ASSESSING THE PERFORMANCE OF ASPEN PLUS AND PROMAX FOR THE SIMULATION OF CO₂ CAPTURE PLANTS

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In Partial Fulfillment of the Requirements
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by
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Fakhteh Sadat Ahmadi, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Assessing the Performance of Aspen Plus and Promax for the Simulation of CO₂ Capture Plants*, in an oral examination held on April 23, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

Carbon dioxide is a prominent greenhouse gas whose emissions have significantly increased due to human activities. Fossil fuel-fired power plants are the largest source of CO\textsubscript{2} emissions, which results in a need for CO\textsubscript{2} capture at these power plants. Prior to building a large scale CO\textsubscript{2} capture plant, a pilot or demonstration plant is set up to confirm the feasibility of the plant. Simulation techniques are needed before actually constructing the plant, in order to improve the reliability and to increase productivity. A number of simulation software tools have been developed and are widely used to complete the simulation of a power plant integrated with a CO\textsubscript{2} capture plant. Therefore, the capability of the software to model and simulate the plant correctly, and to generate accurate and reliable results, is of particular importance.

In this work, the performance of two of the most commonly used process simulators for CO\textsubscript{2} capture, namely ASPEN Plus and PROMAX, was evaluated and compared. In order to achieve this goal, eight data series from two CO\textsubscript{2} capture pilot plants were selected and simulated with the above-mentioned simulators. The pilot plant data came from the International Test Centre for CO\textsubscript{2} Capture (ITC) and the Esbjerg CO\textsubscript{2} from Capture to Storage (CASTOR) project. Simulations were compared to experimental results using several parameters, including CO\textsubscript{2} recovery, lean and rich loadings, steam and heat duties, CO\textsubscript{2} percentage in the product stream, and the temperature and concentration profiles in the columns. Results showed that both software packages could predict the behavior of the system accurately and generate reliable results. The obtained results showed that in most cases, particularly in predicting the absorber and stripper profile
along the column, PROMAX generated results that were closer to the actual experimental data, when compared to ASPEN.
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- Dr. Hallvard F. Svendsen for providing the Esbjerg CASTOR plant data.
- Dr. Raphael Idem and Dr. Amr Henni, for the valuable technical discussions.
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Dedication

To my beloved parents and family.
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CHAPTER 1: INTRODUCTION

1.1 Greenhouse Gases and CO₂ Emission

Global warming, a recent temperature increase of the Earth's surface and lower atmosphere, is a result of the greenhouse effect. Human activities such as deforestation and burning fossil fuels are the most significant reason for the increased concentrations of greenhouse gases (GHGs).

There are several greenhouse gases that are present in the atmosphere, primarily water vapor, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), sulphur hexafluoride (SF₆), perfluorocarbons (PFCs), and hydrofluorocarbons (HFCs) (Derakhshanfar et al., 2011). The atmospheric concentrations of carbon dioxide, methane and nitrous oxide have been increased significantly as a result of human activities since 1750 (IPCC, 2005).

For clear skies, water vapor is the most prominent greenhouse gas, accounting for 60% of the total radiative contribution. The second most important greenhouse gas is CO₂, with a contribution of 26% (Kiehl and Trenberth, 1997). Because the human contributions to water vapor are negligible, it is not measured as part of anthropogenic greenhouse gas emissions and it is not possible to regulate it.

Therefore, carbon dioxide is considered as the major greenhouse gas that emits both naturally through the carbon cycle and also from human activities. The increasing use of crude oil, natural gas and coal as the main source of power generation globally has caused considerable increase of CO₂ level in the atmosphere (Derakhshanfar et al., 2011). Figure 1.1 shows the contribution of greenhouse gases emissions to the atmosphere.
Figure 1.1- Greenhouse gas emissions by gas, 2009 (percent based on Tg CO$_2$ Eq.) (U.S. Environmental Protection Agency, 2011)
The unit teragrams of CO\textsubscript{2} equivalents (Tg CO\textsubscript{2} Eq) is conventionally used in GHG inventories prepared worldwide. One teragram (Tg) is equal to one million metric tons.

Large point sources of CO\textsubscript{2} include large fossil fuel or biomass energy facilities, major CO\textsubscript{2}-emitting industries, natural gas production, synthetic fuel plants and fossil fuel-based hydrogen production plants. The world CO\textsubscript{2} emissions by sector in 2009 were tabulated by the International Energy Agency (IEA) and are presented in Figure 1.2.
Figure 1.2- World CO$_2$ emissions by Sector in 2009 (IEA, 2011a)
In terms of fuels, according to the latest reports by the International Energy Agency (IEA, 2011b), 44% of the estimated CO₂ emissions came from coal, 36% from oil, and 20% from natural gas.

Figure 1.3 shows the growth of CO₂ emissions over the past twenty years. Between 2003 and 2008, emissions rose at a fast rate. The dip in 2009, was caused by the global financial crisis, resulting in a decline from 29.4 billion tons (gigatons, or Gt) CO₂ in 2008, to 29.0 Gt in 2009. However, despite the slow global economic recovery, we recently had the largest single year increase in global human CO₂ emissions from energy (fossil fuels) in 2010, growing a giant 1.6 Gt from 2009, to 30.6 Gt (IEA, 2011b, Skeptical Science, 2011).
Figure 1.3- Observed CO₂ emissions from fossil fuels (Skeptical Science, 2011)
1.2 Carbon Capture and Storage (CCS)

Carbon capture and storage (CCS) is a technique that is used to reduce CO₂ emissions from human activities. It could be applied to emissions from large power plants or industrial facilities.

The process involves three main steps:

1. Capture: Separating CO₂ from other gases produced by an industrial process.
2. Transportation: Captured CO₂ is compressed and transported to a suitable storage location (typically in compressed form).
3. Storage: Transported CO₂ is then stored in geological formations, in the oceans or in mineral carbonates, as a means for preventing its release into the atmosphere (IPCC, 2005).

Fossil-fuel combustion has the most significant portion of CO₂ emissions which is primarily coming from the power generation sector. Three different methods are used for capturing CO₂ from power plants: pre-combustion, Oxyfuel combustion and post-combustion. Post-combustion CO₂ capture using amine-based chemical absorption system is the most common and preferred technology, which is applied these days (Wang et al., 2011). Further details about these technologies follow in Chapter 2.
1.3 Scope of the Work

One of the first steps prior to building a large scale CO₂ capture plant is to confirm the feasibility of the plant by setting up a pilot or demonstration plant. Simulation techniques are needed before actually constructing the plant, in order to improve the reliability and to increase productivity. Although pilot plant tests are important to get a good view for the process design, they are expensive because of the materials and energy consumption. In this case, process simulators are helpful and can be used to complement pilot plant tests and reduce the costs. A number of simulation software tools have been developed and widely used to complete the simulation of a power plant integrated with a CO₂ capture plant.

The goal of this work was to evaluate the performance of two of the most commonly used process simulators for CO₂ capture, namely ASPEN Plus and PROMAX. In this regard, two CO₂ capture pilot plants (the International Test Center for CO₂ capture (ITC) and Esbjerg CASTOR pilot plant) were selected, and eight different data series were simulated.

The performance of ASPEN and PROMAX were evaluated by comparing the simulation results to the experimental data, which included plant recovery, lean and rich loadings, heat duties, absorber temperature and concentration profiles, and stripper temperature profile.
CHAPTER 2: LITERATURE REVIEW

2.1 Current Status of CCS

Today, available technologies can capture about 85–95% of the CO$_2$ at an industrial facility. A power plant with a CCS system (with access to geological or ocean storage) would need roughly 10–40% more energy (11–22% in Natural Gas Combined Cycle plants, 24–40% in Pulverized Coal plants, and 14–25% in Integrated Gasification Combined Cycle plants) than a plant of equivalent output without CCS, and most of that extra energy is for capture and compression (IPCC, 2005).

Challenges that CCS technologies face in order to be a full-scale demonstration and commercial deployment include issues such as: financing large-scale projects and integration of CCS into GHG policies, the higher cost and efficiency penalty of CCS technologies, the development and financing of adequate CO$_2$ transport infrastructure, the development of legal and regulatory frameworks to ensure safe and permanent CO$_2$ storage, adequate public consultation, and developing capacity and awareness in rapidly growing fossil-based economies. There is a large and growing body of work underway to address these issues at the international and national levels. However, the critical next step is to verify the performance of CCS at scale, with capture from a variety of different industries and storage in a variety of geologic settings.

Some of the technologies needed for the CCS process are more developed than others. Table 2.1 indicates the maturity of the CCS components.
**Table 2.1**- Current maturity of system components for the CCS. The X indicates the highest level of maturity for each component (IPCC, 2005)

<table>
<thead>
<tr>
<th>CCS component</th>
<th>CCS technology</th>
<th>Research Phase</th>
<th>Demonstration phase</th>
<th>Economically feasible under specific conditions</th>
<th>Mature market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capture</td>
<td>Post-combustion</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pre-combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxyfuel combustion</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Industrial separation (natural gas processing, ammonia production)</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Transportation</td>
<td>Pipeline</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shipping</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Geological storage</td>
<td>Enhanced Oil Recovery (EOR)</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas or oil fields</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saline formations</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Enhanced Coal Bed Methane recovery (ECBM)</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Ocean storage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Mineral carbonation</td>
<td>Natural silicate minerals</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Waste materials</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Industrial uses of CO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>
To date, only a few fully-integrated, commercial-scale CCS projects are in operation (see Table 2.2). Due to a number of technological, infrastructure, cost and legal challenges, CCS has not yet been applied to large-scale power generation plants.

Table 2.2- Large-scale CCS Projects (IEA, 2009, National Mining Association, 2011)

<table>
<thead>
<tr>
<th>Project</th>
<th>Operator</th>
<th>From</th>
<th>Geological reservoir</th>
<th>Injection start date</th>
<th>Injection rate (Million tons of CO₂ per year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sleipner West (Norway)</td>
<td>Statoil and IEA</td>
<td>natural gas field</td>
<td>Saline formation</td>
<td>1996</td>
<td>1.00</td>
</tr>
<tr>
<td>Weyburn CO₂ Flood Project (Canada)</td>
<td>EnCanada and IEA</td>
<td>EOR</td>
<td>Oil pools</td>
<td>2000</td>
<td>1.75</td>
</tr>
<tr>
<td>In Salah (Algeria)</td>
<td>Sonatrach, BP and Statoil</td>
<td>natural gas production</td>
<td>depleted gas reservoirs</td>
<td>2004</td>
<td>1.00</td>
</tr>
<tr>
<td>K12B (Netherlands)</td>
<td>Gaz de France</td>
<td>natural gas</td>
<td>depleted natural gas reservoirs</td>
<td>2004</td>
<td>0.20</td>
</tr>
<tr>
<td>Snohvit (Norway)</td>
<td>Statoil</td>
<td>gas production</td>
<td>beneath the sea bed</td>
<td>2008</td>
<td>0.70</td>
</tr>
<tr>
<td>La Barge (Wyoming)</td>
<td>ExxonMobil</td>
<td>gas production</td>
<td>depleted gas reservoirs</td>
<td>2008 2010</td>
<td>4.00 6.00</td>
</tr>
</tbody>
</table>
2.2 CO₂ Capture Technologies

According to Korre et al. (2010) about 86% of global energy utilization and 75% of anthropogenic CO₂ emissions are from fossil fuels.

A fossil fuel-fired power plant is a power station that burns fossil fuels, such as coal, natural gas or petroleum (oil), to produce electricity. The flue gas stream contains CO₂ that can be captured before release into the atmosphere.

One of the major ways of reducing the CO₂ emissions from fossil-fired power generation is to maximize the efficiency of new plants, which are built for replacing older or inefficient plants to meet future demand growth. New plants are designed and operated at highest efficiency.

Three common power generation technologies include Pulverized Coal-fired power plants (PC), Natural Gas Combined Cycle (NGCC) and Integrated coal Gasification Combined Cycle (IGCC). In Pulverized Coal-fired power plants (PC), pulverized coal is combusted with excess air in a boiler and a high-pressure/temperature steam is produced. It burns more rapidly and efficiently because finely ground coal has more surface area per unit weight than larger particles. The steam is then used in a steam turbine to generate electricity. The efficiency depends on steam pressure and temperature (Damen et al., 2006). In Natural Gas Combined Cycle plants (NGCC), natural gas is combusted and the hot flue gas then goes to the turbine, which is driving the air compressor and a generator. A gas turbine generator generates electricity and the waste heat is used to make steam to generate additional electricity, via a steam turbine. The efficiency depends on the turbine inlet temperature (Damen et al., 2006). Lastly,
Integrated coal Gasification Combined Cycle (IGCC) is a combination of two technologies:

- Coal gasification, using coal to create a clean-burning gas (syngas).
- Combined-cycle, an efficient method of producing electricity from gas. A gas turbine generator generates electricity and the waste heat is used to make steam to generate additional electricity via a steam turbine.

IGCC allows for the reduction of NO\textsubscript{x} and SO\textsubscript{2} emissions, and to improve the fuel efficiency of coal combustion.

Three different methods are used for CO\textsubscript{2} capture with the power generation systems: Pre-combustion, Oxyfuel combustion and Post-combustion. The concentration of CO\textsubscript{2} in the flue gas, the pressure of the gas stream, and the fuel type are important factors in selecting the capture system.

- **Pre-Combustion:** As the name suggests, CO\textsubscript{2} is separated before burning the fuel. The feed is converted to hydrogen and CO\textsubscript{2} through a number of processes. After capturing the CO\textsubscript{2}, the remaining hydrogen can be used for combustion or another purpose (Damen et al., 2006; Wang et al., 2011).

- **Oxyfuel Combustion:** In this process, a fuel like coal is combusted using nearly pure oxygen instead of air. This results in a flue gas mainly consist of CO\textsubscript{2} and water vapor. Cooling the remaining flue gas enables the CO\textsubscript{2} to be separated from the steam, which condenses to water at low temperatures.
• **Post-Combustion**: In post-combustion systems, a primary fuel such as coal or natural gas is mixed with air and burned. The steam is generated at high pressure by using the heat of combustion, and expanded through turbines to produce power. A number of separation technologies can be employed with post-combustion capture such as adsorption, chemical absorption, physical absorption, membranes and cryogenics separation (Korre et al., 2010, Wang et al., 2011).

Due to a low concentration (typically 3-15% by volume) and low partial pressure of CO$_2$ in the flue gas stream, the chemical absorption method for CO$_2$ capture can be applied to remove CO$_2$ from the flue gas (Wang et al., 2011). To date, all commercial post-combustion CO$_2$ capture plants use chemical absorption process with monoethanolamine (MEA)-based solvents (Herzog et al., 2009).

Post-combustion capture is important because it has:

• Good potential for retrofitting: It can be easily retrofitted to the existing power plants without requiring substantial changes in basic combustion technology.

• Flexible operating features: In the other two capture options, if capture fails, the entire plant must shut down due to their integration with power plant. But in a post-combustion system, if the capture plant shuts down, the power plant can still operate.

**2.3 CO$_2$-MEA System**

To date, the most feasible option for the removal of carbon dioxide from coal- and natural gas-fired plants is capturing CO$_2$ by amine absorption and stripping. Monoethanolamine
(MEA) is the proven and most commonly used solvent for this application (Plaza et al., 2010).

In this section, a brief review of the chemistry of the system is provided and the absorption/stripping capture process is explained.

### 2.3.1 Chemistry of the system

The main reactions occurring in the aqueous MEA-CO$_2$ system are (Hilliard, 2008):

\[
\begin{align*}
2 \text{H}_2\text{O} & \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \quad (a) \\
\text{CO}_2 + 2 \text{H}_2\text{O} & \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \quad (b) \\
\text{MEA} + \text{H}_3\text{O}^+ & \leftrightarrow \text{MEA}^+ + \text{H}_2\text{O} \quad (c) \\
\text{MEA} + \text{HCO}_3^- & \leftrightarrow \text{MEACOO}^- + \text{H}_2\text{O} \quad (d) \\
\text{HCO}_3^- + \text{H}_2\text{O} & \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad (e)
\end{align*}
\]

Additional reactions may also occur but these degradation reactions are not considered important in the basic MEA absorption/stripping process for CO$_2$ removal (Liu et al., 1999).

The equilibrium constants for the above reactions are represented by the following temperature function:

\[
\ln K_{eq} = A + B/T + C \ln T + DT \quad (2.6)
\]
$K_{eq}$ is the equilibrium constant which is dimensionless and $T$ is the temperature in K. A, B, C and D are constant parameters and are given in Table 2.2 for each reaction (Austgen and Rochelle, 1989)
Table 2.3- Values of constant parameters for equilibrium constant in CO$_2$-MEA system

(Austgen and Rochelle, 1989)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction a</th>
<th>Reaction b</th>
<th>Reaction c</th>
<th>Reaction d</th>
<th>Reaction e</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>132.899</td>
<td>231.465</td>
<td>2.1211</td>
<td>2.8898</td>
<td>216.049</td>
</tr>
<tr>
<td>B</td>
<td>-13445.9</td>
<td>-12092.10</td>
<td>-8189.38</td>
<td>-3635.09</td>
<td>-12431.70</td>
</tr>
<tr>
<td>C</td>
<td>-22.4773</td>
<td>-36.7816</td>
<td>0</td>
<td>0</td>
<td>-35.4819</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>0</td>
<td>-0.007484</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
2.3.2 Amine CO\textsubscript{2} capture by absorption/stripping

Chemical absorption systems are one of the best options for CO\textsubscript{2} capture from power plants. The typical flowsheet for a CO\textsubscript{2} capture plant is displayed in Figure 2.1. It mainly consists of the absorber, stripper, rich/lean heat exchanger, and the reboiler.

![Figure 2.1- Typical absorption/stripping flowsheet of CO\textsubscript{2} capture plant](image)
The inlet flue gas is cooled before going to the absorber to reach the temperature of around 45-50 °C to improve CO₂ absorption and reduce solvent losses due to evaporation.

The cooled flue gas, with a low CO₂ concentration (typically 3-5% for natural gas and 10-15% for coal combustion), flows through the absorber from the bottom of the column and comes into direct contact with the lean solvent, usually with a CO₂ loading of about 0.1-0.2 mol CO₂/mol MEA. Then CO₂ absorbs into the aqueous amine and the rich solvent leaves the absorber with the loading of about 0.4-0.5 mol CO₂/mol MEA (Freguia and Rochelle, 2003, Khan et al., 2011). The scrubbed gas undergoes a water wash section to remove any solvent droplets and is then vented to the atmosphere (Dave et al., 2009).

For the amine solvents, the lean solvent inlet temperature to the absorber is assumed to be around 40 °C. The lean amine gradually heats up while absorbing CO₂ in the column, resulting in an absorber temperature typically around 40-60 °C (Dave et al., 2009, Wang et al., 2011). Plaza et al. (2010) used absorber intercooling to optimize the process conditions, which reduced the packing height and increased the performance of the absorber allowing for 90% CO₂ removal.

The regeneration of the solvent is carried out in the regenerator (stripper). The rich solvent from the absorber is pumped to the top of the stripper after being pre-heated in a cross heat exchanger by the regenerated lean solvent. Heat is supplied to the reboiler to produce the stripping steam requirement, which is the major energy penalty of the process and is estimated about 15-30% of the net power production of the coal-fired power plant (Oyenekan and Rochelle, 2005, Pellegrini et al., 2011). The reboiler steam requirement for MEA-based processes was typically 4000-4200 MJ/ton CO₂ captured for
coal and natural gas respectively (Svendsen et al., 2011).

The temperature in the reboiler is normally about 120 °C to keep a low amine loading. This means the pressure should be around 1.8-2 bar. Because of the low pressure drop in the stripper, the stripper top’s pressure will also be 1.8-2 bar. Since the partial pressure of CO$_2$ at the top of the stripper is much below this level, the steam pressure is needed to make up this total pressure at the top. The gas leaving the stripper should contain a high fraction of steam. Increased temperature in the stripper helps desorption of CO$_2$ from the solvent and this will reduce the stripping steam requirement, but on the other hand it also leads to higher absorbent degradation rates. A temperature range of 118-125 °C has been found to be a good compromise between degradation rate and steam consumption (Wang et al., 2011, Svendsen et al., 2011).

2.4 Modeling Chemical CO$_2$ Capture Process

2.4.1 Previous works

Process simulators have become an essential tool for process engineers nowadays. By using these simulators, various process modifications can be applied easily in a short time without any large scale testing and money expenditure (Halim and Srinivasan, 2009).

A number of studies have been done on modeling, simulation and optimization of CO$_2$ capture processes. Several commercial and non-commercial programs are available and have been used for this purpose. This includes GateCycle, GT Pro, PROATES, EBSILON, ASPEN Plus, HYSYS, CHEMASIM, PROMAX and ProTreat. Language
codes such as FORTRAN or Visual Basic can also be developed to go along with these software packages. Basically, all the simulators give reasonable predictions for the overall process performance, but some of them are more rigorous.

Tobiesen et al. (2008) validated a rigorous simulation program with data from their in house pilot plant facility. The model is developed in FORTRAN 90 and yielded a predictive tool for CO₂ removal from flue gases with MEA. They used advanced numerical techniques to develop a gas/liquid interface model based on the penetration theory. The following assumptions were made to create the model: the flow regimes in both phases are highly turbulent so the radial gradients in concentration and temperature along the tower are negligible; all reactions take place in the liquid phase; the gas film is assumed to be steady for all interfacial mass transfer models.

Comparing the results obtained from the model to the experimental data gave the total absolute standard deviation of 20.58% with a relative absolute deviation of 22.6%. The temperature profiles of simulation and experimental data, which are important because they show how the absorption takes place through the absorber, matched well at lower loading ranges while they had larger deviations for higher loadings (above 0.4).

A simulation-optimization framework to evaluate a CO₂ capture process from flue gas using diethanolamine (DEA) solvent was proposed by Halim and Srinivasan (2009). HYSYS was used as the modeling tool. The amines property package was selected as the thermodynamic model, using tray column for the absorber and stripper with equilibrium stages. Amine flowrate, concentration and reboiler temperature were considered as the variables to simultaneously optimize two objective functions- maximization of CO₂
capture and minimization of cost. With the model they showed that for 80-93% of CO$_2$ removal, the cost would be between $52 and $68 per tonne of captured CO$_2$.

Luo et al. (2009) used sixteen data sets from four different pilot plants (The Esbjerg CASTOR pilot plant in Denmark, ITC pilot plant at University of Regina, The University of Keiserslautern mini plant and The SINTEF/NTNU pilot rig) to validate a set of both commercial and in-house simulators. All cases were using conventional CO$_2$ capture system using 30 wt% MEA. ASPEN Plus, Protreat, PROMAX and in-house codes CHEMASIM from BASF SE and CO2SIM from SINTEF/NTNU are the simulators were chosen for their work.

ASPEN Plus is the most used process modeling software and has been used widely for simulating CO$_2$ capture plants. Lots of work has been done by researchers using this software to validate their models, optimize their plants or for cost estimation. Freguia and Rochelle (2003) chose ASPEN Plus as a framework to model a CO$_2$ removal process. Both the absorber and stripper were modeled with a rate-based model called Ratefrac. The simulation was not closed loop as it was kept open at the absorber inlet. The reactions in absorber were described with a kinetic model while the reactions in stripper were set to equilibrium due to the higher temperature. The consistency of the rate model in the absorber was achieved using the e-NRTL thermodynamic framework by integrating with the interface-pseudo-first-order (IPFO) model for mass transfer, through a FORTRAN user kinetic subroutine. The validation of the model showed 10 to 30% over-prediction for the reboiler duty and up to 4% under-prediction for CO$_2$ removal.
Kucka et al. (2003) suggested a rigorous rate-based model for reactive sour gas absorption by aqueous amine solution. In this model resistances to mass and heat transfer were considered according to the two-film theory and each of the gas and liquid phases was balanced separately. The acceleration of mass transfer was also taken into account due to a complex system of chemical reactions in the liquid phase without applying an enhancement factor concept. For the system thermodynamics, the electrolyte-NRTL method was applied for the liquid phase while the Soave-Redlich-Kwong equation of state was used for the gas phase due to non-ideality of this phase.

The model was implemented into the ASPEN Custom Modeler and then validated by two data sets taken from literature pilot plant data for CO₂ absorption by aqueous MEA solution. Good agreement between experimental and simulated data showed a good predictivity of this model for pilot plant data and also industrial scale applications.

The decomposition approach was used by Alie et al. (2005) to simulate the entire CO₂ capture process flow sheet. In this approach a standalone absorber was simulated with different column heights and inlet solvent loadings, while the CO₂ recovery was kept constant as a target. The next step was to simulate a standalone stripper using the inlet stream conditions obtained from the absorber. For the stripper, the reflux ratio and feed ratio were varied to maintain a fixed loading in the lean MEA recycle and 98% CO₂ purity in the overhead stream.

Simulations were performed in ASPEN Plus using the RATEFRAC unit operation model, a rigorous model with a nonequilibrium tray approach, for both the absorber and stripper. The similar results from decoupled and integrated process simulations illustrated the
validity of this approach. Sensitivity analyses for the reboiler duty were also provided. Increasing the lean loading up to 0.3, higher temperature of the lean MEA stream to the stripper and increasing the trays number were the factors that lead to a decrease in steam duty.

Lawal et al. (2009) compared two different approaches for modeling the absorber, the equilibrium stage versus a rate-based model, and also studied the effect of disturbances in the stripper on the absorber behavior is also investigated. ASPEN Plus was used to develop the equilibrium-based approach while the rate-based model was implemented in gPROMS. The models were validated using data from the University of Texas at Austin. Comparing temperature profiles and MEA loadings from the experiment and simulations showed that the rate-based model yielded better predictions and can be a more reliable approach for absorber modeling.

The CO₂ capture plant at university of Texas at Austin was modeled with ASPEN RateSep, a second generation rate-based multistage separation unit operation model in ASPEN Plus (Zhang et al., 2009). It showed an excellent match with the experimental data and the superiority of the rate-based models over the equilibrium-stage models. The study concluded that ASPEN RateSep with proper model parameters successfully simulated the University of Texas-Austin pilot plant, and it can be a very useful tool for the design of CO₂ capture processes.

A new MEA model in ASPEN Plus RateSep was developed by Plaza et al. (2010) in which they used a rigorous thermodynamic model by Hilliard (2008) and kinetics extracted from Aboudheir (2002). This model was validated with experimental data from
pilot plant runs at the University of Texas at Austin. The absorber model gave good results with an error of 1% for the loadings and CO$_2$ removal, and 2 to 8°C off the reported value for the temperature profile. For the stripper, all regressions failed to produce close agreement initially, but after specifying heat duties to account for heat loss the model and experiment matched well with an average deviation of 3.8%.

Dugas et al. (2009) created an ASPEN Plus RateSep absorber model to simulate 12 runs from the CO$_2$ capture pilot plant in the CASTOR project. The study showed that the model is capable of simulating the CASTOR pilot plant absorber performance for wide range of lean solvent conditions. The temperature and CO$_2$ concentration profiles were fairly accurate when comparing to the experimental data. The authors concluded that since they did not use any fitting parameters to match the results to the pilot plant, the ASPEN RateSep absorber model can be a reliable tool to predict CO$_2$-MEA capture performance for different operating conditions.

PROMAX® process simulation software from Bryan Research & Engineering has also been used recently for the CO$_2$ capture process. At the ITC, most of the researchers are using PROMAX to model CO$_2$ capture. The researchers found that the PROMAX simulation results are closer to the experimental values, in comparison with ASPEN.

Liang et al. (2011) validated CO$_2$ capture process from four existing pilot plants (the International Test Center of CO$_2$ capture (ITC), the Esbjerg CASTOR, the Institute of Thermodynamics and Thermal process engineering, Stuttgart and the SINTEF/NTNU pilot plant), using PROMAX. Almost all the parity plots of CO$_2$ concentration, reboiler heat duty, CO$_2$ mass balance and temperature profile between simulation and experiment
have $R^2$ values greater than 0.8, indicating a good agreement between the model and experimental results.

### 2.4.2 Modeling tools

Reviewing the previous work on simulating CO$_2$ capture plants shows that most people have used ASPEN Plus as a simulator program (See Table 2.4).

**Table 2.4-** Modeling tools used for the simulation of CO$_2$ capture processes

<table>
<thead>
<tr>
<th>Author</th>
<th>Modeling Tool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freguia &amp; Rochelle (2003)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Kucka et al. (2003)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Alie et al. (2005)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Tobiesen et al. (2008)</td>
<td>FORTRAN 90</td>
</tr>
<tr>
<td>Halim &amp; Srinivasan (2009)</td>
<td>HYSYS</td>
</tr>
<tr>
<td>Lawal et al. (2009)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Zhang et al. (2009)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Dugas et al. (2009)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Plaza et al. (2010)</td>
<td>ASPEN</td>
</tr>
<tr>
<td>Liang et al. (2011)</td>
<td>PROMAX</td>
</tr>
</tbody>
</table>

The use of PROMAX in industry has been growing over the past decade. Alstom Power, American Electric Power, E.ON UK, RWE Npower, Tata Power and Southern Company Services are industrial companies using PROMAX for CO$_2$ capture projects.
2.4.2.1 ASPEN Plus

ASPEN Plus is a process modeling tool for design, optimization, and performance monitoring for different industries such as chemical, polymer, metals and minerals, and coal power plants. ASPEN Plus is a core element of ASPENTech’s ASPENONE® Engineering applications.

According to their corporate website, some of the most important features in ASPEN Plus are (Aspen Plus, 2011):

- By updating data from the U.S. National Institute of Standards and Technology (NIST), process engineers can access to the best available experimental property data easily and save months of effort when developing chemical process models. The software includes the largest database of pure component and phase equilibrium data for conventional chemicals, electrolytes, polymers, and solids.

- Because the software is integrating with ASPENTech’s industry-leading cost analysis software and heat exchanger design software, the relative costs of proposed designs can be estimated rapidly based on capital and operating cost estimates. Fundamental equipment such as distillation columns and heat exchangers can be rigorously sized within the simulation environment.

- Having a library of more than 300 different types of packings and 5 tray types with fitted parameters provides a flexible design environment for process engineers.
• By using rate-based distillation technology, ASPEN Plus enable users to do the distillation calculations by applying rigorous mass transfer on trays or on packings. This technology has been used for amines-based carbon capture processes and also other separations.

• It can be linked to Microsoft Excel® using ASPEN Simulation Workbook or Visual Basic®.

**ASPEN Rate-Based Distillation**

ASPEN Rate-Based Distillation, called ASPEN RateSep, is a second-generation rate-based technology that extends the functionality of the ASPEN Plus® RadFrac distillation model and includes more accurate predictions for more ranges of operating conditions. ASPEN RateSep eliminates the need for efficiency factors or HETPs with using state-of-the-art mass and heat transfer correlations to predict column performance.

Some features of ASPEN Rate-based are:

• Using the extensive databases of pure component and also phase equilibrium data.

• Providing reactive distillation, including electrolytic, equilibrium, and kinetic reactions.

• Full set of interfaces to link in user-defined correlations for transfer coefficients, pressure drop, interfacial area, and kinetics.

• Offering design mode, which allows users to calculate column diameter based on the approach to flooding.
Benefits:

The benefits that customers have reported for ASPEN RateSep are given below:

- Reducing the capital expenditure by more than 10%.
- Improving the model accuracy significantly by generating the Rete-based distillation model compared to an equilibrium-based model.
- Improving ROI (Return of Investment) and better investment decisions by reducing the risks of inadequately sizing key columns (ASPEN Plus, 2011)

2.4.2.2 PROMAX

PROMAX is a powerful process simulation package that is used by engineers to design and optimize gas processing, chemical, and refining facilities.

According to their website, PROMAX contains over 2300 components, over 50 thermodynamic package combinations and crude oil characterization (Bryan Research & Engineering Inc., 2011). It also has specifiers, solvers, and Microsoft Excel® spreadsheet embedding. They are all offered by PROMAX with amazing flexibility and ease of use.

PROMAX’s predecessors, TSWEET and PROSIM, have been used by industry for over the past 30 years and are widely recognized because of their accuracy and efficiency. With PROMAX, Bryan Research & Engineering, Inc. (BR&E) has focused on several key processes such as amine sweetening, glycol dehydration, equipment rating/sizing, crude oil refining, LPG/NGL recovery & fractionation, and caustic treating. BR&E continues to build on its reputation as a proven leading provider of simulation
technology. PROMAX is a great simulation resource for engineers throughout the oil, gas and chemical industries because it is created by engineers for engineers.

**Amine Sweetening**

BR&E has now incorporated TSWEET into PROMAX to serve the clients in a better way. Before that, TSWEET was known and used for simulating amine sweetening facilities. Benefits of PROMAX include more complete thermodynamic models, calculation of more thermo-physical properties, and better integration with hydrocarbon packages and unit operations. They allow you to model more complex processes such as absorber/stripper configurations, oils in amine units and three-phase flashes. The amine solvents such as MEA, DEA, DGA, MDEA, DIPA, TEA, and AMP are available individually or as blends. PROMAX introduces BR&E’s new Electrolytic-ELR model, which is a significant improvement to the NRTL model in TSWEET. The sweetening package also has the TSWEET’s ability, which is modeling selective absorption by using CO$_2$ kinetics (Bryan Research & Engineering Inc., 2011).

**Benefits:**

- Any amine unit configuration can be modeled virtually.

- Amine solutions-acid gas VLE (Vapor-Liquid Equilibrium) can be predicted along with the actual plant data.

- Real or ideal stages in absorbers and strippers can be modeled properly.

- The type of amine, amine flow rate, and reboiler duty can be optimized.
CHAPTER 3: METHODOLOGY

3.1 ITC Pilot Plant

The International Test Center for CO\textsubscript{2} Capture (ITC) is located on the campus of the University of Regina, Canada. The ITC vision is to focus on developing technologies for capturing CO\textsubscript{2} from flue gases through research and demonstration of a range of amine-based solvent scrubbing. The major goal of the First Phase of the Centre's research was to establish baseline conditions and results for CO\textsubscript{2} capture with MEA and then investigate cost improvements for the base process. Mixed amine solvents were examined later to investigate cost/energy optimization (ITC, 2011).

The ITC pilot plant is operated to capture CO\textsubscript{2} from flue gas that is generated by a natural gas boiler. The plant includes two packed columns that operate as the absorber and stripper. The absorber is comprised of three packed sections with a total packing height of 6.55 m and diameter of 0.30 m. On the top of the absorber is a water wash section to cool down the gas in order to minimize MEA loss. The wash column has the same diameter as the absorber with the height of 2.03 m. The stripper is comprised to two sections with a total packing height of 4.37 m and diameter of 0.30 m. Structured packing (Flexipac 700Y) is used in all the columns. A shell and tube heat exchanger is used instead of a kettle reboiler to supply heat for the stripper.

The ITC pilot plant layouts are shown in Figure 3.1 and Figure 3.2. In 2007, the plant included a reflux stream to the stripper, which was removed for the new design in 2011. The reason for this new configuration is that the temperature of the reflux stream is much
lower than the stripper (30 C and 120 C) and by returning this stream back to the column, the performance of the stripper will decreased. Therefore in the new design of the plant, the reflux stream is returned back to the system directly before the make-up tank, instead of being returned to the stripper (Figure 3.2).

Figure 3.1- ITC pilot plant layout in 2007
Figure 3.2- ITC pilot plant layout in 2011
3.2 Esbjerg CASTOR Pilot Plant

The flowsheet of the Esbjerg pilot plant is shown in Figure 3.3. The plant is located at the Elsam power station in Esbjerg along the West coast of Denmark and treats the flue gas from the 400 MW coal-fired power plant. The absorber consists of four 4.15 m beds of packing while the stripper consists of two 5.00 m beds. Both columns have diameter of 1.1 m and use IMTP50 random packing. A wash water section is located at the top of the absorber with a total packed height of 3.00 m, using MELLAPAK 252Y packing type (Luo et al., 2009, Dugas et al., 2009).

CASTOR, which stands for CO\textsubscript{2} from Capture to Storage, was funded by the European Commission and was carried out by 30 partners including R&D organizations, oil & gas companies, research institutes and universities from 11 European countries. The CASTOR objective was to enable the capture and geological storage of 10\% of European CO\textsubscript{2} emissions, which corresponds to about 30\% of the emissions from power and industrial plants. The project conducted four test campaigns in order to develop and validate the innovative technologies needed for CO\textsubscript{2} capturing in the post-combustion stage and also for CO\textsubscript{2} storage (European Commission, 2007). In January, 2007, Campaign 2 of the CASTOR project was completed, which consisted of 12 runs of CO\textsubscript{2} capture using 30\% MEA with varying solvent flow rates and lean loadings.
Figure 3.3- Esbjerg CASTOR pilot plant layout
3.3 Simulation Modeling

The objective of this work was to compare two of the top software packages for simulating CO₂ capture processes, namely ASPEN and PROMAX, which are used extensively by process engineers. In order to achieve this goal, two CO₂ capture pilot plants were selected for simulation with both software packages. Below is the description of the modeling framework with each simulator. Results are presented in the Chapter 4.

3.3.1 PROMAX Framework

The first step to simulate a process is to select the property package for that process. For amine sweetening, PROMAX presents a model called: Electrolytic Gibbs Excess/Activity Coefficient Model. Gibbs Excess/Activity Coefficient models calculate liquid properties for mixtures rather than pure properties. Electrolytic models are applied for systems in which dissociation of compounds is important (like amine sweetening or systems containing ammonia and an acid gas such as H₂S or CO₂). Therefore, the model is suitable for CO₂ capture processes and can be applied to simulate a CO₂ capture plant.

The available Electrolytic models in PROMAX that are mostly used for CO₂ capture processes are: Amine Sweetening, Electrolytic ELR and Electrolytic NRTL. The Amine Sweetening property package is the same as the Electrolytic ELR based on the Pitzer-Debye-Hückel model (Pitzer and Mayorga, 1974) with significant modifications. Due to recommendations for amine sweetening provided by PROAMX, which can be found in the help section of the software, the Electrolytic ELR-PR package was selected for this work. ELR-PR predicts liquid phase properties by the Electrolytic ELR model and predicts vapor phase properties using the Peng-Robinson property package, which is an
Equation of State (EOS) model and is similar to the Redlich-Kwong EOS. It can model light and heavy hydrocarbon systems, including systems that form a separate aqueous liquid phase or hydrates. Systems containing glycols, water, propylene carbonate and oils can be modeled using Peng-Robinson. It can also predict hydrate formation, water freezing point, and CO$_2$ freeze out. For supercritical fluids, the density of the fluid phase is closer to measured values than that of SRK. Peng-Robinson can be used for nearly pure CO$_2$ systems, even in the critical region (SRK is not recommended for this application).

TSWEET Kinetics was selected as a column type for absorber and stripper. It estimates the kinetic effects based on the residence time on a stage and calculates simultaneous distillation and chemical reaction to account for the CO$_2$-amine reaction rate.

To validate the model with the experiments, the recovery of the system was kept the same as that in the plant and the rich and lean loadings, temperature and concentration profiles, steam duty, and %CO$_2$ in the product were compared with the experimental results.

Figure 3.4 represents the simulation flowsheet that was simulated in PROMAX.
Figure 3.4- PROMAX simulation flow sheet of CO₂ capture plant
3.3.2 ASPEN Framework

ASPEN Plus provides many data packages to model important industrial processes. These data packages have been developed using publicly available literature data and will be updated as new data becomes available. It includes special data packages for amines systems: MDEA, DEA, MEA, DGA and AMP.

These packages allow users to accurately model amine gas treating processes by using the electrolyte capabilities and by also considering CO$_2$ kinetic reactions in the liquid phase.

For MEA-CO$_2$ system with the temperature up to 120 °C, the KEMEA data package is suggested by ASPEN (ASPEN Technology, Inc., 2000) and so selected for this work. This data package uses ELECNRTL as a property method. ELECNRTL uses Electrolyte NRTL for the liquid phase activity coefficient method, which reasonably represents the physical interactions of species in an aqueous multicomponent electrolyte solution. For the vapour phase, ELECNRTL uses the Soave-Redlich-Kwong model for determining the fugacity coefficient, in which the non-idealities of the gas phase are taken into account. ELECNRTL is recommended by ASPEN for rigorously modeling electrolyte systems such as acid gas absorption with amines.

For the system with chemical reactions the default base property method is NRTL, which contains wide applications for low-pressure ideal and non-ideal chemical systems. If the process involves electrolyte reactions, the NRTL method will be replaced by ELECNRTL and the Electrolytes Wizard should be used to define the reactions and ionic species. By using the KEMEA, there is no need to define the reactions for the MEA-CO$_2$
system, since the data package includes all of the equilibrium reactions and kinetics of the system for the whole simulation itself.

The traditional way of modeling absorption and desorption columns is using the equilibrium model. In this model the column is divided into a number of stages and it assumes that the vapor and liquid phase leaving a stage are at equilibrium (Treybal, 1981). This assumption is used to simplify the modeling and rarely happens in reality. The departure from equilibrium is corrected by applying tray efficiency like the Murphree efficiency for tray columns or the height equivalent to a theoretical plate (HETP) for packed columns (Peng et al., 2002). For reactive separation processes, the deviations from the equilibrium model are very large and the use of efficiencies does not work well (Aspiron, 2006). Hence, rate-based models are suggested for modeling these systems. This model assumes that the vapour-liquid equilibrium occurs only at interface

In this work, the RadFrac distillation model was used to model the absorber and stripper columns. It is a rigorous model for simulating absorption and stripping where chemical reactions are occurring. The rate-based mode of RadFrac, called ASPEN RateSep, allows for the rate-based modeling of absorption and desorption columns and uses the two-film theory in mass and heat transfer models. It also provides a number of options for film discretization. To describe the accelerating effect of chemical reactions on mass transfer, a subdivision of the liquid film into several regions is necessary. The Discrnxn option was chosen for the liquid film since there are rapid reactions occur in the liquid film for the MEA system. This is the most robust of the methods that ASPEN offers to consider
reactions in the film and is the most applicable one when the reactions are fast. The *Film* option was chosen for the vapour film, since there no reactions occur in the vapour phase.

Mixed flow was selected as a flow model in this work. In this model, the bulk properties for each phase are same as the outlet conditions of that phase when it leaves that stage (Kothandaraman, 2010). This model is also the default flow model in ASPEN RateSep.

Table 3.1 shows the property models used in PROMAX and ASPEN.

**Table 3.1- Property models used in PROMAX and ASPEN**

<table>
<thead>
<tr>
<th></th>
<th>PROMAX</th>
<th>ASPEN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calculation Type</strong></td>
<td>TSWEEt Kinetics</td>
<td>Rate-based Model</td>
</tr>
<tr>
<td><strong>Property Package</strong></td>
<td>Electrolytic ELR-PR</td>
<td>ELECNRTL</td>
</tr>
<tr>
<td><strong>Liquid Phase Property Model</strong></td>
<td>Electrolytic ELR</td>
<td>Electrolyte NRTL</td>
</tr>
<tr>
<td><strong>Vapor Phase Property Model</strong></td>
<td>Peng-Robinson</td>
<td>Redlich-Kwong</td>
</tr>
</tbody>
</table>

Unlike PROMAX, the packing height for absorber and stripper can be defined in ASPEN, and we can compare the recovery of the model to the experiment like other parameters. In PROMAX, the height of the column cannot be defined and the recovery would change with different residence times and different number of stages. Therefore, we need to try and obtain recovery results that are close to the experimental values by changing these parameters and then compare the loadings and other parameters.

Simulations were done without any problem in PROMAX, but in ASPEN the closed loop could not converge. Therefore, the simulation was kept open at the absorber inlet and the lean solvent became an input to the model. In this case the simulation was running until
the specifications of the streams LEAN-1 and LEAN-2 (shown in Figure 3.2) got fairly close. This condition is close to the closed loop system and was applied for all of the simulations. Figure 3.6 shows the ASPEN simulation flowsheet.
Figure 3.5 - ASPEN simulation flow sheet of CO$_2$ capture plant
3.4 Experimental Data from Pilot Plants

To compare the simulation performance of PROMAX and ASPEN, 8 different sets of data were selected. Four runs were used from the CASTOR project (Campaign 2) and four runs were used from the International Test Center for CO₂ Capture (ITC). The CASTOR project runs had varying liquid flow rates and solvent lean loadings. The ITC runs came from two different plant configurations (2007 and 2011). All the used data were generated from a conventional CO₂ capture process with the chemical absorption, using an approximately 5 M (30 wt%) monoethanolamine (MEA) solvent.

The results of each run are presented in the next chapter. For more convenience the experimental data used for each simulation are given at the beginning of each section.
CHAPTER 4: RESULTS AND DISCUSSIONS

Four data sets from CASTOR pilot plant and four from ITC pilot plant were simulated using PROMAX and ASPEN. The models were validated by comparing the predicted results to the experimental data. This included the comparison of the recovery, the lean and rich loadings, steam and heat duties, CO\(_2\) percentage in the product stream and the temperature and CO\(_2\) concentration profiles in the absorber and the temperature profile in the stripper.

4.1 CASTOR Simulation

Table 4.1 represents the data from Esbjerg plant. Varying solvent flowrates and lean loadings were tested in CASTOR project.

Table 4.1- Experimental data from Esbjerg plant, the CASTOR project

<table>
<thead>
<tr>
<th>Inlet Gas</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (kmol/h)</td>
<td>219.30</td>
<td>222.60</td>
<td>223.93</td>
<td>220.18</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>47.30</td>
<td>47.21</td>
<td>46.86</td>
<td>46.37</td>
</tr>
<tr>
<td>Pressure (kPa(g))</td>
<td>-2.0</td>
<td>-4.0</td>
<td>-4.0</td>
<td>-3.0</td>
</tr>
<tr>
<td>Mole Percent CO(_2) (Dry) (mol% )</td>
<td>13.20</td>
<td>13.13</td>
<td>13.24</td>
<td>11.33</td>
</tr>
<tr>
<td>Mole Percent CO(_2) (mol% )</td>
<td>11.77</td>
<td>11.68</td>
<td>11.81</td>
<td>10.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid Solvent</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (kmol/h)</td>
<td>1005.70</td>
<td>552.62</td>
<td>683.54</td>
<td>756.77</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>40.00</td>
<td>40.00</td>
<td>40.00</td>
<td>40.00</td>
</tr>
<tr>
<td>Lean Loading (mol CO(_2)/mol MEA)</td>
<td>0.275</td>
<td>0.166</td>
<td>0.270</td>
<td>0.224</td>
</tr>
</tbody>
</table>
A good agreement between the simulation values and the experimental data was achieved. In Table 4.2 the results from each case were illustrated.

Comparing the results for recovery showed that the values from PROMAX are closer to the experiment than ASPEN. The reason is, in PROMAX the close recovery to the experiment can be achieved by changing the residence time in the absorber while in ASPEN there is no need to put any fitting parameter to get the close recovery. In Run I, both software packages could not repeat the experimental recovery rate of 89.5%. Interestingly, the maximum recovery in both programs was 81%, which may call into question the accuracy of the reported experimental value.

Lean loading in ASPEN was same as the experiment because it was used as an input to the simulation. As explained in Chapter 3, ASPEN did not converge for a closed loop system hence the simulation was done in an open loop manner that closely resembled the closed loop system. PROMAX also gave fairly close results.

Rich loading values obtained from the simulators are more than the experimental values. Higher loadings mean more CO\textsubscript{2} is absorbed in the column. The explanation could be that in reality the system faces many factors that it does not in the simulation. In a simulation model, everything is considered to be constant in a steady state condition while this is not happening in a real situation. This result could also be due to maldistribution of the liquid through the column, which means liquid is not covering all the packings along the absorber.
The \%CO$_2$ in the product stream coming out off the top of the stripper matches well to the experiment for both ASPEN and PROMAX.

Comparing the heat duties in Table 4.2 shows that the heat needed for stripping in the simulations (both simulators) is less than the experiment. This is because of the heat loss that exists in a real plant but not in the simulation.

Overall, both software package simulations matched very well to the experiment but in comparison, PROMAX even gave more accurate results than ASPEN.
Table 4.2- Results from simulation for CASTOR plant

<table>
<thead>
<tr>
<th>Run I</th>
<th>Experiment</th>
<th>PROMAX</th>
<th>ASPEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>90</td>
<td>90.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.275</td>
<td>0.276</td>
<td>0.36</td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.456</td>
<td>0.469</td>
<td>2.85</td>
</tr>
<tr>
<td>% CO₂ in product</td>
<td>96.9</td>
<td>96.86</td>
<td>-0.04</td>
</tr>
<tr>
<td>Heat Duty, kW</td>
<td>1130.3</td>
<td>1127.84</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run II</th>
<th>Experiment</th>
<th>PROMAX</th>
<th>ASPEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>89.5</td>
<td>81.1</td>
<td>-9.39</td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.166</td>
<td>0.189</td>
<td>13.86</td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.475</td>
<td>0.5</td>
<td>5.26</td>
</tr>
<tr>
<td>% CO₂ in product</td>
<td>96.89</td>
<td>96.83</td>
<td>-0.06</td>
</tr>
<tr>
<td>Heat Duty, kW</td>
<td>1106.21</td>
<td>1104.3</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run III</th>
<th>Experiment</th>
<th>PROMAX</th>
<th>ASPEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>66.3</td>
<td>66.46</td>
<td>0.24</td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.27</td>
<td>0.251</td>
<td>-7.04</td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.471</td>
<td>0.473</td>
<td>0.42</td>
</tr>
<tr>
<td>% CO₂ in product</td>
<td>96.89</td>
<td>96.82</td>
<td>-0.07</td>
</tr>
<tr>
<td>Heat Duty, kW</td>
<td>837.7</td>
<td>834.13</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run IV</th>
<th>Experiment</th>
<th>PROMAX</th>
<th>ASPEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>93.27</td>
<td>93.16</td>
<td>-0.12</td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.224</td>
<td>0.235</td>
<td>4.91</td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.464</td>
<td>0.477</td>
<td>2.8</td>
</tr>
<tr>
<td>% CO₂ in product</td>
<td>96.07</td>
<td>96</td>
<td>-0.07</td>
</tr>
<tr>
<td>Heat Duty, kW</td>
<td>1076.58</td>
<td>1057.35</td>
<td>-1.79</td>
</tr>
</tbody>
</table>
A good model exists if it is able to describe both the temperature and composition profiles along the column, rather than only calculate the values at the top and the bottom. In this regard, the profiles of temperature and concentration are also discussed for all cases. The diamond line (♦) represents the experimental profile while the solid line (—) shows the PROMAX profile and the dashed line (--) shows the ASPEN one, for all the plots in this chapter.

The temperature profile of the absorber from the experimental data and simulations are shown in Figure 4.1 for each run.

The results show that both software packages could simulate the temperature profile. In all cases the PROMAX and ASPEN profiles followed the same trend as the experiment. The place of the temperature bulge was also predicted correctly by both simulators at the top of the absorber. Overall, both software packages predicted the temperature profile behavior in the absorber accurately. But by comparing the results of each run it can be seen that the temperature values obtained from PROMAX is much closer to the experimental values and the profile is more similar.
Figure 4.1 Temperature profile in absorber, CASTOR plant: (a) Run I, (b) Run II, (c) Run III, (d) Run IV
Figure 4.2 shows the concentration profile in the absorber. In Run I, the results from PROMAX matched well with the experiment and showed an accurate profile.

In Run II, both software packages gave similar trend that showed higher concentrations in the upper portions of the column, with more accurate results at the bottom of the absorber.

In Run III, a good agreement between the PROMAX simulation and experimental data was achieved. In this case, like Run I and II, ASPEN predicted higher CO$_2$ concentrations in upper portions of the column compared to the experiment. The experimental results indicate that CO$_2$ is getting absorbed along the column and the concentration decreases in the lower portions, while in the ASPEN simulation the concentration remained high up to the upper stages of the column.

In Run IV, the reported experimental values gave an unusual curve. This is likely due to some experimental errors. ASPAN and PROMAX gave similar concentration profiles.
Figure 4.2  Dry CO$_2$ concentration profile in absorber, CASTOR plant: (a) Run I, (b) Run II, (c) Run III, (d) Run IV.
The profile of the stripper temperature is illustrated in Figure 4.3. The number of data points from the experiment (three) makes it difficult to compare simulation results.

In Run I, the results obtained from both software packages showed good agreements with the experimental data.

In Run III, ASPEN generated a good matching profile while the results from PROMAX gave the same behavior but at higher temperature.

In Run II and IV, the predictions obtained from PROMAX and ASPEN are similar and both show higher temperatures along the column.

The reason of these over-predictions for temperature profile by simulators is the heat loss that exists in a real plant, especially in the stripper.
Figure 4.3  Temperature profile in stripper, CASTOR plant: (a) Run I, (b) Run II, (c) Run III, (d) Run IV
4.2 ITC Simulation

Table 4.3 presents the data from ITC plant. Data for Runs ‘a’ and ‘b’ are from the plant configuration in 2007 and the ones from Runs ‘c’ and ‘d’ are from 2011.

Table 4.3- Experimental data from ITC plant

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet Gas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow Rate (kmol/h)</td>
<td>7.42</td>
<td>7.44</td>
<td>7.43</td>
<td>5.32</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>50.67</td>
<td>48.37</td>
<td>41.40</td>
<td>39.10</td>
</tr>
<tr>
<td>Pressure (kPa(g))</td>
<td>7.3</td>
<td>8.5</td>
<td>10.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Mole Percent CO₂ (mol% )</td>
<td>8.03</td>
<td>8.05</td>
<td>11.20</td>
<td>11.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid Solvent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow Rate (kmol/h)</td>
<td>20.01</td>
<td>20.10</td>
<td>20.30</td>
<td>15.20</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>47.6</td>
<td>37.6</td>
<td>39.3</td>
<td>40.8</td>
</tr>
<tr>
<td>Lean Loading (mol CO₂/mol MEA)</td>
<td>0.275</td>
<td>0.232</td>
<td>0.1902</td>
<td>0.194</td>
</tr>
</tbody>
</table>
The results obtained from simulations for the ITC pilot plant are presented in Table 4.4.

Overall, good agreement was found between the experimental measurements and the model results.

In all cases the recovery from ASPEN and PROMAX matched very well with the experimental value except in Run b, in which ASPEN predicted more recovery (95% instead of 91%).

As explained for the CASTOR results, the lean loading from ASPEN is pretty close to the experimental value. Since Aspen could not run as a closed-loop system, the simulation was kept open at the absorber inlet and the lean solvent became an input to the model. The simulation was running until the specifications of the input lean stream and the outlet lean stream from the make-up tank got fairly close.

Comparing the rich loading results shows that for the first two runs ASPEN gave better results while for Runs ‘c’ and ‘d’ PROMAX had better agreement.

For %CO₂ in the product stream, both software packages generated good predictions, but PROMAX gave better results overall.

The obtained values for heat duty and steam duty from the simulations also matched well with the experimental data.
Table 4.4- Results from simulation for ITC plant

<table>
<thead>
<tr>
<th>Run</th>
<th>Experiment</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>80.83</td>
<td>80.52</td>
<td>-0.38</td>
<td>80.01</td>
<td>-1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.275</td>
<td>0.293</td>
<td>6.55</td>
<td>0.273</td>
<td>-0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.467</td>
<td>0.497</td>
<td>6.42</td>
<td>0.475</td>
<td>1.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%CO₂ in product</td>
<td>97.03</td>
<td>98.03</td>
<td>1.03</td>
<td>96</td>
<td>-1.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Duty, kBtu/hr</td>
<td>67.693</td>
<td>67.846</td>
<td>0.23</td>
<td>68.685</td>
<td>1.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Duty, kg/kg</td>
<td>1.589</td>
<td>1.6</td>
<td>0.69</td>
<td>1.75</td>
<td>10.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run b</td>
<td>Experiment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>91.24</td>
<td>91.1</td>
<td>-0.15</td>
<td>95.96</td>
<td>5.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.232</td>
<td>0.266</td>
<td>14.66</td>
<td>0.231</td>
<td>-0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.453</td>
<td>0.498</td>
<td>9.93</td>
<td>0.477</td>
<td>5.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%CO₂ in product</td>
<td>96.4</td>
<td>96.7</td>
<td>0.31</td>
<td>94.9</td>
<td>-1.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Duty, kBtu/hr</td>
<td>79.743</td>
<td>79.897</td>
<td>0.19</td>
<td>74.461</td>
<td>-6.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Duty, kg/kg</td>
<td>1.65</td>
<td>1.66</td>
<td>0.61</td>
<td>1.67</td>
<td>1.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run c</td>
<td>Experiment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>88.7</td>
<td>88.64</td>
<td>-0.07</td>
<td>87</td>
<td>-1.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.19</td>
<td>0.201</td>
<td>5.63</td>
<td>0.191</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.545</td>
<td>0.514</td>
<td>-5.69</td>
<td>0.497</td>
<td>-8.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%CO₂ in product</td>
<td>96.4</td>
<td>97.13</td>
<td>0.76</td>
<td>97.125</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Duty, kBtu/hr</td>
<td>NA</td>
<td>111.642</td>
<td>-</td>
<td>112.942</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Duty, kg/kg</td>
<td>1.714</td>
<td>1.71</td>
<td>-0.23</td>
<td>1.702</td>
<td>-0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run d</td>
<td>Experiment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
<td>PROMAX</td>
<td>ASPEN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
<td>Value</td>
<td>%Dev.</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>90.7</td>
<td>90.71</td>
<td>0.01</td>
<td>89.91</td>
<td>-0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.194</td>
<td>0.216</td>
<td>11.34</td>
<td>0.194</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich Loading</td>
<td>0.534</td>
<td>0.523</td>
<td>-2.06</td>
<td>0.498</td>
<td>-6.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%CO₂ in product</td>
<td>97.9</td>
<td>97.7</td>
<td>-0.2</td>
<td>97.7</td>
<td>-0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat Duty, kBtu/hr</td>
<td>NA</td>
<td>77.969</td>
<td>-</td>
<td>78.877</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Duty, kg/kg</td>
<td>1.637</td>
<td>1.632</td>
<td>-0.31</td>
<td>1.651</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The temperature profile of the absorber is shown in Figure 4.4. Both software package simulations followed the same trend as experiment did. They also predicted the location of the temperature bulge fairly accurately. The profile obtained from PROMAX was very close to the experimental values and the software could calculate the maximum temperature in the column. The results achieved by ASPEN showed more deviation from the reported experimental data.

In Run ‘d’, both software packages worked well and the simulation profiles really matched the experimental values.

As can be seen in Figure 4.4, the experimental data showed a different behavior and generated a strange profile curve, which happened because of Data Points 6 and 11. The reason for these deviated points was the location of the thermocouples in the absorber, which are embedded along the column to read the temperatures. Figure 4.5 shows that two of these thermocouples are placed in the gap areas between the packing beds and the gas and liquid streams are not in contact as they are in the packing area. In this case, the reported temperature would not be accurate and has deviation from the real value.
Figure 4.4  Temperature profile in absorber, ITC plant: (a) Run a, (b) Run b, (c) Run c, (d) Run d
Figure 4.5- Thermocouple arrangement in the absorber, ITC plant
Figure 4.6 illustrates the CO₂ concentration profile in the absorber. Again the effect of the placement of the two sensors for measuring CO₂ concentration is obvious in the experimental profile. The arrangements of these sensors are same as the thermocouple shown in Figure 4.5.

Both ASPEN and PROMAX predicted the concentration values to have the same trend as the experimental data while PROMAX gave a better profile when compared to ASPEN.

In Run ‘d’, a really good agreement achieved between the simulation results and experimental values.
Figure 4.6  CO₂ concentration profile in absorber, ITC plant: (a) Run a, (b) Run b, (c) Run c, (d) Run d
The stripper temperature profile is given in Figure 4.7. The ITC stripper includes two beds of packing so there is one gap area for this column. This results in having one deviated data point which is placed in the middle of the column (Point 5), which can be seen in Figure 4.7.

The concavity and convexity of the experimental curves were followed by the simulations profiles correctly. The over-predicted temperatures for run ‘c’ and ‘d’ are because of the stripper heat loss in the pilot plant stripper.
Figure 4.7  Temperature profile in stripper, ITC plant: (a) Run a, (b) Run b, (c) Run c, (d) Run d
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, eight data series from the ITC and Esbjerg CASTOR pilot plants were simulated with PROMAX and ASPEN. The models were validated with existing experimental data and the simulation results from both simulators were compared to each other. Results were generated for the CO₂ recovery, lean and rich loadings, steam and heat duties, CO₂ percentage in the product stream, and the temperature and concentration profiles of the columns. The results showed that both software packages could predict the behavior of the MEA-CO₂ capture system efficiently and generate reliable results.

Comparing the performance of PROMAX and ASPEN led to the following conclusions:

- Good agreements between the simulation results from ASPEN and PROMAX and the experimental data were achieved. In most cases, particularly in predicting the absorber and stripper profile along the column, PROMAX simulation results were closer to the experimental data than ASPEN.

- The Rate-based model in ASPEN is more rigorous than the TSWEET Kinetics model in PROMAX, because it considers the mass transfer rate and reaction system. The TSWEET Kinetics model in PROMAX only considers chemical reactions and does not calculate mass transfer resistance and rates.

- A closed-loop CO₂ capture plant model could be simulated in PROMAX, but it could not converge in ASPEN in this work.

- The software interface in PROMAX was more convenient, user friendly and up to date when compared to ASPEN. The call-out or property tables can be added to
the flowsheet and show changes in the stream or block results when the simulation is running. The way to show and report the results was more advanced and convenient in PROMAX.

5.2 Recommendations

To better compare the performance of the simulators, the following recommendations are suggested for future work:

- In this work, two pilot plants were simulated. It is recommended to use data from more CO₂ capture plants with different plant configurations, column types, and column sizes.
- More data series should be used, which can result in a better understanding of the weaknesses and drawbacks of the simulators and giving stronger conclusions.
- Different ranges of process conditions, such as temperature, pressure and CO₂ concentration of the inlet gas, lean loading, solvent concentration, and liquid to gas ratio should be used, which will help to give a better comparison.
- Different kinds of solvents, such as DEA, TEA, MDEA, AMP and mixed amine solvents, should be used rather than just simulating the MEA-CO₂ capture systems.
REFERENCES


IEA. (2011b). *Prospect of limiting the global increase in temperature to 2°C is getting bleaker.* http://www.iea.org/index_info.asp?id=1959


Oyenekan, B., Rochelle, G. (2005). *Performance of innovative stripper options for CO₂ capture*. Department of Chemical Engineering, The University of Texas at Austin, Austin, TX.


