Aspen Plus simulation-based parametric study of Benfield process using hot potassium carbonate promoted by diethanolamine

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Abstract

Simulating Benfield process that uses hot potassium carbonate as a chemical absorbent is a challenging task given the absence of the electrolyte system package in the more widely used simulation software such as Aspen Hysys and the fact that all of the existing simulation works have featured either the absorption column or the stripping column as a stand-alone process scenario. In this work, Benfield process is simulated using the Aspen Plus software as a whole process where the absorption column is integrated to the stripping column in a closed-loop mode. The chemical absorbent, i.e., hot potassium carbonate (K$_2$CO$_3$) is promoted by 3 wt.% of diethanolamine (DEA) to enhance the solubility of the carbon dioxide in the absorbent via higher reaction rate. The absorption column is simulated using rate-based approach while the stripping column is simulated using equilibrium approach. The simulation is validated against the industry data. The effects of stripping column boil-up ratio, solvent circulation rate, and K$_2$CO$_3$ concentration on the reboiler duty and the sweet gas CO$_2$ concentration are studied. The lowest reboiler duty of 48 GCal h$^{-1}$ and the lowest CO$_2$ concentration of less than 50 ppmv are obtained using a boil-up ratio of 0.3, a solvent circulation rate of 35,000 kmol h$^{-1}$, and K$_2$CO$_3$ concentration of 15 wt.%.

Keywords: Aspen Plus; Benfield; CO$_2$ capture; parametric study; potassium carbonate

1. Introduction

Natural gas has become one of the primary sources for energy generation in the present time. It is considered as a cleaner fuel relative to the other fossil-based fuels such as coal, gasoline, and diesel given its dominant methane constituent and low carbon dioxide (CO$_2$) emission per unit of energy produced [1]. Natural gas can be obtained directly from natural gas field as a concentrated product or as a purified product from co-product stream of crude oil refining processes. Natural gas generally contains organic gases such as methane (CH$_4$), ethane (C$_2$H$_6$), propane (C$_3$H$_8$), butane (C$_4$H$_{10}$), and pentane (C$_5$H$_{12}$), a minor amount of inorganic gases such as carbon dioxide (CO$_2$), hydrogen sulphide (H$_2$S), sulphur dioxide (SO$_2$), oxygen (O$_2$), and nitrogen (N$_2$), and a trace amount of inert gases such as helium (He), Xenon (Xe), and Neon (Ne) [2]. Untreated natural gas that contains significant amount of inorganic gases components are generally known as sour gas given their acidic behaviour [3]. The presence of
these inorganic gases especially CO$_2$ and H$_2$S is undesirable since these two components do not contribute to the energy content of the natural gas and in large amount, they may cause major problems during the subsequent transportation and utilisation processes such as pipelines corrosion and sulphide stress cracking [4]. The process to remove acid gases from the natural gas stream is known as gas sweetening process. Over the past decades, five different types of gas sweetening processes have been developed that rely on different mechanisms, i.e., absorption, adsorption, cryogenic distillation, membrane separation, and chemical conversion [5]. Among these processes, absorption is currently the most established process for industrial scale operation [6].

There are two types of absorption processes, i.e., physical absorption and chemical absorption. Physical absorption relies upon the physical contact between the gas stream and the solvent stream to achieve the mass transfer of the acidic gases components from the gas stream to the solvent stream. In chemical absorption, on the other hand, chemical reactions between the acidic gases and the solvent is also present in addition to the physical contact, which enhances the mass transfer rate significantly relative to the physical absorption [7].

1.1. Amine-based Absorption

In present time, the most commonly used and established chemical absorption uses amine-based solvent, which has become the dominant topic for most studies in this field [8]. Some examples of the more commonly used amines in industry are monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), triethanolamine (TEA), disopropylamine (DIPA), and diglycolamine (DGA). However, despite its widespread usage, various limitations manifest during the actual operation using amine-based solvent. One of them is the limited CO$_2$ loading, which hinders complete removal of CO$_2$ from the feed gas. As a result, higher circulation rate of the solvent is required to achieve high CO$_2$ removal rate. Other limitations include pipeline corrosion, high energy consumption for the solvent regeneration process, and the degradation of the solvent [8, 9].

1.2. Potassium Carbonate Absorption

These limitations have prompted the advent of extensive research programs to develop an alternative, improved version of the solvent, which are free from these issues. One of them are potassium carbonate ($K_2$CO$_3$). Compared to the amine-based solvents, $K_2$CO$_3$ is more attractive in terms of its low toxicity, low degradation rate, and low energy consumption for regeneration [10, 11]. Nevertheless, $K_2$CO$_3$ also has some limitations such as the poor reaction kinetics, which translates to large absorption column area requirement [8]. This issue can be overcome by adding small amount of promoter to $K_2$CO$_3$ [10]. The effects of different types of promoters to the absorption performance and their optimum concentrations have been discussed in several recent studies [12, 13]. These studies however mainly focus on the experimental aspect of the absorption. Simulation-based process design and modification studies in this topic is considered sparse since the currently available ones present only the absorption column or the stripping column as an individual process. This work aims to simulate both processes as a single integrated process and perform parametric study on the final CO$_2$ concentration in the final sweet gas and the reboiler duty as functions of stripping column boil-up ratio, solvent circulation rate, and $K_2$CO$_3$ concentration.

1.3. Process Chemistry

The chemical absorption process using potassium carbonate solution is typically conceptualize using the overall reaction represented by Equation (1) [14, 15]:

$$CO_2 + K_2CO_3 + H_2O \leftrightarrow 2KHC O_3$$  \hspace{1cm} (1)

The above reaction can be broken down into nine reactions represented by Equations (2)-(10):

$$K_2CO_3 \rightarrow 2K^+ + CO_3^{2-}$$ \hspace{1cm} (Dissociation) \hspace{1cm} (2)
\[ KHCO_3 \rightarrow K^+ + HCO_3^- \]  
(Dissociation) \quad (3)

Considering the strong ionisation tendency of \( K_2CO_3 \) and \( CO_3^{2-} \), it can be assumed that potassium is present only in its ionic form, i.e., as \( K^+ \) (Equations (2) and (3)).

\[ H_2O \leftrightarrow OH^- + H_3O^+ \]  
(Equilibrium) \quad (4)

\[ CO_2 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \]  
(Equilibrium) \quad (5)

\[ HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \]  
(Equilibrium) \quad (6)

\[ CO_2 + OH^- \rightarrow HCO_3^- \]  
(Kinetic) \quad (7)

\[ HCO_3^- \rightarrow CO_2 + OH^- \]  
(Kinetic) \quad (8)

Addition of small amount of amine promoter generally enhance the diffusion rate of \( CO_2 \) into the bulk liquid through the formation of a carbamate ion (DEACOO-) following Equations (9) and (10):

\[ DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+ \]  
(Equilibrium) \quad (9)

\[ DEACOO^- + H_2O \leftrightarrow DEA + HCO_3^- \]  
(Equilibrium) \quad (10)

The chemical equilibrium expression for the chemical equilibrium reactions is as follows:

\[ \ln K_{eq} = A + \frac{B}{T} + C \ln(T) + DT \]  
(11)

Where the parameters \( A, B, C \), and \( D \) are given in the work of Borhani et al. [15]. For the kinetic reactions, the reaction rate expression is assumed to have a power law form:

\[ r = k \left( \frac{T}{T_0} \right)^n \exp \left( \frac{-E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) \]  
(12)

Where \( r \) is the rate of reaction, \( k \) is the pre-exponential factor, \( T \) is the absolute temperature, \( E \) is the activation energy, and \( R \) is the gas law constant. In Equation (12), the concentration is expressed in molarity. The values of \( k \) and \( E \) are given in the work of Borhani et al. [15].

2. Process Description

The schematic process flow diagram for a conventional gas sweetening process that uses \( K_2CO_3 \) solvent is shown in Figure 1. Sour gas feed is introduced directly into the absorption column from the bottom stage and rises in a counter-current manner against the \( CO_2 \)-lean \( K_2CO_3 \) solvent stream, which enters the column from the top stage of the absorption column. The absorption column operates at temperature and pressure ranges of 313-393 K (40-120 °C) and 2,000-6,000 kPa, respectively [9]. The cross-contact between the solvent and the sour gas facilitates the absorption process of \( CO_2 \) into the solvent. The sour gas leaves the top of the absorption column as a \( CO_2 \)-depleted product gas (i.e., sweet gas). The solvent that contains \( CO_2 \), on the other hand, leaves the bottom of the absorption column as a \( CO_2 \)-rich solvent. To reduce the pressure of solvent that goes to the stripping column, which generally operates at 100–180 kPa [16], the high-pressure \( CO_2 \)-rich solvent stream is passed through pressure reducing valve. At lower pressure, flash evaporation of \( CO_2 \)-rich solvent stream occurs in Flash Drum 1, where a substantial
amount of CO\(_2\) vaporises out from this stream. The CO\(_2\)-rich solvent stream is then heated as it passes through a heater, to achieve desired operating temperature for the stripping column. The CO\(_2\)-rich solvent stream enters the stripping column from the top stage and flows downward, during which its CO\(_2\) constituent are released and removed from the top of the stripping column. The top product of the stripping column generally contains large amount of water, which is separated from CO\(_2\) in Flash Drum 2 and is recycled back to the stripping column. The CO\(_2\)-lean solvent comes out at the bottom of the stripping column and is recycled back to the top of the absorption column. Continuous operation of these absorption and stripping columns for extended time duration leads to the solvent loss, which is compensated via the additional solvent make-up flow.

![Process Flow Diagram](image)

**Figure 1.** Process flow diagram for natural gas sweetening by absorption using potassium carbonate solvent.

### 3. Methodology

**Figure 2** shows the simulation methodology framework of this work, which consists of two different main sections. The first section focuses on the reproduction of the simulation work on the existing cases, which forms the base case while the second section aims to achieve optimised operating parameters. The absorption column and the stripping columns were simulated using the operating condition and parameter obtained from literature and the results were validated [15, 17]. The effects of the process parameters, i.e., boil-up ratio, K\(_2\)CO\(_3\) concentration and circulation rate are evaluated in the second section.
Figure 2. Simulation methodology framework.

The simulation was performed using Aspen Plus software. The compositions of the input feed were obtained from the work of Borhani et al. [15] (Table 1). The specifications for the absorption column and the stripping column, on the other hand, are taken from the works of [15, 17] (Table 2).

Table 1. Characteristics of sour gas and lean solvent [15].

| Name                | Sour Gas  | Lean Solvent |
|---------------------|-----------|--------------|
| Temperature (K)     | 388.2     | 401          |
| Total molar flow (kmol hr\(^{-1}\)) | 8,459     | 46,259.6     |
| Mole fraction       |           |              |
| CO\(_2\)            | 0.17150   | 0            |
| CH\(_4\)            | 0.00187   | 0            |
| CO                  | 0.00376   | 0            |
| H\(_2\)             | 0.57510   | 0            |
| N\(_2\)             | 0.18590   | 0            |
| Ar                  | 0.00217   | 0            |
| H\(_2\)O            | 0.05970   | 0.92943      |
| K\(_2\)CO\(_3\)     | 0         | 0.03663      |
| KHCO\(_3\)          | 0         | 0.02527      |
| DEA                 | 0         | 0.00722      |
| KVO\(_3\)           | 0         | 0.00145      |
Table 2. Absorption and stripping column characteristics [15, 17].

|                        | Absorption column | Stripping column |
|------------------------|-------------------|------------------|
| Diameter (m)           | 4                 |                  |
| Number of trays        | 13                | 10               |
| Type of contactor      | Glitsch Ballast   |                  |
| Weir height (mm)       | 60                |                  |
| Column pressure (kPa)  | 6,000             |                  |
| Calculation type       | Rate-based        | Equilibrium      |

The stripping column, on the other hand, was simulated using the equilibrium model [18] since the desorption process matches well the equilibrium process criterion given its high operating temperature compared to absorption column and fast reaction kinetic. Literature reports that the results obtained by applying rate-based model are typically identical to those obtained by applying equilibrium-based model [18]. Thus, equilibrium model is applied here to shorten the computational time.

This work extends the work of Borhani et al. [15] by simulating the complete Benfield process flowsheet that integrates both the absorption column and the stripping column to evaluate the effects of the stripping column boil-up ratio, solvent circulation rate, and K₂CO₃ concentration to the sweet gas CO₂ concentration and the reboiler duty of stripping column.

4. Results and Discussion

This work simulates a conventional natural gas sweetening process, where the absorption column and the stripping column are connected in a closed-loop mode. Benfield solvent with a circulation rate of 46,259.6 kmol hr⁻¹ and a concentration of 20 wt.% K₂CO₃ promoted with 3 wt.% DEA is used. Table 3 lists the simulation results in terms of mole fraction of sweet gas. The results were validated against Borhani et al. [15], where the percentage difference between the current simulation and Borhani’s work is less than 8%. Such minor discrepancy validates the accuracy of our simulation.

Table 3. Comparison of the sweet gas composition (in mole fraction) obtained in this work to that obtained in the work of Borhani et al. [15].

| Name | Sweet gas simulated by Borhani et al. (2013) | Sweet gas simulated in this work | Error (%) |
|------|---------------------------------------------|----------------------------------|-----------|
| CO₂  | 0.00198                                     | 0.00185                          | 6.3463    |
| CH₄  | 0.00241                                     | 0.00230                          | 4.4119    |
| CO   | 0.00479                                     | 0.00470                          | 1.9115    |
| H₂   | 0.74119                                     | 0.74568                          | -0.6060   |
| N₂   | 0.24029                                     | 0.23239                          | 3.2891    |
| Ar   | 0.00283                                     | 0.00261                          | 7.9217    |
| H₂O  | 0.00989                                     | 0.01103                          | -5.8569   |
Sensitivity analysis with respect to the stripping column boil-up ratio, the solvent circulation rate, and K$_2$CO$_3$ concentration was performed to evaluate the effect of these parameters on the reboiler duty and the CO$_2$ concentration in the sweet gas.

Figure 3 shows the flowrate of CO$_2$ that comes out from the top of the stripping column and the reboiler duty as functions of boil-up ratio of the stripping column between 0.1 and 0.8. Both the CO$_2$ flowrate and the reboiler duty increases with increasing boil-up ratio. This is since the increase in boil-up ratio increases the amount of steam generated at the bottom of the stripping column, which enhances the desorption of CO$_2$. As a result, higher amount of CO$_2$ comes out from the top of the stripping column. Based on the result shown in Figure 3, the rate of change of the CO$_2$ flowrate coming out from the top of the stripping column decreases as the boil-up ratio increase. The reboiler duty increases linearly with increasing boil-up ratio. We selected boil-up ratio of 0.3 as the optimum value since increasing boil-up ratio beyond 0.3 increases the reboiler duty significantly while only giving minor enhancement in the amount of CO$_2$ stripped from the CO$_2$-rich solvent.

![Figure 3. Effect of boil-up ratio on the CO$_2$ flowrate in stripping column overhead product and the reboiler duty.](image)

Figure 4 shows the CO$_2$ mole fraction in sweet gas and the reboiler duty as a function of solvent circulation rate. When the solvent circulation rate increases, the total amount of absorbent increases, resulting in the increase in CO$_2$ absorption rate. CO$_2$ concentration in sweet gas decreases as the solvent circulation rate increases (Figure 4). However, with increasing solvent circulation rate, the reboiler requires more heat supply to maintain the boil-up ratio, thus resulting in the linear increase in the reboiler duty. The amount of CO$_2$ decreases to a fixed value when the solvent circulation rate increases beyond 35,000 kmol hr$^{-1}$. Therefore, an optimum solvent circulation rate is obtained at 35,000 kmol hr$^{-1}$ with the reboiler duty of 47 GCal hr$^{-1}$. This shows a decrease in the solvent usage as compared to the base case (46,259.6 kmol hr$^{-1}$), which represents a reduction of 24% achieved through this sensitivity analysis.
Another important parameter for CO₂ removal is the K₂CO₃ concentration. We varied K₂CO₃ concentration between 5 to 30 wt.% at an optimum solvent’s circulation rate of 35,000 kmol hr⁻¹ to study its effect on the CO₂ concentration in the sweet gas and the stripping column’s reboiler heat duty (Figure 5). It is worth noting that we only changed the concentration of K₂CO₃, while the concentration of DEA was kept constant at 3 wt.%. CO₂ concentration in sweet gas decreases while the reboiler duty increases with increasing K₂CO₃ concentration. An optimum K₂CO₃ concentration of 15 wt.% is obtained where the concentration of CO₂ in the sweet gas decreases to nearly zero. This optimum K₂CO₃ concentration is obtained at the reboiler heat duty of 48 GCal hr⁻¹, which is identical to the results shown in Figure 4, where we used 20 wt.% K₂CO₃ concentration at an optimum solvent circulation rate of 35,000 kmol hr⁻¹. Thus, K₂CO₃ concentration exhibits marginal effect on the stripping column reboiler duty.

Figure 4. Effect of solvent circulation rate on the CO₂ concentration in sweet gas and the reboiler duty.
Figure 5. Effect of K$_2$CO$_3$ concentration on the sweet gas CO$_2$ concentration and the reboiler duty.

5. Conclusion

A closed-loop mode of gas sweetening unit was simulated in Aspen Plus that integrates the rate-based model absorption column with equilibrium-based model stripping column. The results of the simulation show an acceptable agreement with experimental data from literature. The sensitivity analyses of stripping column boil-up ratio, solvent circulation rate, and K$_2$CO$_3$ concentration on the reboiler duty of stripping column and the sweet gas CO$_2$ concentration is investigated. Optimum reboiler heat duty of 48 GCal h$^{-1}$ and CO$_2$ concentration of less than 50 ppmv are obtained at a boil-up ratio of 0.3, solvent circulation rate of 35,000 kmol h$^{-1}$, and K$_2$CO$_3$ concentration of 15 wt.%. Our future work will be dedicated to the integration of the system with downstream process (i.e., dehydration) to study the energy requirement (i.e., heat duty).

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References

[1] Dong K, Sun R, Dong X. CO$_2$ emissions, natural gas and renewables, economic growth: Assessing the evidence from China. Science of The Total Environment. 2018;640-641:293-302.

[2] Ikoku CU. Natural gas production engineering: Wiley; 1984.

[3] Mokhatab S, Poe WA, Mak JY. Handbook of Natural Gas Transmission and Processing: Principles and Practices: Elsevier Science; 2018.

[4] Goodwin MJ, Musa OM, Steed JW. Problems Associated with Sour Gas in the Oilfield Industry and Their Solutions. Energy and Fuels. 2015;29(8):4667-82.
[5] Rao AB, Rubin ES. A technical, economic, and environmental assessment of amine-based CO$_2$ capture technology for power plant greenhouse gas control. Environmental Science and Technology. 2002;36(20):4467-75.

[6] Yildirim Ö, Kiss AA, Hüser N, Leßmann K, Kenig EY. Reactive absorption in chemical process industry: A review on current activities. Chemical Engineering Journal. 2012;213:371-91.

[7] Aresta M. Carbon Dioxide Recovery and Utilization: Springer Netherlands; 2013.

[8] Isa F, Zabiri H, Ng NKS, Shariff AM. CO$_2$ removal via promoted potassium carbonate: A review on modeling and simulation techniques. International Journal of Greenhouse Gas Control. 2018;76:236-65.

[9] Thee H, Nicholas NJ, Smith KH, da Silva G, Kentish SE, Stevens GW. A kinetic study of CO$_2$ capture with potassium carbonate solutions promoted with various amino acids: Glycine, sarcosine and proline. International Journal of Greenhouse Gas Control. 2014;20:212-22.

[10] Borhani TNG, Akbari V, Hamid MKA, Manan ZA. Rate-based simulation and comparison of various promoters for CO$_2$ capture in industrial DEA-promoted potassium carbonate absorption unit. Journal of Industrial and Engineering Chemistry. 2015;22:306-16.

[11] Kohl AL, Nielsen R. Gas Purification: Elsevier Science; 1997.

[12] Cullinan JT, Rochelle GT. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. Chemical Engineering Science. 2004;59(17):3619-30.

[13] Thee H, Suryaputradinata YA, Mumford KA, Smith KH, Silva Gd, Kentish SE, Stevens GW. A kinetic and process modeling study of CO$_2$ capture with MEA-promoted potassium carbonate solutions. Chemical Engineering Journal. 2012;210:271-9.

[14] Kothandaraman A, Nord L, Bolland O, Herzog HJ, McRae GJ. Comparison of solvents for post-combustion capture of CO$_2$ by chemical absorption. Energy Procedia. 2009;1(1):1373-80.

[15] Borhani TNG, Akbari V, Hamid MKA, Manan ZA. Rate-based simulation of DEA promoted potassium carbonate process2013.

[16] Ochieng R, Berrouk A, Elkamel A. Multiobjective Optimization of a Benfield HiPure Gas Sweetening Unit. Journal of Industrial Mathematics. 2013;2013.

[17] Rahimpour MR. Desorption of carbon dioxide from promoted hot potassium carbonate in an industrial stripper using penetration theory. Chemical Technology An Indian Journal. 2007;2(1):13-23.

[18] Mudhasakul S, Ku H-m, Douglas PL. A simulation model of a CO$_2$ absorption process with methyl-diethanolamine solvent and piperazine as an activator. International Journal of Greenhouse Gas Control. 2013;15:134–41.

[19] Zhang Y, Chen H, Chen C-C, Plaza JM, Dugas R, Rochelle GT. Rate-Based Process Modeling Study of CO$_2$ Capture with Aqueous Monoethanolamine Solution. Industrial & Engineering Chemistry Research. 2009;48(20):9233-46.