Research Article

Reduction of Energy Consumption and Greenhouse Gas Emissions in a Plant for the Separation of Amines

The chemical industry comprises of the companies that produce industrial chemicals. It is central to the modern world economy, converting raw materials into more than 70,000 different products. However, environmental regulations and the risk of climate change are putting pressure on the chemical industry to minimize greenhouse gas emissions. In this work, we use the concept of process intensification (using thermally coupled distillation) to reduce energy consumption and CO2 emissions in a plant for the separation of amines. The results show that the use of thermally coupled distillation sequences can be related to a reduction in energy consumption, greenhouse gas emissions, and good theoretical control properties in the re-designed plant.

Keywords: Distillation, Energy consumption, Greenhouse gas emissions

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1 Introduction

Global warming has recently become a growing source of environmental concern. There is a scientific consensus that emissions of what are known as greenhouse gases may have a serious effect on atmospheric composition and, therefore, induce gradual climate change. When greenhouse gas emissions are discussed, CO2 is generally the gas that receives the most attention because of its greenhouse effect. CO2 is emitted in large amounts into the atmosphere and has a rather long atmospheric lifetime [1]. Production of CO2 globally has recently been brought into sharp focus through declarations such as the Kyoto Protocol, which applies to various industries. The chemical industry is considered an emitter or contributor to climate change. For instance, the combustion of fuel in furnaces is considered as the main source of CO2 in chemical industries, accounting for about 90% of CO2 emissions [2]. It is recommended that we reduce CO2 emissions by over 50% in order to stabilize their impact on global warming. One way in which we can address this is through judicious use of process intensification technology. Process intensification may be defined as any engineering development that leads to a substantially smaller, cleaner, safer, and more energy-efficient technology. It is most often characterized by an enormous reduction in plant volume (orders of magnitude) but its contribution to reducing greenhouse gas emissions may also be significant [3].

Thermally coupled distillation sequences (TCDS) are an example of process intensification [4]. TCDS have been proposed to perform distillation separation tasks with the incentive of lower energy consumption levels (and consequently, reduction in CO2 emissions) with respect to conventional distillation sequences [5]. Through implementation of a vapor-liquid interconnection between two columns, a condenser or a reboiler of one of the columns is eliminated, and if a proper optimization of the operating conditions is performed, such an interconnection can provide energy savings [6, 7]. TCDS for ternary mixtures have received special attention and their analysis is of special interest. One of the schemes that has received special attention is the system with a side column [8, 9], namely, the thermally coupled system with a side stripper, TCDS-SS (shown in Fig. 1). Oftentimes, the design of integrated systems creates operational and control problems that do not affect simpler designs. In particular, the presence of recycle streams for TCDS schemes has led to the notion that control problems might be expected during the operation of these systems; this, compared to the rather well-known behavior of conventional distillation sequences. The foregoing has been one of the main reasons for the lack of industrial implementation of TCDS schemes.

Recently, Ramírez and Jiménez [10] have studied one arrangement that emerges from modifications to the systems shown in Fig. 1. Such a new system is shown in Fig. 2. In the modified arrangement (an indirect sequence with a side stream from the first column, ISS), the vapor interconnection of the...
TCDS-SS is eliminated and the top section of the first column (section 3) is added to the second column, affecting the original side stripper. Therefore, the new arrangement eliminates the intercolumn vapor transfer, does not contain recycle streams, and the second column of each sequence is transformed into a conventional distillation column. The resulting new structure, therefore, seems to provide simpler systems to control and operate. Segovia-Hernandez et al. [11] have shown that TCDS-SS and ISS systems are thermodynamically equivalent.

In this work, we study process intensification (using TCDS-SS or its thermodynamically equivalent arrangement) in an industry of amine separation (azeotropic mixture). Results show that the use of process intensification is a better option than conventional distillation sequences (Fig. 3) in terms of energy savings, reductions in greenhouse gas emissions, capital investment, and control properties.

2 Design Method

For the design of the TCDS arrangements, conventional sequences were first obtained (the indirect sequence (Fig. 3b)) for the TCDS-SS. The sections performing similar tasks in the two types of systems were identified to produce the tray arrangement of the thermally coupled design. Such a design was then tested and optimized for energy consumption through rigorous simulations. The optimization procedure requires a rigorous model for each equilibrium stage in the distillation columns that can be obtained from a generic equilibrium stage. Eqs. (1–5) describe the equilibrium stage model.

Total mass balance in stage $j$:

$$L_{j-1} + V_{j+1} + F_j^L + F_j^V - (L_j + U_j) - (V_j + W_j) = 0$$  \(1\)
Component mass balances in stage $j$:

$$L_{i-1}X_{i,j-1} + V_{j+1}Y_{j+1} + F_j^L Z_{i,j}^L + F_j^V Z_{i,j}^V - (L_j + U_j)X_{i,j} - (V_j + W_j)Y_{i,j} = 0 \quad (2)$$

Equilibrium relation in stage $j$:

$$Y_{i,j} = K_{i,j} X_{i,j} \quad (3)$$

Summation constraint in stage $j$:

$$\sum_{i=1}^{C} K_{i,j}X_{i,j} - 1.0 = 0 \quad (4)$$

Energy balance in stage $j$:

$$L_{i-1} - \frac{h_i}{h_j} + V_{j+1} - \frac{h_j}{h_j} + F_j^L - \frac{h_j}{h_j} + F_j^V - \frac{h_j}{h_j} - (L_j + U_j) - \frac{h_j}{h_j} - (V_j + W_j) = 0 \quad (5)$$

Further details on the design procedure are given by Hernández and Jiménez [12].

The equivalent scheme can be obtained directly from the TCDS-SS arrangement, following the simple tray section analogies depicted in Fig. 1. The new systems should also be subjected to an optimization procedure to detect the values of side stream flow rates from the first column that minimizes their energy consumption. It should be noted that the range for the optimization procedure for these structures is more restricted than for the TCDS-SR structure because of mass balance considerations. The bounds for columns with side streams are explained by Glinos and Malone [12].

## 3 Case Study

We studied the purification process of a mixture of amines (Tabs. 1 and 2). The original process is shown in Fig. 4. This is a real case study and due to confidentiality policies; we cannot reveal the identity of the three amines. The amine of industrial interest is component C (a ternary amine) with a purity of 99% in mole percentage in stream 8. According to Fig. 4, a feed of three amines is introduced into a conventional distillation column that removes the ternary homogeneous azeotrope (Fig. 5). The bottom product of the first distillation column is mostly component C and the top products is principally a mixture of A and B. More details about the process are given in Tab. 3. The separation of the bottom products in the other two columns may be re-designed (use of process intensification). The first conventional distillation column and the columns for the separation of top products are needed in the two new configurations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular weight [g/mol]</th>
<th>Boiling temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>59</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>87</td>
<td>65</td>
</tr>
<tr>
<td>D</td>
<td>60</td>
<td>97.8</td>
</tr>
<tr>
<td>E</td>
<td>156</td>
<td>157</td>
</tr>
</tbody>
</table>

Table 2. Properties of the mixture.

The first option uses a TCDS-SS. As indicated in Fig. 6, component C is obtained at the top of the main column of the complex arrangement. The second option uses an ISS arrangement. As shown in Fig. 7, component C is obtained at the top of both columns of the sequence.

The UNIQUAC model was used to predict thermodynamic properties. In the new schemes, the design pressure for each separation was chosen to ensure the use of cooling water in the condensers. The pressure drop for a single tray is given based on the heuristics of Kister [13].

## 4 Results

The results presented here correspond to the separation of component C with a high mole fraction (0.99), using different alternatives of the original flowsheet. In the case of the first option, using a TCDS-SS (Fig. 6), Tab. 4 displays the energy consumption of all columns, including the coupled distillation scheme. When we compared the original scheme with the option-1 flowsheet, the modified separation process shows energy savings, reduction in CO$_2$ emissions (calculated according to Appendix A), and reduction in total annual cost (TAC) calculated according to Turton et al., 2004 (see Appendix B). In general, the savings are $\sim$ 25% (Tab. 5). In the case of the option-2 flowsheet displayed in Fig. 7 (Tab. 4 shows energy con-

<table>
<thead>
<tr>
<th>Specifications of the columns in the original process.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-204</td>
</tr>
<tr>
<td>Number of stages</td>
</tr>
<tr>
<td>Feed stage</td>
</tr>
<tr>
<td>Reboiler duty [W]</td>
</tr>
<tr>
<td>Pressure [kg/cm$^2$]</td>
</tr>
</tbody>
</table>

Table 3. Specifications of the columns in the original process.
sumption of all columns including the ISS arrangement), that modified process shows savings of \( \sim 9\% \) in energy consumption, \( \text{CO}_2 \) emissions, and TAC in comparison with the original process (Tab. 5). The results show the advantage of using process intensification to obtain savings in reboiler duty, greenhouse gas emissions, and TAC. In the case of the plant for the separation of amines, the use of a TCDS-SS showed the greatest savings.

As a complement to this study, we analyzed the control properties of the original process with the best case using process intensification (option 1). We used the singular value decomposition technique (SVD) for this purpose. First, open-loop dynamic responses to changes in the manipulated variables around the assumed operating point were obtained. The responses were obtained using Aspen Dynamics. Transfer function matrices \( (G) \) were then collected for each case (Tabs. 6 and 7), and they were subjected to singular value decomposition (SVD):

\[
G = UVW^H
\]

where \( \Sigma = \text{diag} (\sigma_1, \ldots, \sigma_n) \), \( \sigma_i \) = singular value of \( G = x_k^{1/2} (GO_k^H) \); \( V = (v_1, v_2, \ldots) \), matrix of the left singular vectors, and \( W = (w_1, w_2, \ldots) \), the matrix of right singular vectors. Two parameters of interest are the minimum singular value, \( \sigma_m \), and the ratio of maximum to minimum singular values, or condition number:

\[
\gamma = \sigma / \sigma_m
\]

The minimum singular value is a measure of the invertibility of the system and represents a measure of the potential problems of the system under feedback control. The condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control [14].

For the case study of the original process and option 1, we obtained the following results (Figs. 8 and 9): the alternative using process intensification
presents higher minimum singular values and a lower condition number for the entire frequency range. Therefore, it can be expected that the modified process exhibits better control properties than the original process under feedback control and is better conditioned to the effect of disturbances than the other flow sheet.

According to the results, option 1 is the best alternative to separate the mixture of amines. Additionally, the use of a complex distillation sequence (TCDS-SS) can more effectively reduce capital costs when implemented in a single distillation column, using a dividing wall. This is important to highlight because the industrial implementation of the TCDS options is being carried out using a single shell divided by a wall. This eliminates potential operational and control problems associated with flooding and operating pressure.

5 Conclusions

The separation of an azotropic mixture of amines was studied using process intensification through a coupled distillation scheme or its alternative sequence. The results show that the use of TCDS-SS can produce total savings (in energy, TAC and CO2 emissions) of around 25% over the original process. In the case of the use of the ISS arrangement, the total savings are ~9%. Furthermore, it was found that control properties of option 1 are better than the original scheme. The results imply that the proposed modification using a coupled distillation sequence can achieve significant total energy savings that can be translated into reductions in TAC and CO2 emissions. The theoretical control properties indicate that cost savings and lower greenhouse gas emissions can be obtained without additional control properties; i.e., the expected dynamic behavior could be even better than the process using conventional distillation sequences.

Acknowledgements

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Appendix A

Table 4. Energy consumption in modified process.

<table>
<thead>
<tr>
<th>Option 1</th>
<th>T-204</th>
<th>T-205</th>
<th>T-305</th>
<th>T-306</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reboiler duty [W]</td>
<td>260 000</td>
<td>268 000</td>
<td>260 000</td>
<td>96 000</td>
</tr>
<tr>
<td>Option 2</td>
<td>T-204</td>
<td>T-205</td>
<td>T-305</td>
<td>T-306</td>
</tr>
<tr>
<td>Reboiler duty [W]</td>
<td>260 000</td>
<td>275 000</td>
<td>260 000</td>
<td>172 000</td>
</tr>
</tbody>
</table>

Table 5. Comparison of results using the various alternatives.

<table>
<thead>
<tr>
<th></th>
<th>Original flowsheet</th>
<th>Option 1 flowsheet</th>
<th>Option 2 flowsheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reboiler duty [W]</td>
<td>1 040 000</td>
<td>884 000</td>
<td>967 000</td>
</tr>
<tr>
<td>TAC [$/y]</td>
<td>629 261</td>
<td>471 945</td>
<td>585 212</td>
</tr>
<tr>
<td>CO2 emissions [Ton/h]</td>
<td>3.48</td>
<td>2.61</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Table 4. Energy consumption in modified process.

Table 5. Comparison of results using the various alternatives.

Fuel combusts when mixed with air, producing CO2 according to the following stoichiometric equation:

\[ C_nH_y + (x + y/4) O_2 \rightarrow x CO_2 + y/2 H_2O \]  
(A.1)

where \( x \) and \( y \) denote the number of carbon, C, and hydrogen, H, atoms, respectively, present in the fuel compositions, and where complete oxidation of carbon is assumed.

In the combustion of fuels, air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed. CO2 emissions, \( [CO_2]_{\text{Emiss}} \) (kg/s), are related to the amount of fuel burnt, \( Q_{\text{fuel}} \) (kW), in a heating device as follows [5]:

\[ [CO_2]_{\text{Emiss}} = \frac{Q_{\text{fuel}}}{NHV} \left( \frac{C\%}{100} \right) a \]  
(A.2)
where $\alpha$ (= 3.67) is the ratio of molar masses of CO$_2$ and C, while NHV (kJ/kg) represents the net heating value of a fuel with a carbon content of C%. Eq. (A.2) shows that both the fuel used and the heating device affect the amount of CO$_2$ produced.

Boilers produce steam from the combustion of fuel. This steam is delivered to the process at the temperature required by the process or obtained at a higher temperature and then throttled. In distillation systems, steam is used either for heating purposes, indirectly in the reboilers, or as a direct stripping agent in so-called steam distillations, such as crude oil units. The flame temperature is lower in a boiler than in a furnace because the heat of combustion is immediately removed from the steam. However, the same theoretical flame temperature of 1800°C may still be used. The stack temperature of 160°C is also used in the calculations. The amount of fuel burnt can be calculated from Gadalla et al., 2005:

$$Q_{\text{Fuel}} = \frac{Q_{\text{Proc}}}{\lambda_{\text{Proc}}} (\rho_{\text{Proc}} - 419) \frac{T_{\text{FTB}} - T_0}{T_{\text{FTB}} - T_{\text{Stack}}} \quad (A.3)$$

where $\rho_{\text{Proc}}$ (kJ/kg) and $\lambda_{\text{Proc}}$ (kJ/kg) are the latent heat and enthalpy of steam delivered to the process, respectively, while $T_{\text{FTB}}$ (°C) is the flame temperature of the boiler flue gases. The above equation is obtained from a simple steam balance around the boiler to relate the amount of fuel necessary in the boiler to provide a heat duty of $Q_{\text{Proc}}$; the boiler feed water is assumed to be at 100°C with an enthalpy of 419 kJ/kg. Eqs. (A.2) and (A.3) can be used to calculate the CO$_2$ emissions from steam boilers.

**Appendix B**

For a given number of theoretical trays, Aspen Plus One simulator calculates column diameter and height (for 24-in tray spacing) after converging for selected valve tray column with 2 in weir height. Glitsch valve trays are considered. Distillation column cost (carbon steel construction) was estimated by the cost equations showed in Turton et al. [16], which are adjusted using the CEPCI (Chemical Engineering Process Cost Index). For comparison, a single value from CEPCI is selected (October 2007), as of the year this study begun. The total column cost is the sum of the installation cost of the column shell and the installation cost of the column trays. Moreover, the sizing and costing of heat exchangers were carried out. The cost of heat exchangers can be calculated as a function of the surface area assuming shell and tube, floating head, and carbon steel construction. Installation prices are adjusted using the CEPCI.
Figure 8. Minimum singular values.

Figure 9. Condition numbers.
index. Capital cost (purchase plus installation cost) is annualized over a period which is often referred to as plant lifetime:

\[
\text{Annual capital cost} = \frac{\text{Capital cost}}{\text{Plant lifetime}} \quad \text{(B.1)}
\]

Total annual cost (TAC) = Annual operating cost + Annual capital cost \quad \text{(B.2)}

Operating costs were assumed to be only utility costs (steam and cooling water).

Plant life = 5 years
Operating hours = 8400 h/y.

References