

Modeling and Optimization of Ionic Liquid Enabled Extractive Distillation of Ternary Azeotrope Mixtures

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Abstract

To help slow climate change, international efforts have begun to mandate the phase-out of high global warming potential (GWP) hydrofluorocarbons (HFCs) throughout the next decade. Most HFC refrigerant mixtures form azeotropes, complicating separation into the individual HFC components for reuse and recycling. In this paper, we design and analyze ionic liquid (IL)-enabled extractive distillation processes for ternary HFC separations using AspenPlus. Specifically, we design processes to separate three commercially important HFC refrigerant mixtures (R-404A, R-407C, and R-410A) into high purity HFC streams. We find added value of the separation of R-410A of 0.58 \$/kg with current market conditions, specifically laboratory-scale IL manufacturing costs (1000 \$/kg of IL) and a low-price differential of 1.00 \$/kg between raw materials and separated products. If the IL purchase cost decreases 90 % due to mass production, consistent with prior adoption of ILs for niche separations, the added value increases to 0.76 \$/kg. Moreover, under proposed reductions in HFC manufacturing, the price of recovered products may dramatically increase in the future. For example, if the price of R-32 increases by 50 %, the added value would reach 3.08 \$/kg. In summary, we find IL-based recycling of HFCs is economically viable based on simple technoeconomic analysis. Moreover, this paper reports capital and operation cost curves and a general analysis framework to analyze evolving market conditions.

Keywords: Extractive Distillation; Azeotrope; Ionic Liquid; Modeling; Economic Analysis.

1. Introduction

Thousands of tons of HFC refrigerant mixtures, commonly used in industrial, commercial, and residential applications, are scheduled for phase-out worldwide under the 2016 Kigali amendment to the Montreal Protocol, the European Union F-Gas regulations (2015), and the American Innovation and Manufacturing (AIM) Act of 2020. The latter directs EPA to phase down production and consumption of HFCs in the US by 85 percent over the next 15 years. Common HFC mixtures such as R-410A (50 % R-32, 50 % R-125), R-404A (44 % R-125, 4 % R-134a, 52 % R-143a), and R-407C (23 % R-32, 25 % R-125, 52 % R-134a) are targeted for phase-out because of their high global warming potential (GWP): R-410A with 2088 GWP, R-404A with 3922 GWP, and R-407C with 2107 GWP, where CO₂ has a GWP of 1 by definition. However, R-32 and other HFCs have a low GWP and could be reused as part of global phase-out. R-134a is used in R-450A, offering similar performance but with a lower GWP (547) (Honeywell, 2021). Unfortunately, there is no means to easily separate HFC mixtures due to their

azeotropic or near azeotropic nature. Without a new economically viable separation process, the phase-out will require all HFCs to be collected and incinerated.

Extractive distillation, the most common method for separating azeotropic or close-boiling mixtures, is a promising approach to separate HFC mixtures. Moreover, tailored IL solvents can enable extractive distillation of near-azeotropic HFC mixtures. In 2003, Lei et al. first proposed extractive distillation with ILs as entrainers, and (Lei et al., 2005) discussed the use of ILs in extractive distillation in detail. ILs have exhibited high capacity as entrainers to separate azeotropic or close-boiling mixtures (Pereiro et al., 2012). ILs can be recycled in separation processes, reducing the material demands and improving the economics (Zhao et al., 2005, Zhao et al., 2017). Shiflett and Yokozeki (2006) proposed extractive distillation to separate fluorinated refrigerant mixtures using ILs.

2. Methods

2.1. HFC Separation Process Development and Modeling

In this work, we design three extractive distillation processes to separate three ternary azeotrope mixtures, R-404A, R-407C, and a mixture of R-410A and R-22 using an IL entrainer. Table 1 summarizes these three case studies (Finberg 2021). We use the Peng-Robison (PENG-ROB) equation of state to calculate thermodynamic properties. We fit the HFC binary interaction parameters similar to Shiflett and Yokozeki (2006a, 2006b, 2007).

Table 1. Compositions of HFCs mixtures separated and IL used.

HFC	R-404A mol/mol	R-407C mol/mol	R-410A mol/mol
R-32	0.00	0.23	0.45
R-125	0.44	0.25	0.45
R-134a	0.04	0.52	0.00
R-143a	0.52	0.00	0.00
R-22	0.00	0.00	0.10
IL used	[emim][Tf ₂ N]	[bmim][PF ₆]	[bmim][PF ₆]
IL (kg/h)	2000	400	750

Figure 1 shows the process flow diagram for the R-404A case study. The process flow diagrams for the other case studies are nearly identical and not shown for brevity.

2.2. Sensitivity analysis

We performed single-parameter sensitivity over eight variables. The base case used 20 theoretical stages, a flowrate of IL of 1000 kg/h, IL is feeding in stage 2, and the HFC mixture feeding stage is stage 15, the inlet temperature of 25 °C, the pressure of 10 bar, a reboiler temperature of 130 °C, and a reboiler ratio of 2.5. We found that the extractive distillation column's pressure and reflux ratio are most important to minimize energy consumption while obtaining 99.5 mol% purity of all HFC products. Through our sensitivity analysis, we look to obtain the desired purity (99.5 mol%) of R-134a in the distillate of the extractive distillation in the presence of [emim][Tf₂N] with moderate energy consumption. We found that it is impossible to reach the required purity without 25 theoretical stages and a flowrate of IL of 2000 kg/h, even though they significantly influence the capital cost. The IL is fed in stage 2, and the HFC mixture is fed in stage 20 at a temperature of 20 °C. We selected a pressure of 7 bar in the column and a reboiler

[illegible]
$$i = \frac{i' - f}{1 + f} \quad (4)$$

As shown in Figure 2, the capital and operating costs (\$/kg of HFC feed) of the R-404A, R-407C, and R-410A separation increase as we decrease the mixture feed flow rate. We

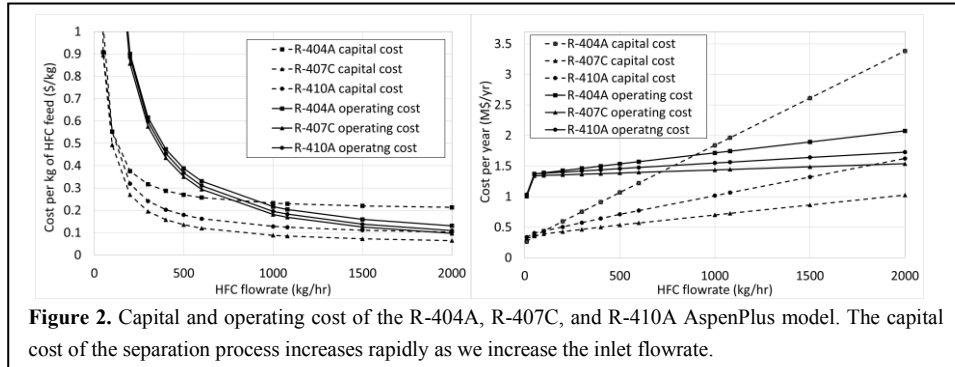


Figure 2. Capital and operating cost of the R-404A, R-407C, and R-410A AspenPlus model. The capital cost of the separation process increases rapidly as we increase the inlet flowrate.

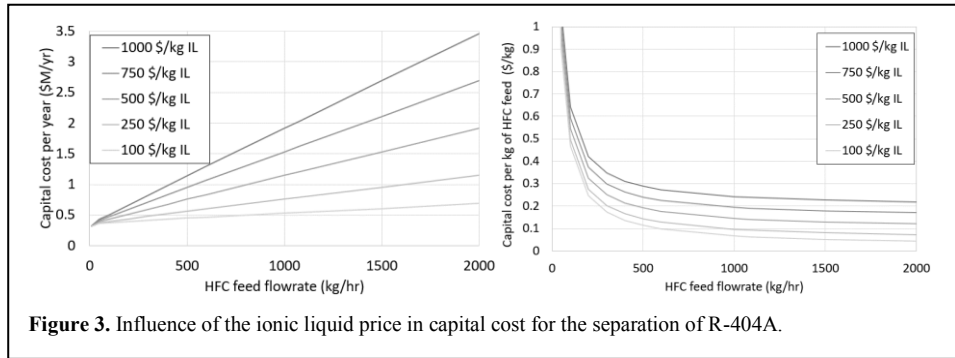


Figure 3. Influence of the ionic liquid price in capital cost for the separation of R-404A.

observe that the significant increase in the capital cost is due to the amount of IL necessary to achieve the 99.5 mol% purity of HFCs desired in the separation. The cost of equipment and installation have minor variations as the size of the equipment is nearly minimum or standard size. As observed in Figure 2, the capital cost may increase to up to 60 % of the total cost. The rise in total capital cost is dependent on the ratio of IL/HFC mixture required for each process. 1 % to 2 % of IL degradation per year corresponds to an increase of the operating cost of 0.03 \$/kg to 0.05 \$/kg, respectively.

Currently, most ILs are only available in high purity for laboratory-scale experiments at high prices of \$1,000/kg. Historically, after an IL is selected for a commercial application and production increases, the price decreases by 90-92 % (Shiflett et al., 2020). In anticipation of a similar economy of scale, we consider five IL price scenarios: 1,000 \$/kg, 750 \$/kg, 500 \$/kg, 250 \$/kg, and 100 \$/kg. Figure 3 shows the impact of IL price on capital costs. Specifically, the capital cost (M\$/y) increases linearly with the IL flowrate (kg/h) at a given IL price. As expected, changing the IL price changes the slope of this relationship. Moreover, the capital cost is extremely sensitive to the IL price. For example, at 5000 kg/h IL flowrate, decreasing the IL price from 1000 \$/kg (laboratory scale specialty chemical) to 100 \$/kg (commercial IL) decreases the capital cost from 8

M\$/y to 1.5 M\$/y. We reiterate that previous commercialization of ILs suggests a 90 % reduction in IL price is reasonable (Shiflett et al., 2020).

$$\text{Added value} \left(\frac{\$}{\text{kg}} \right) = \underbrace{\text{Sell price low GWP components} \left(\frac{\$}{\text{kg}} \right) - \text{Cost of recovery HFC mix.} \left(\frac{\$}{\text{kg}} \right)}_{\text{Price differential}} - \underbrace{\text{Capital Cost} \left(\frac{\$}{\text{kg}} \right) - \text{Operating cost} \left(\frac{\$}{\text{kg}} \right)}_{\text{Costs}} \quad (5)$$

Next, we propose added value, with units \$/kg of HFC feed, as a metric to easily compare different hypothetical scenarios. Eq. (5) calculates added value from the price differential and costs. The selling price of low GWP components is the value of the recycled products, and the cost of recovery HFC mixture corresponds to the value of the used HFC refrigerant mixtures (half of the cost of production and transportation of the HFC mixture used as a base and worst-case scenario). A negative cost of recovery HFC mixture is possible with government subsidies incentivizing HFC recycling (instead of illegal venting). Figure 2 reports the operating and capital costs (\$/kg) as a function of the HFC feed rate. Similarly, Figure 3 shows the dependence of capital cost (\$/kg) on IL price. Because the added value metric represents profit per kilogram of HFC processed, it allows quick evaluation of different market scenarios (e.g., HFC and IL prices).

Using values from these plots, the added value metric can quickly evaluate the benefits of new ILs for the separation process; for example, if a new hypothetical IL required 20 % less mass than the analyzed ILs, the cost in Figure 3 can be proportionally reduced. Likewise, if a new hypothetical IL reduces the separation energy requirement by 50 %, the operating cost value used in Eq. (5) can be reduced by approximately 50 %. This metric gives valuable insights and enables fast “what if” analyses to guide IL and process design.

Under current market conditions, we found that R-410A separation has an added value of 0.55 to 0.72 \$/kg with an IL price of 1000 \$/kg and 100 \$/kg, respectively. Under a futuristic scenario where phase-outs in production doubles the market price for R-32, the added value of the separation of R-410A could be as high as 5.60 \$/kg to 5.78 \$/kg with an IL price of 1000 \$/kg and 100 \$/kg respectively. If the price of R-32 increases by 50 %, the added value would reach 3.08 \$/kg. We found that the price of ILs has the most significant impact on the capital cost, and the price differential between the HFC mixture and the pure HFC impacts the added value and the payback period.

4. Conclusions

In this paper, we show that separating and recycling HFCs with extractive distillation utilizing ILs is economically attractive, especially under anticipated future scenarios. It is important to note that ILs are viscous, and a rate base model is needed for rigorous design and more accurate technoeconomic analyses.

The presented results are based on currently available ILs [bmim][PF₆] and [emim][Tf₂N]. However, ILs can be tailored for specific purposes due to the vast diversity of anions and cations available. For example, tailored ILs with higher selectivity would reduce the amount of IL required and thus capital costs. Tailoring other properties of the

ILs, such as the density, viscosity, and thermal capacity could reduce the operating costs of the process.

There are also unexplored opportunities to optimize the extractive distillation process. While the one and two-dimensional sensitivity analyses presented here show 25 theoretical stages and the amount of IL necessary for the separation, rigorous optimization may find additional opportunities for improvement by exploiting interactions across multiple design decision variables. Moreover, simultaneous process optimization (e.g., flowrates, temperatures) and heat integration may further reduce the energy intensity of the process by systematically balancing reboiler duty and compression costs (e.g., by changing column pressure).

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