Greener Solvent Selection and Solvent Recycling for Carbon Dioxide Capture

Ghinwah Hachem
University of Dayton, OH 45469

Juan Salazar and Urmila Diwekar
Vishwamitra Research Institute, Clarendon Hills, IL 60559

Carbon capture and storage (CCS) constitutes an extremely important technology that is constantly being improved to minimize the amounts of carbon dioxide (CO$_2$) entering the atmosphere. According to the Global CCS Institute, there are more than 320 worldwide CCS projects at different phases of progress. However, current CCS processes are accompanied with a large energy and efficiency penalty. This paper models and simulates a post-combustion carbon capture system, that uses absorption as a method of separation, in Aspen Plus V7.2. Moreover, the CAPE-OPEN Simulated Annealing (SA) Capability is implemented to minimize the energy consumed by this system, and allow coal-fired power plants to use similar carbon capture systems by losing around 10 % of the plant’s output instead of 20 to 40 %.

Introduction

Coal-fired power plants provide 44.9 % of the electricity consumed in the United States of America (USA). Thus, coal is the largest source of energy for electricity generation in the USA. Moreover, researchers claim that there are 847 billion tons of coal supplies worldwide. These reserves are estimated to last around 119 years at current rates of production. Furthermore, scientists believe that countries will continue to rely on coal since it only costs $1 to $2 to generate 1 MMBtu of usable energy, and it is found all around the world and specifically in China, India, the Persian Gulf, and the USA. Coal-fired power plants have several harmful effects, one of which is their major contribution to the greenhouse effect. For instance, in the USA, they generate around 36 % of the annual CO$_2$ emissions. Hence carbon capture systems are important for reducing the environmental impact of coal-fired power plants.

There are three different carbon capture systems: oxy-fuel combustion, pre-combustion and post-combustion. Oxy-fuel combustion uses pure oxygen (O$_2$) instead of air to burn the coal, and yields a flue gas that consists mostly of CO$_2$ and Water (H$_2$O). This makes the carbon capture process easier as it does not have to consider other pollutants like NOx. Also, oxy-fuel combustion systems can capture maximum carbon emissions, and can be retro-fitted to already existing plants. Still, obtaining pure O$_2$ from air is a high energy consuming process. In Pre-combustion systems, the fossil fuel reacts with air to produce a synthesis gas mostly composed of hydrogen (H$_2$) and carbon monoxide (CO). Then, CO is converted to CO$_2$. After that, CO$_2$ is captured and H$_2$ undergoes combustion. Pre-combustion systems are very effective since they can capture about 90 % of the CO$_2$ produced, but they cannot be integrated to already existing plants. In post-combustion systems, 95 % of the CO$_2$ can be captured after the fossil fuel reacts with air. Moreover, post-combustion systems can be added to existing power plants. Finally, the post-combustion technology is the closest to commercial, since it is the one that is most widely studied and comprehended. Carbon capture systems can use four different separation techniques: absorption; physical or chemical, adsorption, membrane separation, or cryogenic separation. This paper considers a post-combustion carbon capture system that utilizes chemical absorption as a separation technique because this method has been shown to be the cheapest and most efficient in similar applications.

The carbon capture flow sheet used in this system is shown in Figure 1. The FLUE-GAS containing CO$_2$ enters the absorber where it interacts with the LEAN-IN amine solvent; usually containing an aqueous amine solution and some CO$_2$. A chemical reaction occurs, during which the solvent absorbs a large amount of the CO$_2$ contained in the FLUE-GAS. As for the loaded amine solvent, it leaves the absorber as the RICH-OUT stream and is pumped and heated before it enters the stripper as the RICH-IN stream. Once in the stripper, the loaded amine solvent is further heated using steam to release the absorbed CO$_2$. This is known as solvent regeneration. The CO$_2$ stripped off from the loaded solvent constitutes the CO$_2$-OUT.
stream that is compressed to a pressure appropriate for transfer, and transported in order to be permanently and safely stored. The regenerated solvent is usually cooled and recycled back for reuse. Figure 1 does not show the recycle stream, since adding it in Aspen makes it more difficult for the system to converge. Therefore, the recycle stream is replaced by a design specification that ensures the mole fraction of CO$_2$ in the LEAN-OUT stream is equal to the mole fraction of CO$_2$ in the LEAN-IN stream.

Multiple studies have been performed on post-combustion carbon capture systems. Scientists have come up with different configurations, several organic and inorganic solvents, appropriate operating conditions such as absorber temperature and pressure, stripper temperature and pressure, solvent flow-rate, and distillate flow-rate, and suitable design conditions for example maximum number of trays in absorber or stripper. They have also identified a lot of problems with these carbon capture systems such as corrosion, solvent dissociation, cost burdens, and large energy consumption. This paper attempts to solve some of these problems by looking at different solvents, and performing numerical optimization to reduce the energy penalty imposed by carbon capture systems.

The above objective will be accomplished by performing parametric studies that consist of varying one model parameter while keeping the other parameters constant, and monitoring the change in percent of CO$_2$ captured and stripper reboiler duty. These results will provide the information needed to specify the suitable ranges of variables that will be used to generate the matrix that serves as input data for the CAPE-OPEN SA Capability.

Problem Definition

In a coal-fired power plant that uses a post-combustion carbon capture system, coal and air undergo combustion in a burner and produce flue gas. The flue gas then passes through a desulfurization unit, and after that it enters the absorber which constitutes the first part of the carbon capture system. In the absorber, the flue gas interacts with a solvent. The solvent absorbs a large amount of the CO$_2$ present in the flue gas and then it enters a stripper where it is regenerated. The clean gas is then released into the atmosphere, and the CO$_2$ is properly transported and permanently stored. The objective of this paper is to identify the configuration, design conditions, and operating conditions that minimize the amount of energy consumed by a post-combustion carbon capture system.

The assessed solvents are: Monoethanolamine (MEA), Diethanolamine (DEA), a MEA-DEA mixture, and a new solvent that has been selected using the solubility parameter approach: solvents with solubility parameters close to that of CO$_2$, which is 21.8 MPa$^{1/2}$. A rate based model will be used when experimental data are available: with the MEA, DEA, and MEA-DEA systems. As for the system using the new solvent, an equilibrium model will be used since no experimental data has been collected yet for this particular solvent. Rate based models usually give more accurate results, however they may require more parameters than the equilibrium model. Still, in both cases the following variables will be manipulated in order to observe the system’s responses to change: Lean solvent flow-rate, CO$_2$ loading (moles CO$_2$ / mole MEA), lean solvent temperature, absorber pressure, stripper pressure, reflux ratio, maximum number of trays in absorber, maximum number of trays in stripper, possible feed tray locations in absorber, and possible feed tray locations in stripper. The first six variables listed above constitute continuous variables since they can take any value within a specific range. However, the rest are referred to as integer or discrete variables because they can only take specific integer values. The number of possible combinations that would have to be applied to the system to obtain a minimum energy results can be calculated using the following:

\[ 100^6 \times N_a \times N_s \times N_a! \times N_s! \]

\[ = 100^5 \times 20 \times 20 \times 20! \times 20! \]

\[ = 2.37 \times 10^{51}, \]

where 100$^6$ stands for the 100 samples of each of the 6 continuous variables; $N_a$ is the maximum number of trays in absorber; $N_s$ is the maximum number of trays in stripper; $N_a!$ is the possible absorber feed tray locations; $N_s!$ is the possible stripper feed tray locations.

This shows that it would be impossible to go through these combinations in a reasonable period of time. Thus, SA will be used to obtain a global minimum energy. SA is a probabilistic optimization method that mimics the process of physical annealing. If properly applied, it guarantees obtaining a global minimum and eliminates the risks of getting stuck at a local minimum. So, although this problem has been previously solved using Sequential Quadratic Programming (SQP), SA is definitely a better option. This is because SQP presents higher risks of getting caught at a local minimum. In order to properly apply SA, one has to fully understand how the system operates with each of the solvents, and how it responds to changes in the previously listed variables. This requires performing parametric studies on each specific solvent model.

Parametric Studies

Parametric studies were performed on the Aspen model that uses a 30 weight percent MEA solution as a solvent. One parameter was varied holding all other parameters constant. The constant values were based on the model’s default parameters, which are quite similar to the conditions present in the actual plant. The initial values were:

- Lean solvent flow-rate = 2311 kg / hr
FIG. 2: Temperature profiles for multiple lean solvent flow-rates.

FIG. 3: % CO$_2$ captured for multiple lean solvent flow-rates.

FIG. 4: Stripper reboiler duty for lean solvent flow-rates. Stripper did not converge for a lean solvent flow-rate of 2000 kg/hr.

FIG. 5: Temperature profiles for multiple CO$_2$ loadings.

- CO$_2$ loading = 0.28 moles CO$_2$ / mole MEA
- Lean solvent temperature = 40.2 °C
- Absorber pressure = 1.7 × 10$^5$ Pa
- Stripper Pressure = 2.1 × 10$^5$ Pa
- Reflux ratio = 1 (mass basis)
- Distillate flow-rate = 100 kg / hr
- Number of Trays in Absorber = 20
- Number of trays is Stripper = 20

Varying the flow-rate of the LEAN-IN stream from 2000 to 2900 kg / hr yielded the results shown in Figures 2 - 4.

Figure 2 shows that the exothermic reaction between MEA and CO$_2$ occurs in the intermediate stages of the absorber, leading to an increase in temperature. Also, as the solvent flow-rate increases, the maximum temperature attained in the absorber increases. This constitutes a constraint, since a 30 weight percent MEA solution dissociates at 260 °C. So, one should make sure, before selecting the appropriate solvent flow-rate, that the maximum temperature reached does not exceed 260 °C.

Figures 3 and 4 show that as the solvent flow-rate increases, the amount of CO$_2$ captured increases and the stripper reboiler duty increases. Therefore, one should keep in mind that the higher the lean solvent flow-rate, the more the CO$_2$ captured but the more the energy spent and the higher the risk of solvent degradation.

Varying the CO$_2$ loading (moles CO$_2$ / mole MEA) from 0.25 to 0.3 yielded the results shown in Figures 5 - 7. Figure 5 shows that as the moles CO$_2$ / mol MEA decrease, the maximum temperature attained in the absorber increases. This also constitutes a constraint, since a 30 weight percent MEA solution dissociates at 260 °C. So, the LEAN-IN stream cannot have zero moles of CO$_2$ since this will lead to a large increase in temperature.

FIG. 6: % CO$_2$ captured for multiple CO$_2$ loadings.
and possible solvent dissociation. Figure 6 shows that as the moles CO$_2$ / mole MEA decrease the amount of CO$_2$ captured increases. Figure 7 shows that as the CO$_2$ loading increases, the stripper reboiler duty decreases and then becomes constant. This is because the energy in the stripper is being used to strip the CO$_2$ off the solvent, and to remove some of the water from the RICH-IN stream in order to retain the 30 weight percent MEA solution. One has to keep in mind that the mole fraction of CO$_2$ in the LEAN-OUT stream is equal to the mole fraction of CO$_2$ in the LEAN-IN stream. Therefore, even if less CO$_2$ needs to be stripped off at higher CO$_2$ loadings, which means less energy spent on stripping, the same amount of energy needs to be spent on water removal. This explains the steady curve starting at 0.27 moles CO$_2$ / mole MEA.

Varying the temperature of the LEAN-IN stream from 41 °C to 60 °C yielded the results shown in Figures 8 and 9. Figure 8 shows that as the temperature of the lean solvent entering the absorber increases, the amount of CO$_2$ captured increases reaching a maximum around 54 °C and then decreasing. This can be explained by realizing that the amount of CO$_2$ captured in the absorber is affected by the rate of the reaction occurring between CO$_2$ and MEA, and solubility of CO$_2$ in MEA. In this case, as the temperature increases, the exothermic reaction slows down and the solubility of CO$_2$ in MEA increases. However, this drop in reaction rate starts affecting the system and decreasing the amount of CO$_2$ captured only when the reaction becomes very slow. Figure 9 shows that as the temperature of the lean solvent entering the absorber increases, the stripper reboiler duty decreases. So, in this case, having a LEAN-IN temperature around 55 °C would allow capturing the largest amount of CO$_2$, while maintaining a low stripper reboiler duty.

Varying the number of trays in the absorber from 6 to 20 yielded the results shown in Figures 10 and 11. Fig-
FIG. 12: % CO\textsubscript{2} captured for multiple numbers of trays in stripper.

FIG. 13: Stripper reboiler duty for multiple numbers of trays in stripper.

ure 10 shows that as the number of trays in the absorber increases, the amount of CO\textsubscript{2} captured increases. However, as we approach 20 trays, the number of trays starts having no effect on the amount of CO\textsubscript{2} captured. Figure 11 shows that as the number of trays in the absorber increases, the stripper reboiler duty decreases. The circled area in Figure 11 denotes a numerical error. Varying the number of trays in the stripper from 6 to 20 yielded the results shown in Figures 12 and 13. Figure 12 shows that the amount of CO\textsubscript{2} captured in the absorber is independent of the number of trays in the stripper. Figure 13 shows that as the number of trays in the stripper increases, the stripper reboiler duty decreases. The above parametric studies allow us to understand how our carbon capture system behaves when using a 30 weight percent MEA solution, and how changing certain variables will affect the amount of CO\textsubscript{2} captured by the absorber, and the stripper reboiler duty.

**Optimization Algorithm**

After completing the parametric studies, the CAPE-OPEN SA capability was used to optimize the performance of the system that uses a 30 weight percent MEA solution. The post-combustion carbon capture system is the object of a Mixed Integer Non-linear Programming problem (MINLP). MINLP problems consist of a non-linear objective function, energy in this case, and contain both discrete and continuous variables. These problems can be solved using the Branch-and-bound method, generalized Bender’s decomposition method, outer-approximation (OA) algorithm, variants of OA: equality relaxation, and augmented penalty function, and probabilistic methods: simulated annealing and genetic algorithms.\textsuperscript{5} In this paper simulated annealing is used to solve the MINLP problem. Simulated annealing is a probabilistic method that mimics the process of physical annealing.\textsuperscript{5} Physical annealing comprises heating of a material followed by controlled cooling, which allows the atoms to move from an initial high energy configuration to a final low energy state. If this algorithm is properly formulated, a global minimum will certainly be obtained. Applying SA requires:

1. Specifying the objective function, which is the energy, expressed in terms of stripper reboiler duty, in this case.

2. Identifying the binary and discrete variables: The carbon capture system has continuous and discrete variables, but no binary variables. The continuous variables need to be discretized by specifying an acceptable range of values for each one.

3. Listing the equality and inequality constraints besides the ones that are already accounted for by Aspen Plus such as the material balance and the reaction kinetics.

4. Selecting an initial temperature and a freezing temperature, keeping in mind that temperature represents a parameter.

5. Choosing a temperature decrement that is neither too small in order for the optimization not to require too much processing time, nor too large to minimize the risks of getting caught at a local minimum.

The temperature decrement that will be used is:\textsuperscript{5}

\[ T_{\text{new}} = \alpha \cdot T_{\text{old}} \]  

All of the above will be used in the SA algorithm, which obtains the global minimum in the following way:

1. A configuration space, containing the values of all the variables, is defined: Supposing the problem has two continuous variables, which is not the case here, Figure 14 would represent the configuration space where each point constitutes a configuration.

2. A move generator, that picks a path based on probability is defined: Assuming the algorithm starts evaluating the objective function at point A shown in Figure 14, the move generator will decide if the next evaluated point will be A, B or C.

\[ T_{\text{new}} = \alpha \cdot T_{\text{old}} \]
3. A certain number of moves are performed at every temperature. The objective function is evaluated at every configuration.

4. A move is made to the next temperature when the number of specified moves, at the previous temperature, is completed, or when a plateau is reached i.e. multiple equal values for the objective function are obtained.

5. The lowest objective function, obtained at every temperature, is selected. Eventually, the minimum objective function is obtained at the freezing temperature.

The CAPE-OPEN SA capability is programmed to perform all of the above. A detailed User Manual can be obtained by writing to its Author, Urmila Diwekar.

Optimization Results

The CAPE-OPEN SA capability did not function properly in Aspen Plus V7.2, therefore Aspen Plus 2006.5 was used to properly complete the optimization. Figure 15 is a summary of the SA application to the carbon capture system. It shows the initial conditions, the lowest cost obtained at every temperature level (TL) and the final minimum energy.

Figure 15 shows that the optimal cost obtained is 112,157 Watts. Comparing the minimum calculated energy to the initial cost of 239,383 Watts shows that the minimum energy is 127,208 Watts less than the initial energy.

Moreover, the following optimal conditions were obtained:

- Stripper reflux ratio : optimum at 0.017
- RICH-IN Pressure : optimum at 1.05 atm
- LEAN-IN Temperature: optimum at 42.28°C
- Moles CO₂ / Mole MEA: optimum at 0.25
- Stripper feed stage: optimum at stage 6

Conclusion

SA is an extremely essential tool for identifying the best configurations, design conditions, and operating conditions that would improve the efficiency of the carbon capture systems. Similar parametric studies and optimization should be performed on the systems using DEA, MEA-DEA mixture, and the new solvent.

Acknowledgements

We would like to thank the National Science Foundation, Division of Engineering Education and Centers ENG Directorate for Engineering (ENG-1062943) for their funding, P and Drs. Takoudis and Jursich for making this research experience so beneficial and fun.