A Sequential Method for Determining Optimal Stripper Pressure and Terminal Pressure in CO₂ Capture and Liquefaction Process Using MEA

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Abstract: The pressure of a distillation column for regenerating an absorbent is one of the key variables for minimizing the energy in a carbon capture and storage (CCS) chain. The steam drag point in power plant, the regeneration energy in capture process and the compression energy in the liquefaction process are highly dependent on the pressure of regeneration column. In this work, a new method for determining optimal value of stripper pressure is proposed based on the integrated simulation model and sequential optimization method. Total required energy has been represented as a function of the stripper pressure and the terminal pressure. The results show that the higher pressure is generally recommended to reduce the required energy, revealing that the value of the stripper pressure depends on the liquefaction process more than the power plant.

Keywords: CCS, MEA, stripper, carbon dioxide

1. INTRODUCTION

Carbon capture and storage/sequestration (CCS) has been studied for minimizing carbon dioxide (CO₂) emitted from various sources. In general, a whole chain of CCS consists of five stages: power plant, capture process, compression/liquefaction process, transportation (or transmission) process and storage (or utilization). Various combinations from possible options can exist. Since the amount of carbon dioxide emitted from coal power plants is significant, the CCS chain with a conventional coal power plant and capture unit using aqueous monoethanolamine (MEA) is widely studied.

Although the necessity of CCS technology has been increased, its economic feasibility is not yet competitive. The implementation of carbon dioxide capture unit causes the power generation efficiency to drop by 20%(6). Various ideas have been suggested to address the issue. Majority of previous studies have been focused on suggesting alternative designs of the capture and compression/liquefaction processes where over 90% of the total energy is used(1)(2)(3)(5). Oyenekan and Rochelle (6) shows an alternative design for a capture unit to reduce the energy where compression ratio is adjusted to reduce the compression energy in transmission process.(7)

Economic feasibility cannot be evaluated without an integrated process model due to the interactions among the processes. A simple combination of each optimized process may not necessarily lead to an global optimal as a whole process. However, it is difficult to construct an integrated model that covers the whole CCS chain. Only a small number of studies show a global optimal condition with a large number of computations. Whereas this approach can show the optimal value, it is difficult to obtain an insight and physical causality from the results.

In this study, an integrated simulation model for the whole CCS chain was developed with a high convergence performance and a fast calculation speed. Moreover, a new semi-analytical method for determining the optimal pressure of stripper is suggested to minimize the total energy in the CCS chain without performing simulations of each case.

The remainder of the paper is organized as follows: in Process and Model Description, the integrated simulation model and a detailed process has been suggested to develop an optimization algorithm. With this algorithm, the total energy required and the optimal pressure are obtained with two different cases in Results section.

2. PROCESS AND MODEL DESCRIPTION

Pro/II® with Soave-Redlich-Kwong (SRK), Non-Random Two Liquid (NRTL) and Benedict-Webb-Rubin-Starling (BWRS) models were employed. The SRK equation is used for gaseous components while the NRTL and BWRS models were chosen for the CO₂ capture and steam, respectively. The simulated power plant was a conventional coal power plant with a 500-MW power generation capac-
ity. 30wt% of monoethanolamine (MEA) was used as an absorbent. The compression and liquefaction process were composed of a series of compressors. During the liquefaction process, the water content was maintained below 50 vppm to avoid hydrate formation (8)(9). The pipeline was simulated using the specifications reported in (8).

2.1 Power Plant

The plant was designed with a 500-MW power capacity. Illinois No. 6 coal mixed with water was simulated. Flue gas composition is shown in Table 1.

Table 1. Flue Gas Composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>77.41</td>
<td>mol%</td>
</tr>
<tr>
<td>CO2</td>
<td>15.62</td>
<td>mol%</td>
</tr>
<tr>
<td>H2O</td>
<td>6.81</td>
<td>mol%</td>
</tr>
<tr>
<td>O2</td>
<td>0.12</td>
<td>mol%</td>
</tr>
<tr>
<td>Rest</td>
<td>0.04</td>
<td>mol%</td>
</tr>
</tbody>
</table>

2.2 Capture Process

A wet process using 30 wt% MEA was selected. The pressure of the absorption column (absorber) and regeneration column (stripper) set to be 1 bar and 1.5 bar respectively. The composition of the captured CO2 is shown in Table 2.

Table 2. The Composition of the Captured CO2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>94.03</td>
<td>mol%</td>
</tr>
<tr>
<td>H2O</td>
<td>5.10</td>
<td>mol%</td>
</tr>
<tr>
<td>H2</td>
<td>Trace</td>
<td>mol%</td>
</tr>
<tr>
<td>O2</td>
<td>Trace</td>
<td>mol%</td>
</tr>
</tbody>
</table>

2.3 Liquefaction Process

The multistage compression was designed with 4 compressors. Triethylene glycol (TEG) was used to control the water concentration below 50 vppm. Table 3 shows the output data for the compression and liquefaction model.

Table 3. The Composition of the Liquefied CO2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>198</td>
<td>K</td>
</tr>
<tr>
<td>Pressure</td>
<td>10</td>
<td>Bar</td>
</tr>
<tr>
<td>Energy</td>
<td>105</td>
<td>kWh/ton CO2</td>
</tr>
<tr>
<td>H2O concent</td>
<td>50</td>
<td>vppm</td>
</tr>
</tbody>
</table>

3. FORMULATION

In the capture process, the stripper pressure is the key variable that affects the total energy consumption. The capture process decreases the power generation by utilizing steam to compensate the reboiler duty. The operating pressure of the capture process will change the energy requirements of the compression and liquefaction. To determine the optimal pressure of the stripper analytically, it is necessary to express the required energy in terms of pressure. The concept of equivalent work has been applied (6).

In this study, three general assumptions were used. First, both liquid and vapor phases are well mixed in the stripper. Second, the reboiler was in a vapor/liquid equilibrium. Finally, the amount of vaporized amine was negligible.

3.1 Reboiler Duty

The reboiler duty is composed of three terms: the heat required to desorb CO2 (Q_{desorption}), the heat required to vaporize the water (Q_{vaporization}) and the sensible heat (Q_{sensible heat}).

\[ Q_{reboiler} = Q_{desorption} + Q_{vaporization} + Q_{sensible heat} \] (1)

The heat of desorption. The heat of desorption per mole of CO2 can be calculated by differentiating the Vapor/Liquid Equilibrium (VLE) equation for MEA with respect to \( \frac{1}{T} \). If we represent the partial pressure of CO2 in terms of temperature, it is easy to estimate the heat of desorption as in Eq. (3).

\[ \ln P_{CO2} = a + b \gamma + \frac{c}{T} + d \frac{\gamma^2}{T^2} + e \frac{\gamma}{T} + f \gamma \] (2)

\[ -\frac{\Delta H_{des}}{R} = c + 2d \frac{\gamma^2}{T} + 2e \frac{\gamma}{T} + f \gamma \] (3)

where \( \Delta H \) is the heat of desorption, \( R \) is the universal gas constant, \( T \) is the temperature in K, \( \gamma \) is the rich amine loading and \( a, b, c, d, e, f \) are the empirical constants. The values of the constants are shown in Table 4.

Table 4. Heat of desorption obtained by the least squares

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>30.27</td>
</tr>
<tr>
<td>b</td>
<td>-38.87</td>
</tr>
<tr>
<td>c</td>
<td>-11991</td>
</tr>
<tr>
<td>d</td>
<td>1110073</td>
</tr>
<tr>
<td>e</td>
<td>-4896203</td>
</tr>
<tr>
<td>f</td>
<td>31355.6</td>
</tr>
<tr>
<td>R^2</td>
<td>0.995</td>
</tr>
</tbody>
</table>

The heat of vaporization. The heat of vaporization per mole of CO2 can be expressed as follows:

\[ \frac{n_{H_2O}(T)}{n_2} \Delta H(T) \] (4)

The number of moles of vaporized water (\( n_{H_2O}(T) \)) and the enthalpy for vaporizing the water (\( \Delta H(T) \)) varies with the temperature of the reboiler. Because the operational temperature range is small, e.g., 373.15 K to 408.15 K, it is acceptable to fit the data to obtain the heat of vaporization as a function of temperature. In case of \( n_{H_2O}(T) \), the value which varies with the temperature was determined given the pressure value between 1 and 2.1 bar by simulations.

The sensible heat. The sensible heat is the energy for heating the liquid mixture to the reboiler temperature. Sensible heat per mole of CO2 can be expressed as follows:

\[ Q_{sensible heat} = \frac{L_{Cp} \Delta T}{n_{CO2}} \] (5)
\( \Delta T \) is assumed to be 10 K. \( L \) is the flowrate of the inlet to the stripper and \( n_{\text{CO}_2} \) is the number of moles of captured \( \text{CO}_2 \).

**Equivalent work**   
The concept of equivalent work in calculating the reboiler duty is advantageous to estimate the loss in power plant quickly without iterative simulation. The heat required for the stripper can be converted to the equivalent work using the following equation:

\[
W_{\text{eq, reboiler}} = 0.75 \times Q_{\text{reboiler}} \times \frac{(T_{\text{reboiler}} + 10 - 313.15)}{(T_{\text{reboiler}} + 10)}
\]

(6)

where 0.75 is the turbine efficiency and 10 is the reboiler approach temperature. The sink temperature is assumed to be 313.15 K.

### 3.2 Compression work

The energy required for the compression process varies with the possible process configurations. A \( N \) compressors with a constant flow rate was employed, and where the liquid loss after capture process was neglected. In this case, the compression work per a mole of \( \text{CO}_2 \) can be obtained as follows:

\[
W_{\text{comp}} = \frac{\mu kR T_{\text{in}}}{n_{\text{CO}_2}(k-1) \eta} \left( \sum_{i=1}^{n} \left( \frac{P_{i+1}}{P_i} \right)^{\frac{k-1}{k}} - n \right)
\]

(7)

Here, \( \mu \) is the inlet flowrate to the compression process and \( k \) is the heat capacity ratio of the gas mixture. \( R \) is the gas constant, \( T_{\text{in}} \) is the temperature of the inlet flow to the compression process, and \( \eta \) is the compression efficiency of each compressor.

**Number of compressors**   
To evaluate the compression work, it is necessary to specify the terminal pressure, maximal compression ratio, and efficiency. Two cases were considered: for ship transportation, 10 bar was set as the terminal pressure, and 100 bar was chosen for pipeline transmission. The maximal compression ratio and efficiency were set to be 2.5 and 85%, respectively.

1. Determine \( x \) as a real number

Because the maximum value of the compression ratio was set as 2.5, it is possible to find an approximate value of the number of compressors given the stripper and terminal pressures are provided.

\[
p \times (2.5)^x = P_{\text{terminal}}
\]

(8)

A real number \( x \) is obtained and it is necessary to correct the value because the number of compressors must be a natural number.

2. Determine \( n \) as an integer

\[
\text{if } x \text{ is not integer, } n = [x] + 1 = \left[ \log_{2.5} \frac{P_{\text{terminal}}}{p} \right] + 1
\]

\[
\text{if } x \text{ is an integer, } n = x = \log_{2.5} \frac{P_{\text{terminal}}}{p}
\]

(9)

where \( [x] \) is a floor function. Because Eq. (8) will be a rare case, we only consider Eq. (7) in the subsequent discussions.

(3) Find the compression ratio \( \theta \)

After determining \( n \), the number of compressors can be obtained by

\[
p \times \theta^n = P_{\text{terminal}}
\]

(10)

\[
\theta = \log_{\frac{P_{\text{terminal}}}{p}} n_{\text{CO}_2}(k-1) \eta \left( \sum_{i=1}^{n} \left( \frac{P_{i+1}}{P_i} \right)^{\frac{k-1}{k}} - n \right)
\]

(11)

As a result, compression work is expressed as a function of \( p \) and \( P_{\text{terminal}} \) as follows:

\[
\frac{\mu kR T_{\text{in}}}{n_{\text{CO}_2}(k-1) \eta} \left( \sum_{i=1}^{n} \left( \frac{P_{i+1}}{P_i} \right)^{\frac{k-1}{k}} - n \right)
\]

(12)

\[
= \frac{\mu kR T_{\text{in}}}{n_{\text{CO}_2}(k-1) \eta} \left( \log_{2.5} \frac{P_{\text{terminal}}}{p} + 1 \right) \times
\]

\[
\left( \log_{\frac{P_{\text{terminal}}}{p}} \frac{P_{\text{terminal}}}{p} \right)^{\frac{k-1}{k}} - 1
\]

**3.3 Total energy**   

Total energy can be expressed as a sum of the equivalent work for the reboiler and compression work. Note that the liquefaction duty is not included in this research.

\[
E_{\text{tot}} = W_{\text{eq, reboiler}} + W_{\text{comp}}
\]

(13)

If we expand the individual terms, the total is represented as a function of two key variables: pressure and temperature of the stripper. It is necessary to eliminate the temperature term to have the total energy as a function of the pressure.

**3.4 Empirical relation between temperature and pressure in stripper**   

To find an optimal pressure that minimizes \( E_{\text{tot}} \), it is necessary to map \( T \) as a function of \( P \), the pressure of the reboiler. Because it is impossible to have an analytical expression, an empirical relationship was constructed using simulation data.

\[
T(p, \gamma) \approx -4.54p^2 + 34.3p + 346.85 \quad (0.45 \leq \gamma \leq 0.49)
\]

(14)

Thus, we can reduce the degree of freedom and complexity arising from the combination of the different conditions of the flue gas and MEA solution. Because RAL is in the range between 0.45 and 0.52 when MEA is used to capture \( \text{CO}_2 \), our model can represent most cases. Also, the empirical relationship between the stripper temperature and pressure shows that the effect of RAL on the stripper temperature can be neglected.

### 4. RESULTS

#### 4.1 Case study

Two cases were considered with different methods of transmission for captured \( \text{CO}_2 \). The first case is ship transportation, where the terminal pressure of liquefaction process is
set as 10 bar. The second case is pipeline transmission, where the terminal pressure is assumed to be 100 bar.

Case I. Ship transportation (p_{terminal} = 10 bar)
The transmission pressure is usually in the range between 7 and 20 bar to prevent boil-off gas, and 10 bar was used in this study (7). Based on Eq. (13), the reboiler duty, the compression energy and the total energy required were evaluated and shown in Figs. 1 and 2. A high pressure was shown to be favorable in saving the total energy.

Case II. Pipeline transmission (p_{terminal} = 100 bar)
In case II, the value of \( p_{terminal} \) was set as 100 bar. Similar trends were observed as shown in Figs. 3 and 4.

According to Eq. (13), the total energy is composed of 4 parts: \( \text{CO}_2 \) desorption energy, \( \text{H}_2\text{O} \) vaporization energy, the sensible heat and the compression work. As the pressure rises, the temperature also rises in stripper. The desorption energy decreases since the thermal energy is required to remove binding between MEA and \( \text{CO}_2 \). Also, the heat of vaporization and the amount of evaporated \( \text{H}_2\text{O} \) decreases. Because the sensible heat is independent of the stripper pressure, the reboiler duty is reduced as the temperature rises by increasing the pressure. However, the equivalent work for reboiler increases because the increase in the temperature term \( T + 10 \) dominates the decrease in the reboiler duty \( Q_{\text{reboiler}} \). It is reasonable because if we increase the stripper pressure, the high quality steam needs to be withdrawn from the power plant. Although the equivalent work increases, the amount of reduced compression work is larger than that of equivalent
work for reboiler. Hence, the total energy decreases as the pressure rises.

4.3 Simultaneous optimization using the differentiation

The discrete function \([\log_{2.5}\frac{p_{\text{terminal}}}{p}]\) is modified to \((\log_{2.5}\frac{p_{\text{terminal}}}{p})\) for differentiation. Replacing \(T(p)\) with \((-4.54p^2 + 34.3p + 346.85)\) in Eq. (13) yields a fully expanded equation for total energy in terms of pressure. Setting \(\frac{dP}{dp} = 0\), \(p_{\text{optimal}}\) can be obtained. For evaluating an analytical solution of \(p_{\text{optimal}}\), it is necessary to convert the logarithm term to polynomial form using the Taylor series.

\[
\ln(1 + x) \approx x
\]

As a result, \(f(p)\) can be represented as a fractional function with polynomials. Since \(T(p)\) and \(\Delta H(T)\) are \(2^{nd}\) order polynomials in a single variable \(p\) and the degree of polynomial equation \(g(p) = 0\) is more than 5, and a general solution cannot be obtained explicitly according to the Abel-Ruffini theorem. Hence, it is impossible to make an analytical solution for \(p_{\text{optimal}}\), including all possible cases through differentiation.

4.4 Sequential optimization using the separation of variables

Because the simultaneous method is not available to find an optimal solution, a sequential method is applied as an alternative. Recall the Eq. (16).

\[
E_{\text{tot}} = W_{\text{eq, reboiler}} + W_{\text{comp}}
\]

The first term \((W_{\text{eq, reboiler}})\) is a single variable function of the stripper pressure while the second term \((W_{\text{comp}})\) is a multi variable function of the stripper pressure and the terminal pressure. Hence, we can set an optimization problem based on this observation.

Minimize \(G(p, p_{\text{terminal}}) = F_1(p) + F_2(p, p_{\text{terminal}})\)

subject to \(1 \leq p \leq 2.2\) and \(4 \leq p_{\text{terminal}} \leq 200\)

Because \(F_1\) is solely dependent on \(p\), we can evaluate the amount of energy change caused by the pressure increase. As the pressure rises from 1 bar to 2.2 bar, \(F_1\) increases from 16.43 kJ/mole of CO\(_2\) to 19.14 kJ/mole of CO\(_2\). In other words, we will get an energy loss in \(F_1\) with 2.71 kJ/mole of CO\(_2\) if we increase the stripper pressure. In case of \(F_2\), we found that the energy gain \((F_2(1, p_{\text{terminal}}) - F_2(2.2, p_{\text{terminal}}))\) by rising the stripper pressure increases as the value of \(p_{\text{terminal}}\) increases. Fig. 5 shows this trend.

When we calculate the total energy, sum of \(F_1\) and \(F_2\), it is easy to expect that the shape of the total energy according to the stripper pressure can change because the value of the increase in \(F_1\) is constant while the value of decrease in \(F_2\) varies with the terminal pressure. The simulation results show that the total energy has a monotonous decreasing shape if the terminal pressure exceeds 6.3 bar. Here, we can summarize the optimization result as follows:

1. \(4 \leq p_{\text{terminal}} < 6.3 : 1 \leq p_{\text{optimal}} < 2.2\) (The optimal pressure exists in the range 1 bar to 2.2 bar)
2. \(6.3 \leq p_{\text{terminal}} : p_{\text{optimal}} = 2.2\) (The higher pressure is favorable)

4.5 Total energy saved and the energy efficiency

The higher stripper pressure is favorable in energy saving for most cases because the terminal pressure is above 20 bar generally. When it comes to the effectiveness, however, the conclusion is different. Fig. 6 shows the amount of energy saved and the efficiency.

When we calculate the total energy, sum of \(F_1\) and \(F_2\), it is easy to expect that the shape of the total energy according to the stripper pressure can change because the value of the increase in \(F_1\) is constant while the value of decrease in \(F_2\) varies with the terminal pressure. The simulation results show that the total energy has a monotonous decreasing shape if the terminal pressure exceeds 6.3 bar. Here, we can summarize the optimization result as follows:

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2. \(6.3 \leq p_{\text{terminal}} : p_{\text{optimal}} = 2.2\) (The higher pressure is favorable)

Fig. 5. Energy gain

Fig. 6. Energy saved and the efficiency

As the terminal pressure increases, the amount of energy saved increases while the efficiency hardly change in the vicinity of 0.063. From this observation, the recommended terminal pressure can be defined near 150 bar. Also the optimal stripper pressure can be recommended as a value of 1.5 bar considering the safety factor and MEA thermal degradation temperature.

5. CONCLUSIONS

In this article, 5 different achievements are presented. (1) Design an integrated CCS simulation model including power plant, capture unit, compression, liquefaction process (2) Develop a new algorithm for determining the optimal stripper pressure to minimize the total energy required (3) Solve an optimization problem by sequential method and obtain reasonable results consistent with the results of previous studies without a repetitive simulation or calculation (4) Reveal that the shape of the total energy with respect to a stripper pressure is highly affected by a terminal pressure (5) Introduce a new concept of energy efficiency for suggesting an optimal stripper pressure and a terminal pressure.

NOMENCLATURE

\(\Delta T\) = temperature approach in cross exchange [K]
\(\gamma\) = CO\(_2\) loading [mol CO\(_2\)/mol MEA+]
\(\eta\) = efficiency of compressor
\(\mu\) = inlet flowrate to the compression process [gmoles/s]
\(\theta\) = compression ratio
\(C_p\) = heat capacity of liquid \([kJ/mol-K]\)
\(E_{tot}\) = total energy required \([kJ/gmol of CO_2]\)
\(\Delta H\) = heat of absorption/desorption \([kJ/gmol CO_2]\)
\(k\) = heat capacity ratio of the outlet flow from the condensor
\(n\) = number of compressors required
\(n_{CO_2}\) = mole of CO_2 \([molde]\)
\(n_{H_2O}\) = mole of H_2O \([moles]\)
\(P_{CO_2}\) = equilibrium partial pressure of CO_2 \([bar]\)
\(p_i\) = pressure of the inlet flow to \(i^{th}\) compressor \([bar]\)
\(Q_{reboiler}\) = reboiler duty \([kJ/gmol CO_2]\)
\(Q_{desorption}\) = heat of desorption of CO_2 \([kJ/gmol of CO_2]\)
\(Q_{H_2Ovaporization}\) = heat of H_2O vaporization \([kJ/gmol of CO_2]\)
\(Q_{sensibleheat}\) = sensible heat required to heat rich solution to reboiler temperature \([kJ/gmol of CO_2]\)
\(R\) = universal gas constant \([J/K-mol]\)
\(T\) = temperature \([K]\)
\(T_{in}\) = temperature of the inlet flow to the compression process \([K]\)
\(T_{reboiler}\) = temperature of reboiler
\(W_{eq,reboiler}\) = equivalent work for reboiler \([kJ/gmol of CO_2]\)
\(W_{comp}\) = isentropic work of compression \([kJ/mol of CO_2]\)

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