective optimization. The goal is to select equally good designs that are both cost effective and energy efficient at the same time. We formulate multiobjective optimization as an ϵ -constrained optimization problem as follows:

min
$$W^{eqv}$$
 (27)

s.t.
$$SC \le \epsilon$$
 (28)

Eqs. 1-22, 23, 25-26, and S1-S34

Here the objective function minimizes the equivalent work of the process, while Eq. 28 is the ϵ -constraint on the separation cost. We vary ϵ to take different values to generate different points on the Pareto front.

With all the constraints discussed above, the goal is to select: (i) the optimal design variables of the ED column, e.g., number of trays, reflux ratio, refrigerant and IL entry stage, (ii) the most appropriate IL regeneration unit (single flash/double flash/stripping column/distillation column), in such a manner that the most optimal process for the ED-based separation of R-410A could be identified.

3 Base-Case Design and Model Validation

We start by considering a previously reported ⁶⁷ process configuration as the base design (Figure 5), and further optimize it. We consider [bmim][PF₆] as the solvent, which is an IL considered for R-410A separation. The values in Figure 5 colored in green are fixed variables, i.e., the same as was in Shiflett and Yokozeki,⁶⁷ whereas all the other variables are for further optimization. To achieve better separation, the feed to the ED column should be in the liquid phase.⁴⁸ However, the experimental solubility data is only available up to 10 bar.²⁴ Therefore, to achieve reliable design, we consider the maximum pressure of the ED column to be 10 bar. The feed R-410A is available at 1 bar and 298.15 K, which can be further compressed before feeding to the ED column. R-32, being more soluble in [bmim][PF₆], leaves the column with the IL at the bottom. R-125 is separated as distillate from the top. The bottom flow rate of the ED column (rich IL) goes to the two sequential flash separators for regeneration. For the base case, the flash separator is pumped, cooled and afterwards sent back to the ED column.

For the base case, we consider a subset of the original superstructure (Figure 5). Specifically, we omit the consideration of SC and CD and consider a 30×4 superstructure. Here we position the ED unit in the first two columns (j = 1 and j = 2). The blocks in the first column (j = 1)are vapor blocks and represent the vapor phase inside the ED column. On the other hand, the blocks in the second column (j = 2) represent the liquid phase of the ED column. Blocks $B_{1,1}$ and $B_{1,2}$ represent the total condenser and blocks $B_{30,1}$ and $B_{30,2}$ represent the partial re-boiler. Therefore, the 28 equilibrium stages of the ED column are represented by blocks from row i = 2to row i = 29. The VLE phase boundary is depicted by the vertical green line. The refrigerant mixture R-410A enters as feed at block $B_{1,3}$. Blocks $B_{1,3}$ to $B_{6,3}$ (vertical white blocks in third column) are the feed compression blocks where R-410A is compressed to the operating pressure of the ED column (i.e., 10 bar). The compressed R-410A from block $B_{6,3}$ enters the ED column at block $B_{22,1}$ as jump inlet. The liquid IL enters the liquid block of ED column at block $B_{3,2}$. After separation, the distillate product is taken out as product P1 from the condenser block $B_{1,2}$, where the rich IL leaves the ED column from block $B_{30,2}$ towards the two flash separators. Block pair $B_{29,3}$ and $B_{29,4}$ represent the first flash separator (Flash 1), from where the R-32 rich product leaves as vapor product (product stream P2 from block $B_{29,3}$). The second flash separator (Flash 2) operating at vacuum condition is presented by block $B_{27,3}$ (vapor block) and $B_{27,4}$ (liquid block). The pump symbol with product stream P3 represent the vacuum pump which is necessary to create the vacuum operation. After regeneration, the IL is pumped to the operating pressure of the ED column at block $B_{26,3}$ and cooled at block $B_{25,3}$. Then from block $B_{25,4}$ the IL leaves as jump outlet and enters at block $B_{3,2}$ as jump inlet.

With this superstructure, we evaluate and improve the base design for energy minimization while achieving at least 99.5 wt% purity for both R-125 rich product (distillate) and R-32 rich product (combined vapors from the two flash separators). Our results show that the overall process has equivalent work consumption of 659 kJ/kg R-410A, emission of 0.058 kg CO₂-eqv/kg, and a separation cost of \$0.081/kg R-410A. Interestingly, Shiflett and Yokozeki⁶⁷ reported a total heat duty of 652 kJ/s for 0.3 kg/s R-410A. This converts to $0.23 \times 652/0.3 = 500$ kJ/kg of equivalent work for heat duty alone. While they did not report the energy consumption in the compressor and the vacuum pump, they are about 145 kJ/kg and 11 kJ/kg, respectively. Therefore, the total energy consumption is about 656 kJ/kg R-410A, which is comparable to the energy consumption that SPICE_ED reports for the same design and operating conditions.



Figure 5: Base design for extractive distillation of R-410A with $[bmim][PF_6]$ as solvent; classical process representation shown in the left and the equivalent building block-based representation shown in the right.

To establish confidence and validate the models used in SPICE_ED, we perform process simulation in Aspen Plus with the pure component physical properties listed in Table 2. We use the same thermodynamic models as employed by Shiflett and Yokozeki,⁶⁷ to ensure that the IL molar volume is temperature dependent. While modeling the solubility in Aspen Plus, the molar liquid volume is assumed to be constant. Moreover, the binary system specific parameter ($\alpha_{k,k''}$) is not required.

Because of differences in property definition, solubility modeling in Aspen Plus using the exact Gamma-Phi parameters leads to solubility isotherms that deviate from the experimental solubility,

Table 2: Physical Properties for [bmim][PF₆].⁴⁸

Property	Correlation	A	В	C
$\rho \; (\mathrm{kg.m^{-3}})$	$A + B \times T$	1609.4	-0.8181	0
$\mu~({\rm mPa.s})$	$A\exp(B/T) + C$	5.271×10^{-6}	5228.5	0
$c_p (\mathrm{J.K^{-1}.mol^{-1}})$	$A+B\times T+C\times T^2$	124.44	1.2403	-9.612×10^{-4}
$\sigma~({\rm mN.m^{-1}})$	$A + B \times T$	63.552	-0.06773	0

as shown in Figure 6. Note that the solubility in NRTL model is modeled by mainly the binary interaction parameters (defined in Eq. 16) as follows: $G_k^{12} = \exp(\lambda \tau_k^{12})$ and $G_k^{21} = \exp(\lambda \tau_k^{21})$, where $\tau_k^{12} = \tau_k^{12(0)} + \tau_k^{12(1)}/T$ and $\tau_k^{21} = \tau_k^{21(0)} + \tau_k^{21(1)}/T$. Here, λ is a constant which was set to 0.2 by Shiflett and Yokozeki.²³ In the SPICE_ED, we modeled the solubility using the exact Gamma-Phi parameters. Our solubility prediction is satisfactory with respect to experimental solubility (dashed blue lines in Figure 6). To ensure that the solubility behavior is sufficiently captured in Aspen Plus, we change the NRTL constant (λ) while employing the same binary interaction parameters as presented in Table 3. The changed NRTL constants for the simulations in Aspen Plus are $\lambda = 0.3625$ and $\lambda = 0.3275$ for R-32/[bmim][PF₆] and R-125/[bmim][PF₆] binary systems, respectively. The solubility with the changed λ in Aspen Plus is presented by the green solid lines in Figure 6. As shown in Table 4, the SPICE_ED based process simulation is very similar to the simulation in Aspen Plus. The maximum deviation is 7%, which is within a reasonable limit. Since the ED column is of our primary interest, we further verify the temperature profile between the SPICE_ED results and the Aspen Plus results, and observe excellent match as shown in Figure 7.

 Table 3: NRTL Parameters for Refrigerant/Ionic Liquid Binary Mixtures.²³

System $(1)/(2)$	$\tau_k^{12(0)}$	$\tau_k^{12(1)}(K)$	$\tau_k^{21(0)}$	$\tau_k^{21(1)}(K)$
$ m R-32/[bmim][PF_6]$	4.4080	-565.89	-1.0275	-199.06
$\operatorname{R-125/[bmim][PF_6]}$	2.7880	-78.28	1.2041	-422.79

4 Process Synthesis and Optimization

After establishing a base case in the previous section, we now focus on generating new and fully optimized designs. To allow SPICE_ED to come up with fully optimized design configurations, we now relax all the decision variables to take their optimized values for 100 kg/hr of refrigerant R-410A. Furthermore, we enforce the minimum separation purity of both R-125 and R-32 to be



Figure 6: Solubility isotherms of R-32 (a) and R-125 (b) in ionic liquid $[bmim][PF_6]$. Here, the experimental solubilities are shown by black circles, whereas the solubility prediction by the original NRTL model in Aspen Plus is shown by the red dashed lines. The dashed blue lines represent the solubility predictions in SPICE_ED and the green solid lines represent the corrected solubility predictions in Aspen Plus.



Figure 7: Comparison between Aspen Plus and SPICE_ED temperature profiles of the base-case extractive distillation column.

99.5 wt%. The pressure of each block in the superstructure is bounded between 0.1 bar to 15 bar. To ensure a reliable solution that conforms with the experimental data, we enforce the partial pressure of the refrigerants (R-32 and R-125) in the vapor phase to be less than 10 bar by imposing $y_{i,j,k}P_{i,j} \leq 10$, $(i,j) \in VB$, $k \in \mathcal{K}^{ref}$. Lastly, the temperature of the entire superstructure is allowed to vary between 273 K to 500 K.

The overall MINLP model size depends on the number of blocks used to represent the columns

	Aspen Plus	SPICE_ED	Gap (%)
Feed compressor (kW)	4.0	4.0	0
Condenser temperature (K)	286.4	287.5	-0.4
Condenser duty (kW)	-0.49	-0.48	3.5
Re-boiler temperature (K)	367.3	367.5	-0.1
Re-boiler duty (kW)	5.8	6.2	-7.1
Distillate purity			
R-125 (wt $\%$)	99.41	99.50	-0.1
Bottom flow rate (kg/h)	1267.0	1267.0	0
Bottom purity			
R-32 (wt%)	4.0	4.0	0
IL (wt%)	96.0	96.0	0
Flash 1			
Vapor flow rate (kg/h)	45.0	45.7	-1.5
R-32 purity (wt%)	99.45	99.47	0
Flash 2			
Vapor flow rate (kg/h)	4.47	4.30	3.9
R-32 purity (wt%)	99.8	99.8	0
Vacuum pump work (kW)	0.3	0.3	0
IL recycle pump work (kW)	0.5	0.5	0
IL recycle cooler duty (kW)	-7.1	-6.8	5.5

Table 4: Comparison Between Aspen Plus and SPICE_ED.

(ED, SC, and CD). The continuous variables vary between 1573 to 3522, the binary variables vary between 79 to 184, and the number of constraints vary between 2268 to 6643. We solve the MINLP problem in GAMS 35.1 environment using ANTIGONE⁷³ as the global solver.

4.1 Minimization of Energy Consumption and Equivalent CO₂ Emission

We optimize the entire superstructure under the design objective of minimizing equivalent work consumption. Under this objective, the optimized design (Figure 8a) requires 338.2 kJ/kg R-410A which is a 48.7% improvement over the base-design. The identical design is obtained under the objective of minimizing CO₂-eqv emission for which the emission is 47.2 % lower than the base design.

The optimized configurations has a higher number of separation stages compared to the base design (47 vs 28 trays). As a result, the quality of separation improves, and the required purity is

achieved. We observe that the column operates at a slightly lower pressure (9.6 bar) than the base design. The improved energy efficiency is mainly due to the heat integration between the re-boiler and the IL recycle cooler. As a result, no external hot utility is consumed by the re-boiler. Also, only 26% of the cooling duty of the recycling IL is provided by the external cooling utility.



Figure 8: Optimal process configurations for (a) minimum equivalent work consumption and minimum CO₂-eqv emission, and (b) minimum separation cost. We also show (c) Pareto optimal process configuration and (d) Pareto space to elucidate the trade-offs between the separation cost and the equivalent work consumption. Points a and b correspond to the most energy efficient and the most economic designs, respectively, whereas point c corresponds to the Pareto optimal design.

4.2 Minimization of Separation Cost

In many cases, the effectiveness and applicability of separation process depend on the overall cost of separation. To that end, we have performed further optimization studies to achieve designs with minimum cost for R-410A separation. For this, we set the separation cost as the objective function. We observe that the total separation cost is largely dependent on the capital investment than the operating cost. For instance, in the base design, the operating and the investment costs contribute equally (approximately 50% each). However, in the energy optimum design, the capital investment becomes 63% of the overall separation cost. This further proves that the separation cost becomes more sensitive to the cost of ED column.

Since the cost of the ED column largely depends on the number of stages, it is intuitive that the SPICE_ED framework under the objective of minimizing cost, proposes design with a lower number of stages (see Figure 8b) than the other design (Figure 8a). For instance, the optimal cost-effective ED column requires 18 trays to achieve the required purity with a separation cost of 0.059/kg R-410A. Due to a lower number of stages, i) the energy consumption and the emission increase which are 394.1 kJ/kg R-410A and 0.036 kg CO₂-eqv/kg R-410A, respectively; ii) higher flow rate of IL is required (19% higher than the base design); ii) ED column operates at the maximum allowable pressure of 10 bar. SPICE_ED, in this case proposes heat integration as well, due to which only 30% of the re-boiler duty is required to be provided by the external hot utility.

4.3 Pareto Optimal Process

To capture the trade-offs between the energy efficiency and the process economics, we perform multiobjective optimization (Figure 8d). We solve a set of optimization problems where the goal is to minimize the energy consumption of the process subject to an ϵ -constrained separation cost. We observe that, as the separation cost is varied, the Pareto front essentially becomes vertical indicating the negligible decrease in energy consumption with the increase of separation cost after reaching a certain threshold. The trade-offs are more prominent with the stricter economic constraints i.e., lower separation cost. Stricter economic constraints lead to a larger energy requirement as it enforces lesser number of separation trays to be used. For example, after the point c in Figure 8d, the reduction in energy consumption becomes less than 1% as the constraints on cost are relaxed. The flowsheet pertaining to the point c is shown in Figure 8c which has an energy consumption of 345.7 kJ/kg R-410A, emission of 0.031 kg CO₂-eqv/kg R-410A, and separation cost of \$0.071/kg R-410A.

Interestingly, both of the flash separators are selected for all cases for solvent regeneration. For efficient use of IL-based solvent, the IL needs to be sufficiently regenerated ($\geq 99.9 \text{ wt\%}$ purity), which requires the regeneration pressure to be at least 0.2 bar or less in the flash separators. To operate in such subatmospheric pressure, vacuum pump is required. As the power consumption and cost of a vacuum pump depend on the flow rate, when only one flash is selected, all the

bottom product from the ED column would be fed to the flash. Hence, the power consumption would increase. For this reason, we observe that the bottom of ED product is first fed to Flash 1 (operating at 1 bar) that separates around 92% of the R-32. Flash 2 is then used for separating the remaining 8% of the R-32 from the IL.

The selection of any stripping/distillation column would lead to the IL being stripped/distilled at higher temperatures. This would require a large amount of heat duty which would directly contribute to the CO₂-eqv emission and operating cost. For this reason, the SPICE_ED considers both of the flash separators and also avoids the stripping and distillation columns. This result regarding the avoidance of stripping column conforms with previous observations.⁴⁸

To summarize, SPICE_ED offers the flexibility to choose between any one of the proposed designs (see Figures 8a, 8b and 8c) with each providing significant improvement over the base design in terms of energy consumption, sustainability and cost.

4.4 Sensitivity Analysis

We perform sensitivity analysis to investigate the impact of the variabilities in raw materials, utility prices and equipment purchase prices on the overall separation cost. Figure 9a shows the percentage deviation from the nominal separation cost as the IL and utility prices are varied between -50% to +50% of the nominal price. The percent deviation exhibits essentially linear relationship. Since the hot utility and the electricity prices have the major contributions to the operating cost, these two exhibit the largest deviations from the nominal cost. Figure 9b shows the sensitivity of the separation cost with respect to the variation of the equipment purchase price (\pm 50% around the nominal price). Since the overall design objective is to minimize the cost, SPICE_ED selects the feasible number of trays that mostly reduces the operating costs. As a result, the sensitivity exhibits concave response at lower ED column prices. On the other hand, at a greater than nominal price of the ED column, SPICE_ED selects the minimum required trays to attain the separation purity. As a result, the overall separation cost increases linearly with the price of the ED column.



Figure 9: Sensitivity of the separation cost with respect to the variation of (a) IL and utility prices and (b) equipment purchase prices.

5 Conclusions

Due to high global warming potential of HFCs, it is imperative to ensure their minimum usage and maximum recyclability. Ionic liquids show promise as a solvent for selective separation of HFC mixtures using extractive distillation. There can be many different process configurations to perform the same separation task. In this work, we put forward a systematic approach and a design framework SPICE_ED for optimal flowsheeting of the R-410A separation process. The framework considered phenomena level design, and was able to identify innovative process configurations achieving significant improvement. We were also able to establish confidence on the new designs based on rigorous process simulation performed in commercial simulator such as Aspen Plus. To the best of our knowledge, this is the first study on R-410A separation that takes energy minimization, sustainability goals, economic objective and multiobjective optimization into account. Our solubility modeling was based on the Gamma-Phi approach. Since the accuracy of the process models is dictated by the rigorousness of the thermodynamic models, one can employ EoS-based solubility models (e.g., Peng-Robinson or RK) to obtain a more realistic process performance prediction at a higher computational time. To that end, data-driven approach⁷⁴ offers exciting prospect to achieve optimal solutions fast, while maintaining the predictive capability of such rigorous models. Also, rather than using the equilibrium based model, one can use rate-based models considering transport properties with appropriate mass transfer-coefficient, viscosity and other thermophysical properties (e.g. conductivity). The separation performance can also vary depending on the selection of the ionic liquid. Further work is necessary to screen the optimal ionic liquid for separating refrigerant mixtures. To that end, SPICE_ED can be used in its current form to identify the properties of a hypothetical ionic liquid that, if discovered, would improve the energy consumption and cost performance of the separation process in the most optimal way. This can be done by optimizing the process configurations and material properties simultaneously. This is a fascinating direction in the areas of process and product design, which is still at its nascent stage of development.

Acknowledgement

The authors gratefully acknowledge support from the NSF EFRI DCheM grant 2029354 and the NSF CAREER award CBET-1943479. Part of the research was conducted with the computing resources provided by Texas A&M High Performance Research Computing.

Supporting Information

Piecewise approximation of refrigerant's liquid phase specific enthalpy, physical parameters, building block superstructure for full scale optimization, and equipment capital cost functions. The Supporting Information is available free of charge on the http://pubs.acs.org.

References

- Sicard, A. J.; Baker, R. T. Fluorocarbon Refrigerants and their Syntheses: Past to Present. Chemical Reviews 2020, 120, 9164–9303.
- Purohit, P.; Höglund-Isaksson, L. Global emissions of fluorinated greenhouse gases 2005–2050 with abatement potentials and costs. Atmospheric Chemistry and Physics 2017, 17, 2795–2816.
- [3] Minor, B. H.; Herrmann, D.; Gravell, R. Flammability characteristics of HFO-1234yf. Process Safety Progress 2010, 29, 150–154.
- [4] Pardo, F.; Gutiérrez-Hernández, S. V.; Zarca, G.; Urtiaga, A. Toward the Recycling of Low-GWP Hydrofluorocarbon/Hydrofluoroolefin Refrigerant Mixtures Using Composite Ionic Liquid-Polymer Membranes. ACS Sustainable Chemistry & Engineering 2021, 9, 7012–7021.
- [5] Asensio-Delgado, S.; Pardo, F.; Zarca, G.; Urtiaga, A. Enhanced absorption separation of hydrofluorocarbon/hydrofluoroolefin refrigerant blends using ionic liquids. *Separation and Purification Technology* 2020, 249, 117136.
- [6] McLinden, M. O.; Huber, M. L. (R)Evolution of Refrigerants. Journal of Chemical & Engineering Data 2020, 65, 4176–4193.
- [7] AIM Act. https://www.epa.gov/climate-hfcs-reduction/aim-act (accessed on December 2021).
- [8] Tian, Y.; Demirel, S. E.; Hasan, M. M. F.; Pistikopoulos, E. N. An overview of process systems engineering approaches for process intensification: State of the art. *Chemical Engineering and Processing-Process Intensification* 2018, 133, 160–210.
- [9] Demirel, S. E.; Li, J.; Hasan, M. M. F. Systematic process intensification. Current Opinion in Chemical Engineering 2019, 25, 108–113.
- [10] Tula, A. K.; Eden, M. R.; Gani, R. Computer-aided process intensification: Challenges, trends and opportunities. AIChE Journal 2020, 66, e16819.
- [11] Sitter, S.; Chen, Q.; Grossmann, I. E. An overview of process intensification methods. Current Opinion in Chemical Engineering 2019, 25, 87–94, Nanotechnology: water-energy nexus Process Systems Engineering: process intensification.
- [12] Werner, S.; Haumann, M.; Wasserscheid, P. Ionic Liquids in Chemical Engineering. Annual Review of Chemical and Biomolecular Engineering 2010, 1, 203–230, PMID: 22432579.

- [13] Faúndez, C. A.; Barrientos, L. A.; Valderrama, J. O. Modeling and thermodynamic consistency of solubility data of refrigerants in ionic liquids. International Journal of Refrigeration 2013, 36, 2242–2250.
- [14] Liu, X.; Lv, N.; Su, C.; He, M. Solubilities of R32, R245fa, R227ea and R236fa in a phosphonium-based ionic liquid. Journal of Molecular Liquids 2016, 218, 525–530.
- [15] Liu, X.; Qi, X.; Lv, N.; He, M. Gaseous absorption of fluorinated ethanes by ionic liquids. Fluid Phase Equilibria 2015, 405, 1–6.
- [16] Shiflett, M. B.; Maginn, E. J. The solubility of gases in ionic liquids. AIChE Journal 2017, 63, 4722–4737.
- [17] Minnick, D. L.; Shiflett, M. B. Solubility and Diffusivity of Bromodifluoromethane (Halon-1201) in Imidazolium Ionic Liquids: [C2C1im][Tf2N], [C4C1im][BF4], and [C4C1im][PF6]. Journal of Chemical & Engineering Data 2020, 65, 3277–3286.
- [18] Minnick, D. L.; Shiflett, M. B. Solubility and Diffusivity of Chlorodifluoromethane in Imidazolium Ionic Liquids: [emim][Tf2N], [bmim][BF4], [bmim][PF6], and [emim][TFES]. Industrial & Engineering Chemistry Research 2019, 58, 11072–11081.
- [19] Mellein, B. R.; Scurto, A. M.; Shiflett, M. B. Gas solubility in ionic liquids. Current Opinion in Green and Sustainable Chemistry 2021, 28, 100425.
- [20] Asensio-Delgado, S.; Viar, M.; Pardo, F.; Zarca, G.; Urtiaga, A. Gas solubility and diffusivity of hydrofluorocarbons and hydrofluoroolefins in cyanide-based ionic liquids for the separation of refrigerant mixtures. *Fluid Phase Equilibria* 2021, 549, 113210.
- [21] Asensio-Delgado, S.; Pardo, F.; Zarca, G.; Urtiaga, A. Vapor-Liquid Equilibria and Diffusion Coefficients of Diffuoromethane, 1,1,1,2-Tetrafluoroethane, and 2,3,3,3-Tetrafluoropropene in Low-Viscosity Ionic Liquids. *Journal of Chemical & Engineering Data* 2020, 65, 4242–4251.
- [22] Shiflett, M. B.; Yokozeki, A. Separation of CO2 and H2S using room-temperature ionic liquid [bmim][PF6]. Fluid Phase Equilibria 2010, 294, 105–113, Ionic Liquids Special Issue.
- [23] Shiflett, M. B.; Yokozeki, A. Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. AIChE Journal 2006, 52, 1205–1219.
- [24] Shiflett, M. B.; Harmer, M. A.; Junk, C. P.; Yokozeki, A. Solubility and diffusivity of 1,1,1,2-tetrafluoroethane in room-temperature ionic liquids. *Fluid Phase Equilibria* 2006, 242, 220–232.
- [25] Shiflett, M. B.; Yokozeki, A. Solubility of CO2 in Room Temperature Ionic Liquid [hmim][Tf2N]. The Journal of Physical Chemistry B 2007, 111, 2070–2074.
- [26] Yokozeki, A.; Shiflett, M. B. Global phase behaviors of trifluoromethane in ionic liquid [bmim][PF6]. AIChE Journal 2006, 52, 3952–3957.
- [27] Yokozeki, A.; Shiflett, M. B. Vapor-liquid equilibria of ammonia+ionic liquid mixtures. Applied Energy 2007, 84, 1258–1273.
- [28] Yokozeki, A.; Shiflett, M. B. Separation of Carbon Dioxide and Sulfur Dioxide Gases Using Room-Temperature Ionic Liquid [hmim][Tf2N]. Energy & Fuels 2009, 23, 4701–4708.
- [29] Morais, A. R. C.; Harders, A. N.; Baca, K. R.; Olsen, G. M.; Befort, B. J.; Dowling, A. W.; Maginn, E. J.; Shiflett, M. B. Phase Equilibria, Diffusivities, and Equation of State Modeling of HFC-32 and HFC-125 in Imidazolium-Based Ionic Liquids for the Separation of R-410A. Industrial & Engineering Chemistry Research 2020, 59, 18222–18235.
- [30] Pereiro, A.; Araújo, J.; Esperança, J.; Marrucho, I.; Rebelo, L. Ionic liquids in separations of azeotropic systems A review. The Journal of Chemical Thermodynamics 2012, 46, 2–28.
- [31] Ayuso, M.; Cañada-Barcala, A.; Larriba, M.; Navarro, P.; Delgado-Mellado, N.; García, J.; Rodríguez, F. Enhanced separation of benzene and cyclohexane by homogeneous extractive distillation using ionic liquids as entrainers. *Separation* and Purification Technology 2020, 240, 116583.
- [32] Ayuso, M.; Navarro, P.; Palma, A. M.; Larriba, M.; Delgado-Mellado, N.; García, J.; Rodríguez, F.; Coutinho, J. A.; Carvalho, P. J. Separation of benzene from methylcycloalkanes by extractive distillation with cyano-based ionic liquids: Experimental and CPA EoS modelling. *Separation and Purification Technology* **2020**, 234, 116128.
- [33] Navarro, P.; Ovejero-Pérez, A.; Ayuso, M.; Delgado-Mellado, N.; Larriba, M.; García, J.; Rodríguez, F. Cyclohexane/cyclohexene separation by extractive distillation with cyano-based ionic liquids. *Journal of Molecular Liquids* 2019, 289, 111120.

- [34] Navarro, P.; Ayuso, M.; Palma, A. M.; Larriba, M.; Delgado-Mellado, N.; García, J.; Rodríguez, F.; Coutinho, J. A. P.; Carvalho, P. J. Toluene/n-Heptane Separation by Extractive Distillation with Tricyanomethanide-Based Ionic Liquids: Experimental and CPA EoS Modeling. *Industrial & Engineering Chemistry Research* 2018, 57, 14242–14253.
- [35] Navarro, P.; de Dios-García, I.; Larriba, M.; Delgado-Mellado, N.; Ayuso, M.; Moreno, D.; Palomar, J.; García, J.; Rodríguez, F. Dearomatization of pyrolysis gasoline by extractive distillation with 1-ethyl-3-methylimidazolium tricyanomethanide. *Fuel Processing Technology* **2019**, 195, 106156.
- [36] Li, W.; Xu, B.; Lei, Z.; Dai, C. Separation of benzene and cyclohexane by extractive distillation intensified with ionic liquid. *Chemical Engineering and Processing - Process Intensification* 2018, 126, 81–89.
- [37] Díaz, I.; Palomar, J.; Rodríguez, M.; de Riva, J.; Ferro, V.; González, E. J. Ionic liquids as entrainers for the separation of aromatic-aliphatic hydrocarbon mixtures by extractive distillation. *Chemical Engineering Research and Design* 2016, 115, 382–393.
- [38] Zhu, Z.; Ri, Y.; Li, M.; Jia, H.; Wang, Y.; Wang, Y. Extractive distillation for ethanol dehydration using imidazolium-based ionic liquids as solvents. *Chemical Engineering and Processing - Process Intensification* 2016, 109, 190–198.
- [39] Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids. AIChE Journal 2004, 50, 2439–2454.
- [40] Aniya, V.; De, D.; Satyavathi, B. Comprehensive Approach toward Dehydration of tert-Butyl Alcohol by Extractive Distillation: Entrainer Selection, Thermodynamic Modeling and Process Optimization. Industrial & Engineering Chemistry Research 2016, 55, 6982–6995.
- [41] Chen, H.-H.; Chen, M.-K.; Chen, B.-C.; Chien, I.-L. Critical Assessment of Using an Ionic Liquid as Entrainer via Extractive Distillation. Industrial & Engineering Chemistry Research 2017, 56, 7768–7782.
- [42] Wu, L.; Wu, L.; Liu, Y.; Guo, X.; Hu, Y.; Cao, R.; Pu, X.; Wang, X. Conceptual design for the extractive distillation of cyclopentane and neohexane using a mixture of N,N-dimethyl formamide and ionic liquid as the solvent. *Chemical Engineering Research and Design* 2018, 129, 197–208.
- [43] Song, Z.; Li, X.; Chao, H.; Mo, F.; Zhou, T.; Cheng, H.; Chen, L.; Qi, Z. Computer-aided ionic liquid design for alkane/cycloalkane extractive distillation process. *Green Energy Environment* 2019, 4, 154–165.
- [44] Zhu, Z.; Ri, Y.; Jia, H.; Li, X.; Wang, Y.; Wang, Y. Process evaluation on the separation of ethyl acetate and ethanol using extractive distillation with ionic liquid. Separation and Purification Technology 2017, 181, 44–52.
- [45] Zhu, Z.; Hu, J.; Geng, X.; Qin, B.; Ma, K.; Wang, Y.; Gao, J. Process design of carbon dioxide and ethane separation using ionic liquid by extractive distillation. Journal of Chemical Technology & Biotechnology 2018, 93, 887–896.
- [46] Shiflett, M. B.; Shiflett, A. D.; Yokozeki, A. Separation of tetrafluoroethylene and carbon dioxide using ionic liquids. Separation and Purification Technology 2011, 79, 357–364.
- [47] Asensio-Delgado, S.; Pardo, F.; Zarca, G.; Urtiaga, A. Absorption separation of fluorinated refrigerant gases with ionic liquids: Equilibrium, mass transport, and process design. Separation and Purification Technology 2021, 276, 119363.
- [48] Finberg, E. A.; Shiflett, M. B. Process Designs for Separating R-410A, R-404A, and R-407C Using Extractive Distillation and Ionic Liquid Entrainers. Industrial & Engineering Chemistry Research 2021, 60, 16054–16067.
- [49] Valencia-Marquez, D.; Flores-Tlacuahuac, A.; Vasquez-Medrano, R. Simultaneous Optimal Design of an Extractive Column and Ionic Liquid for the Separation of Bioethanol–Water Mixtures. *Industrial & Engineering Chemistry Research* 2012, 51, 5866–5880.
- [50] Zhou, T.; Song, Z.; Zhang, X.; Gani, R.; Sundmacher, K. Optimal Solvent Design for Extractive Distillation Processes: A Multiobjective Optimization-Based Hierarchical Framework. *Industrial & Engineering Chemistry Research* 2019, 58, 5777–5786.
- [51] Waltermann, T.; Grueters, T.; Muenchrath, D.; Skiborowski, M. Efficient optimization-based design of energy-integrated azeotropic distillation processes. Computers & Chemical Engineering 2020, 133, 106676.
- [52] Tian, Y.; Pistikopoulos, E. N. A process intensification synthesis framework for the design of extractive separation systems with material selection. Journal of Advanced Manufacturing and Processing 2021, 3, e10097.
- [53] Demirel, S. E.; Li, J.; Hasan, M. M. F. Systematic process intensification using building blocks. Computers & Chemical Engineering 2017, 105, 2–38.
- [54] Li, J.; Demirel, S. E.; Hasan, M. M. F. Building block-based synthesis and intensification of work-heat exchanger networks (WHENS). Processes 2019, 7, 23.

- [55] Demirel, S. E.; Li, J.; Hasan, M. M. F. A general framework for process synthesis, integration, and intensification. Industrial & Engineering Chemistry Research 2019, 58, 5950–5967.
- [56] Li, J.; Demirel, S. E.; Hasan, M. M. F. Process synthesis using block superstructure with automated flowsheet generation and optimization. AIChE Journal 2018, 64, 3082–3100.
- [57] Demirel, S. E.; Li, J.; El-Halwagi, M.; Hasan, M. M. F. Sustainable Process Intensification Using Building Blocks. ACS Sustainable Chemistry & Engineering 2020, 8, 17664–17679.
- [58] Demirel, S. E.; Li, J.; Hasan, M. M. F. Membrane Separation Process Design and Intensification. Industrial & Engineering Chemistry Research 2021, 60, 7197–7217.
- [59] Monjur, M. S.; Demirel, S. E.; Li, J.; Hasan, M. M. F. SPICE_MARS: A Process Synthesis Framework for Membrane-Assisted Reactive Separations. Industrial & Engineering Chemistry Research 2021, 60, 7635–7655.
- [60] Monjur, M. S.; Demirel, S. E.; Li, J.; Hasan, M. M. F. Computer Aided Chemical Engineering; Elsevier, 2021; Vol. 50; pp 287–293.
- [61] Monjur, M. S.; Hasan, M. M. F. Computer-Aided Process Intensification of Natural gas to Methanol Process. AIChE Journal 2021, e17622.
- [62] Yokozeki, A.; Sato, H.; Watanabe, K. Ideal-gas heat capacities and virial coefficients of HFC refrigerants. International journal of thermophysics 1998, 19, 89–127.
- [63] Fernandez, E. S.; Bergsma, E. J.; de Miguel Mercader, F.; Goetheer, E. L.; Vlugt, T. J. Optimisation of lean vapour compression (LVC) as an option for post-combustion CO2 capture: Net present value maximisation. *International Journal* of Greenhouse Gas Control 2012, 11, S114–S121.
- [64] Jung, J.; Jeong, Y. S.; Lee, U.; Lim, Y.; Han, C. New configuration of the CO2 capture process using aqueous monoethanolamine for coal-fired power plants. *Industrial & Engineering Chemistry Research* 2015, 54, 3865–3878.
- [65] US Energy Information Administration. https://www.eia.gov/tools/faqs/faq.php?id=73&t=11 (accessed on June 2021).
- [66] Luo, H.; Bildea, C. S.; Kiss, A. A. Novel heat-pump-assisted extractive distillation for bioethanol purification. Industrial & Engineering Chemistry Research 2015, 54, 2208–2213.
- [67] Shiflett, M. B.; Yokozeki, A. Separation of diffuoromethane and pentafluoroethane by extractive distillation using ionic liquid. *Chimica oggi* 2006, 24, 28–30.
- [68] Sigma-Aldrich. https://www.sigmaaldrich.com/US/en/product/aldrich/70956 (accessed on December 2021).
- [69] Luyben, W. L. Estimating refrigeration costs at cryogenic temperatures. Computers & Chemical Engineering 2017, 103, 144–150.
- [70] Yao, L.; Li, M.; Hu, Y.; Wang, Q.; Liu, X. Comparative study of upgraded CO2 transcritical air source heat pump systems with different heat sinks. *Applied Thermal Engineering* 2021, 184, 116289.
- [71] Woods, D. R. Rules of thumb in engineering practice; John Wiley & Sons; Weinheim, Germany, 2007; pp 376-436.
- [72] Atsonios, K.; Panopoulos, K. D.; Kakaras, E. Investigation of technical and economic aspects for methanol production through CO2 hydrogenation. *International Journal of hydrogen energy* 2016, 41, 2202–2214.
- [73] Misener, R.; Floudas, C. A. ANTIGONE: algorithms for continuous/integer global optimization of nonlinear equations. Journal of Global Optimization 2014, 59, 503–526.
- [74] Iftakher, A.; Aras, C. M.; Monjur, M. S.; Hasan, M. M. F. Data-driven approximation of thermodynamic phase equilibria. AIChE Journal e17624.

TOC Graphic



For Table of Contents Use Only