Rational Design of Extractive Distillation Toward Enhanced Separation of HFPO from HFP/HFPO Mixture

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Abstract

Hexafluoropropyleneoxide (C₃F₆O, HFPO) is highly expensive and it may be used as a raw material for the synthesis of various fluorne based compounds. Currently, extractive distillation method has gained considerable attention to collect the HFPO from a mixture of HFPO / hexafluoropropylene (C₃F₆, HFP). Optimized operating conditions are studied using a theoretical method for the extraction process. Among available solvents for the purification process, the use of 1,1-dichloro-1-fluoroethane exhibits a high purity of HFPO as a top product and minimize the required heat duty. Since the boiling point of the solvent increases as the pressure in the column increases, the enhanced extractive capability of the solvent led to the high purity of HFPO at the high pressure.

Keywords: Hexafluoropropyleneoxide, Hexafluoropropylene, Extractive distillation, Separation, Aspen

1. Introduction

As one of the consequences of the technical scarcity and energy crisis, several efforts for recycling fluorinated composites has been paid to produce fluorine-based primary building block [1]. Hexafluoropropyleneoxide (HFPO) is an important primary building block for the synthesis of a vast number of value-added intermediates in organofluorine chemistry (i.e., fluropolymers) in industrial applications (i.e., anti-reflection/fingerprint coating material, membranes in fuel cells, fluorine-based lubricants etc.) [2-6]. Hexafluoropropylene (HFP) is one of the main sources to produce HFPO via thermal cracking of polytetrafluoroethylene (PTFE) [4,7]. The HFPO can be synthesized by oxidation of such obtained HFP with 80 ~ 90 wt% yields, indicating that the remained HFP should properly be separated and/or removed to produce high purity HFPO.

Negligibly small difference in boiling points (ΔTbp = 2.3 °C) between HFP (-27.3 °C) and HFPO (-29.6 °C) at 1 atm, however, has hampered their effective separation using conventionally applied regular distillation process [8]. Therefore, strategies for proper solving this issue should target another separation process. One of the promising methods to remove HFP species from a HFPO/HFPO mixture can be an extractive distillation method [9]. Since the vapor pressures of HFP and HFPO are quite similar, the relative volatility is about to be 1. Therefore, it is necessary to lower the vapor pressure of HFP by adding a solvent so that the relative volatility is increased. In order to successfully achieve such extractive distillation, proper selection of solvent should firstly be accompanied [10]. The key factors for solvents as an extracting agent are high volatility, needless of stabilizer, recyclable, low cost, nonflammable, and environmentally benign. And then, the separating condition should be optimized properly.

In this study, 1,1-dichloro-1-fluoroethane, dichloromethane, and disopropyl ether were applied and compared as extractive solvents to maximize the purity of HFPO with minimal energy consumption as a function of inlet pressure using Aspen Plus software. One of the most important operating parameters seems to be the proper selection of extractive solvents. After adequate choice of solvents, the next consideration is how to minimize the scale of the extractive distillation tower in terms of the number of stages and the diameter of the tower. To achieve the goal, two factors may be considered: the reflux ratio and the mass flow rate of the solvent. On the other hand, the operating cost is also important: the heat duties for the reboiler and the condenser should be taken into account. Therefore, this theoretical
study focuses on the following targets: optimizing operation parameters such as (1) the type of extractive solvents, (2) the reflux ratio, (3) the number of tray, and (4) the mass flow rate of solvents.

2. Material and Methods

2.1. Physical properties of HFP and HFPO

Table 1 shows the molecular weights, molecular structures and the normal boiling points of HFP and HFPO. Both the molecular structure and the normal boiling point are quite similar between HFP and HFPO, indicating that the separation of these molecules from their mixture is hampered.

Variation of temperature and pressure with respect to the mole fraction of HFP is described in Figure 1. The dew point of a vapor is located quite near from the bubble point of a liquid at any given mole fraction of HFP. It indicates that a normal distillation cannot be successfully used to separate them and another type of distillation such as an extractive distillation has to be considered.

Typical organic materials were chosen as an extractive solvent which has a relatively low boiling point compared to HFP and HFPO so that it can easily be recovered from the mixture of HFP, HFPO, and solvent after the extractive distillation. It should not form an azeotropic solution together with either HFP or HFPO. The solvent has to be an inert material during the synthetic reaction of HFPO. The physicochemical properties are shown in Table 2.

2.2. Computational modeling

The mixture of HFP and HFPO is supplied to the extractive distillation column 1 so that the pure HFPO can be obtained as a top product and the mixture of HFP and the solvent can be separated as a bottom product as shown in Figure 2. The solvent is recycled to the first column after it is separated from the mixture of HFP and the solvent using a normal distillation column. The Aspen Plus software is used to design the extractive distillation process: the number of trays, the reflux

Table 1. Physical properties of HFP and HFPO

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical formula</th>
<th>MW (g mol⁻¹)</th>
<th>Boiling point (°C)</th>
<th>Chemical structure</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexafluoropropylene (HFP)</td>
<td>CF₂CFCF₃</td>
<td>150.02</td>
<td>-29.6</td>
<td></td>
<td>116-15-4</td>
</tr>
<tr>
<td>Hexafluoropropyleneoxide (HFPO)</td>
<td>CF₃COCF₃</td>
<td>166.02</td>
<td>-27.3</td>
<td></td>
<td>684-16-2</td>
</tr>
</tbody>
</table>

Table 2. Physical properties of solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical formula</th>
<th>Aspen form</th>
<th>MW (g mol⁻¹)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-dichloro-1-fluoroethane</td>
<td>CCl₂FCH₃</td>
<td>C₂H₅ClF</td>
<td>116.95</td>
<td>32.0</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>CH₂Cl₂</td>
<td>84.93</td>
<td>39.8</td>
</tr>
<tr>
<td>Diisopropyl ether</td>
<td>CH₃(CH₂)OCH(CH₂)₂</td>
<td>C₆H₁₂O</td>
<td>102.18</td>
<td>68.3</td>
</tr>
</tbody>
</table>
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Figure 2. Layout of columns for extractive distillation and recycle of solvent.

Figure 3. A typical condition for numerical analysis

<table>
<thead>
<tr>
<th>Number of trays in extractive column</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column pressure (atm)</td>
<td>2 ~ 10</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>10</td>
</tr>
<tr>
<td>Solvent</td>
<td>1,1-dichloro-1-fluoroethane</td>
</tr>
<tr>
<td>Flow rate of feedstock (kg d⁻¹)</td>
<td>HFPO 227.2</td>
</tr>
<tr>
<td></td>
<td>HFP 22.8</td>
</tr>
<tr>
<td>Flow rate of solvent (kg d⁻¹)</td>
<td>200 ~ 100,000</td>
</tr>
</tbody>
</table>

3. Results and Discussion

A type of condenser is fixed to be a partial condenser since the top product is collected as a gas so that it can be directly used as an intermediate in the industrial organofluorine chemistry: specifically as a monomer for fluoropolymers. Also several design variables are fixed such as the number of trays of the extractive distillation and the operating pressure by a preliminary design with Aspen Plus so that the required heat duty is controlled to be minimized.

3.1. Effect of tray location for feedstock on purity of HFPO

At the given operating condition shown in Table 3, the purity of HFPO was simulated and the results of it is shown in Figure 3 as a function of flow rate of extractive solvent. The 1,1-dichloro-1-fluoroethane was selected as a model solvent to investigate the optimum locations of both a feed and a solvent tray in the extractive distillation column. At the moderate flow rate of solvent, the purity of HFPO was targeted to be higher than 0.98 in several parameters such as the type of solvent and the reflux ratio. The heat duties of the condenser and the reboiler are also simulated with the same condition. A typical operating condition for a numerical analysis is represented in Table 3.
mole fraction. The results show that the Case 1, Case 4 and Case 6 (see Table 3) are suitable to obtain the target purity of HFPO at over the solvent flow rate of 200 kg d⁻¹. Therefore, the solvent tray was fixed to be 5 and the feed tray can be selected among 15, 20, and 25 depending on the reasonable construction of the distillation column. In this study, the tray number of 20 was selected as a feed tray.

3.2. Screening of solvents

In order to determine the solvent for an efficient extractive distillation of HFP/HFPO mixture, the purity of HFPO were calculated with respect to the mass flow rate of 1,1-dichloro-1-fluoroethane, dichloromethane, and diisopropyl ether, respectively, as shown in Figure 4. the purity of HFPO for all solvents increased as the increase in the mass flow rate, which indicates that the process toward the purification of HFPO is underlying the steady-state. Although the recorded purities of HFPO for diisopropyl ether and dichloromethane were higher than that for the 1,1-dichloro-1-fluoroethane at 5 atm and 10 atm, respectively, the gap of the purity was negligibly low (2 ~ 5%). In other words, all of the extractive solvent candidates exhibit comparable performance toward the purification of HFPO. It should be noted that the level of HFPO purity is over 0.85 at 5 atm, 0.917 at 7 atm, and 0.945 at 10 atm, which are high enough to reach the primary target purity of HFPO. Therefore, examination and comparison of the applied heat at reboiler (bottom) and exchanged heat at condenser (top) in the column for these solvents is important for practical application.

3.3. Heat duties for condenser and reboiler

The heat duties on the condenser and the reboiler depend on the various operating parameters, particularly the type of the solvent for the extractive distillation. The heat capacities of the utilized solvents are different from each other, leading that the different heat duty is required. Since the heat duty is one of the major operating costs, the heat duty is designed to be as low as possible. In Figure 5, the heat duty is represented as a function of the flow rate of the solvent used at the given typical condition such as the operating pressure of 5, 7, and 10 atm. It easily can be seen that the lowest heat duty can be
obtained when 1,1-dichloro-1-fluoroethane is used among the three solvents in both the condenser and reboiler. It should be noted that the operating temperature is also important in the distillation tower for the recovery of solvent. Since the boiling point of 1,1-dichloro-1-fluoroethane is known to be 32 °C, it is much lower than 39.8 °C of dichloromethane. The temperature range will be between 32 °C and -29.6 °C of HFP if 1,1-dichloro-1-fluoroethane is used. Thus, the temperature range will be

Figure 5. Effect of various solvents on heat duties on condenser at (a) 5 atm, (b) 7 atm, and (c) 10 atm, respectively, and also on the reboiler at (d) 5 atm, (e) 7 atm, and (f) 10 atm, respectively.

Figure 6. The effect of reflux ratios on the purity of HFPO with respect to the flow rate of 1,1-dichloro-1-fluoroethane at (a) 5 atm, (b) 7 atm, and (c) 10 atm, respectively.
narrower than with the solvent of dichloromethane, which is much more effective. Furthermore, the heat of vaporization for 1,1-dichloro-1-fluoroethane is 27.8 kJ mol$^{-1}$ and that for dichloromethane is 28.1 kJ mol$^{-1}$. It is believed that the heat duty for the reboiler with 1,1-dichloro-1-fluoroethane in the distillation column 2 will be much smaller than with dichloromethane. As far as there is no big difference on the extractive performance for HFPO, it is required to select the suitable solvent by considering the several factors mentioned above. Moreover, it should be noted that the heat duty decreased as the increase in the feed pressure.

3.4. Effect of reflux ratio on purity of HFPO

A reflux ratio is one of the very important operating parameters. If the reflux ratio is large, the diameter of a distillation column increases, leading to a difficult control of homogeneous flows of gas and liquid. Therefore, the reflux ratio should be designed as small as possible until the target purity of HFPO can be established. Figure 6 shows the calculated HFPO purity as a function of flow rate of 1,1-dichloro-1-fluoroethane with various reflux ratios. The optimum reflux ratio should be determined to obtain the target purity at the low flow rate of the solvent. As a result, the reflux ratios of 2.5 and 5 are insufficient and the reflux ratio of 15 is too large to reach desirable level of HFPO purity. Therefore, the reflux ratio of 10 is determined to be the optimized reflux ratio. Moreover, the mole fraction of HFPO increased as the increase in the feed pressure, which is in good agreement with the results shown in Figure 4.

4. Conclusions

The extractive distillation process was successfully designed using a software of Aspen Plus including the normal distillation process for the recycle of solvent. The optimum tray locations could be selected for the feed mixture and the solvent for the extractive distillation column so that the target purity of HFPO in the top product could be obtained. The reflux ratio was also determined to achieve the purity of HFPO at the top of the distillation column by considering the minimum flow rate of the solvent. In addition to the operating condition, adequate type of solvent was found to be 1,1-dichloro-1-fluoroethane so that the heat duty could be minimized. Those design factors can be directly applied to the real separation of HFPO from its mixture of HFP.

References