Optimized Simulation of CO_2 Removal Process from Coal Fired Power Plants with MEA by Sensitivity Analysis in Aspen plus

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Abstract

The World Energy consumption has been increasing steadily since industrialization, this recent increase is also the major cause for the raise of CO_2 concentration in the atmosphere. Fossil fuels play a central role in our energy consumption; actually the CCS technology and their operations in power systems must get a prominent role in reducing total CO_2 emissions. An attempt to tackle the problem of solvent based Post Combustion Carbon Capture process optimization requires the availability of a rigorous process model along with a design methodology. During the modeling, much physical and chemical process should be considered in order to get more realistic results, this complexity process addressed as Reactive Separation.This report presents detailed descriptions of the process sections as well as technical documentation for the ASPEN Plus simulations including the design basis, models employed, key assumptions, design parameters, convergence algorithms, concentration and temperature profiles and calculated outputs. The main purpose is to minimize the amount of energy required in the desorption process through the optimum operating condition to the actual CO_2 absorption experimental setup. The case of study is on MEA 30wt% in a coal fired power plant. Electrolytic method is considered; the sensitive analysis was used for the Optimization.

Keywords

Coal Fuel. Global Energy. Post-combustion. Carbon capture Amine absorption simulation. Sensitive Analysis.

1. Introduction

The electricity and heating sector are the largest sources of CO_2 emissions, producing over 13 Gt in 2011, being equivalent to more than 40% in 2000 (OECD/IEA, 2013).

The power generation sector plays an important direct role by reducing substantially its carbon intensity, but electricity now plays an indirect role by substituting for fossil fuels in all final demand sectors. As seen in Figure 1:
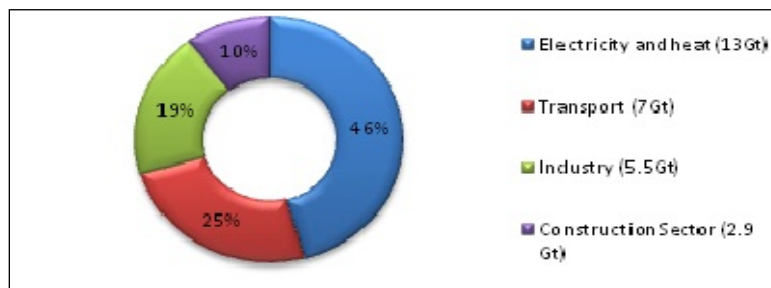

Figure 1. Emission of CO_2 by sector 2011 [1].

According to the data from EIA until August 2013, showing in the Figure 2, the main production of energy of the world comes from Coal and Natural Gas such as fuels (Global CCS Institute, 2013).
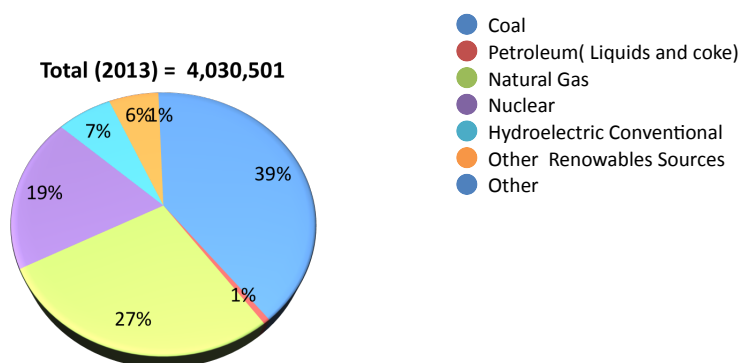

Figure 2. Net Generation by Energy Source: (Thousand Megawatt hours).

1.1. Coal Combustion Pollutants from Coal Fired Power Plant

The National Emissions Inventory prepared by EPA indicates that emissions to the atmosphere from coal-fired power plants (EPA, 2008):

- Contain 84 of the 187 hazardous air pollutant identified by EPA as posing to human health and the environment.
- Release 386,000 tons of hazardous air pollutants annually that account for 40% of all hazardous air pollutant emissions from point sources, more than any other point source category, also are the largest point source category of hydrochloric acid, mercury, and arsenic release to air.
- Coal-fired power plants are also a major source of emissions for several criteria air pollutants; including sulfur dioxide, oxides of nitrogen, and particulate matter.

1.2. Hazardous Air Pollutant Emissions

When talking about the emissions, one should keep in mind that besides CO_2, other pollutants such as particulate matters PM10, PM2.5, SO_2, NO_x, fly ash etc., are also of great importance. HAPs emitted from coal-fired power plants include neurotoxins such as mercury and lead,

corrosive substances such as hydrochloric acid, carcinogens such as arsenic and benzene, radioactive elements such as radium, and potent organic carbon-based toxins such as dioxins and formaldehyde.

2. Modeling Coal Fired Power Plants with CCS Technology

In general various technologies exist for electricity production. Pulverized coal combustion with post combustion CCS (PCC) are modeled and analyzed for Separation of CO_2 with amines. The Advantages and Challenges to CO_2 Capture for Coal-Based Power Generation are:

- In either new build or retrofit application it enables the continued deployment of the well established Pulverized Coal (PC) technology familiar to power industries worldwide.
- The widespread R&D on improved sorbents and capture equipment should reduce the energy penalty of PCC capture.

2.1. Pulverized Coal Plants with Post Combustion CCS (amine system — MEA)

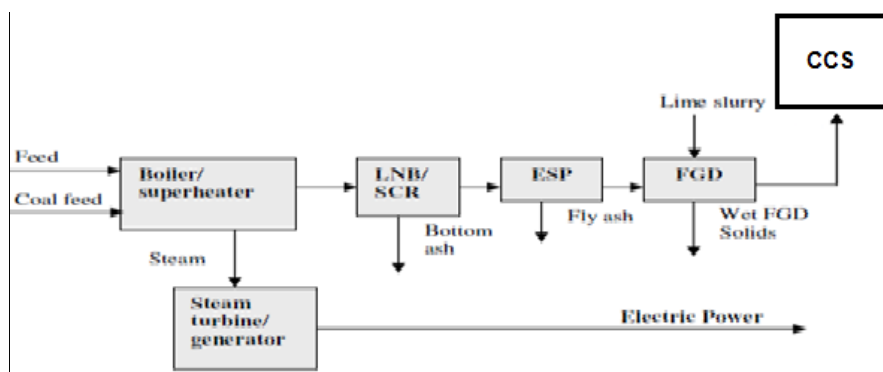The next Figure 3 has shown the Block diagram of this system:

Figure 3. Block diagram of a subcritical PC generating unit. (MIT, 2007).

Control systems. These should be applied for controlling NO_X, SO_2, particulate matter.

- ***Low NO_X burners:*** Here low NO_X burners with 50% maximum efficiency have been applied to all plants.
- ***Selective catalytic reduction (SCR):*** This technology can achieve 90% NO_X removal. The use of this control system also leads to additional multi-pollutant interactions. The level of NO_X reduction depends on coal sulfur level.
- ***Electrostatic precipitator (ESP):*** An electrostatic precipitator or fabric filter can be used for particulate emission control. Plants routinely achieve more than 99% particulate removal.
- ***Wet flue gas desulphurization (FGD):*** FGD applied on the plants has SO_2 removal efficiency of 98%.
- ***Mercury adsorption by activated carbon:*** Mercury can be adsorbed onto the surface of a sorbent material such as activated carbon, or it can be dissolved in an aqueous solution such as in a wet lime or limestone FGD system. For existing coal-fired plants with only a particulate collector such as an ESP, mercury control can be achieved by injecting activated carbon upstream of the ESP.
- ***Fly ash disposal:*** Coal fly ash contains toxic contaminants and should be properly disposed. Solid management has been considered in all the plants and fly ash is disposed with FGD wastes.

2.1.1. Amine-Based Capture Processes

Amine scrubbing technology was established over 60 years ago in the oil and chemical industries, for removal of hydrogen sulphide and CO_2 from gas streams. Commercially, it is the most well

established of the techniques available for CO_2 capture although practical experience is mainly in gas streams which are chemically reducing, the opposite of the oxidizing environment of a flue gas stream.

Mono-ethanolamine (MEA) is a widely used type of amine for CO_2 capture. CO_2 recovery rates of 98% and product purity in excess of 99% can be achieved. Many other amines and, especially in recent years, amine blends such as MEA plus ethyldiethanolamine (MDEA), have also been utilized. Amines react rapidly, selectively and reversibly with CO_2 and are relatively nonvolatile and inexpensive. However, they are corrosive and so require more expensive materials of construction. In addition, they do gradually volatilize (which can be especially problematic in the MEA case) and they degrade, especially in the presence of O-14 and/or SO_2, both of which phenomena necessitate the timely injection of fresh solution.

2.1.2. Energy penalty

No matter which kind of solvent, energy consumption is the biggest obstacle. For chemical absorptions to capture CO_2 in flue gas from coal-fired power plants there are four areas of energy consumption:

- The heat for stripper reboiler.
- The heat to pre-heat the solvent entering stripper.
- Flue gas compression work.
- Carbon dioxide compression energy.

The heat for stripper reboiler is the most considerable; the regeneration of a CO_2-rich amine solution requires a high amount of energy. The related energy demand can be divided into three different proportions: first, apply the desorption enthalpy, which is directly linked with the heat of absorption; second, heating up the amine solution to saturation temperature and third, evaporate water as stripping steam.

2.1.3. Process description

The process consists of two major sections, an absorption section where CO_2 in the flue gas is absorbed into the liquid solvent, and a regeneration section where the absorbed CO_2 is stripped out by means of heat. The flow diagram is shown at the Figure 4.
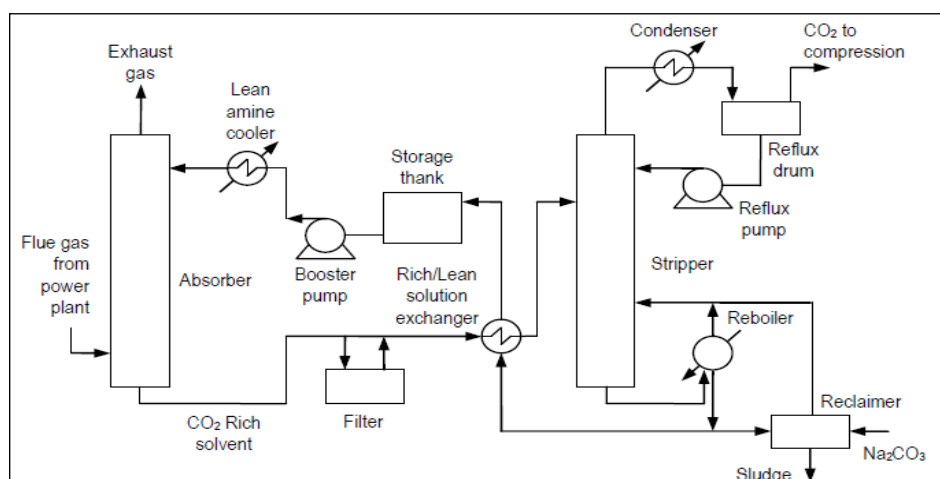
Figure 4. Process flow diagram of an amine-based system. (Kohl, 1997).

3. Aspen Plus — Modeling of CO_2 absorption-stripping processes by Amina MEA

The Table 1 contains a simplified summary of some of the recent academic research of applied simulation modeling of amine based CCS flowsheets. It can be seen, that the use of rate-based calculations is dominant over the equilibrium modeling, with Aspen Plus® being employed as a

frequent platform in the calculations. Note that most of the studies including any advanced configuration reported simulations of the standalone stripper or absorber, and those with advanced configurations on a full CCS flow sheet used only MEA solvent.

Table 1. Previous Simulations work on amine based CCS flow sheets (Chavarro, 2011).

Author(s)	Solvents	Interaction Parameters[1, 2]	Transport	Kinetics[2]	Advanced configurations	Simulator®
[Freguia 2002]	30% wt. MEA	Regressed from data in Augsten 1989 and Jou et al. 1995	Rate-based	Dang 2001 [3]	No	Aspen Plus
[Jassim & Rochelle 2006]	30% wt. MEA	Freguia 2002	Rate Based	Dang 2001 [3]	Multi-pressure stripper, CO₂ compressor integration [6]	Aspen Plus
[Abu-Zahra et al. 2007]	20-40% MEA	Aspen Plus® v.13.1 MEA insert	Equilibrium	Aspen Plus® v.13.1 MEA insert	No	Aspen Plus
[Gabrielsen et al. 2007]	2.9M (~26% wt.) AMP	Regressed from data in Park et al. 2002 and Roberts & Mather 1988 [5]	Rate-Based	Saha et al. 1993	No [4]	Matlab code
[Oyenekan & Rochelle 2007]	Several mixtures of MEA, MDEA and K₂CO₃ with PZ	Cullinae 2005 Freguia 2002 Posey 1996	Equilibrium	Equilibrium	Matrix stripper, vacuum stripper, internal exchange stripper, multi-pressure stripper with split feed [6]	Aspen Custom Modeler
[Plaza et al. 2009]	35% wt. MEA	Hilliard 2008	Rate-based	Aboudheir 2002 [3]	Three stage flash regeneration	Aspen Plus
[Freeman et al. 2010]	8m (~40.8% wt.) PZ 7m (~30% wt) MEA	Hilliard, 2008 modified with extended PZ data	Rate-based	Not specified	Three stage flash regeneration [6]	Aspen Plus
[Schach et al. 2010]	30% wt. MEA	Augsten 1989 and Jou et al. 1995	Equilibrium	Hikita 1977	AIC, matrix stripper, two strippers	Aspen Plus
[Karimi et al. 2011a]	30% wt. MEA	Default Unisim and Protreat amine packages	Rate-based	Barth et al. 1986	Split stream, multi-pressure stripper, ALF, CO₂ compressor integration	Unisim Design and Protreat
[Karimi et al. 2011b]	20-30% wt. MEA 20-50% wt. DEA	Default Unisim and Protreat amine packages	Rate-based	Barth et al. 1986	AIC [4]	Unisim Design with Matlab and Protreat
[Plaza & Rochelle 2011]	5-9m (~30.1-43.7% wt.) PZ	Frailie et al. 2011	Rate-based	Regressed from data in Dugas 2009	No	Aspen Plus
[Tobiesen & Schumann-Olsen 2011]	30-40% wt. MEA	Regressed from data in Ma'Mun et al. 2005 and Jou et al. 1995 [5]	Rate-based	Hoff et al. 2004	No	CO2SIM
[Van Wagener & Rochelle 2011]	9m (~35.5% wt.) MEA 8m (~40.8) PZ	Frailie et al. 2011 Hilliard 2008	Rate-based	Not specified	1&2 stage flash, ALF, IHC [6]	Aspen Plus

[1] Author(s) used the Electrolyte-NRTL activity coefficient model unless otherwise specified.
[2] Interaction parameters and kinetics data as per citations in the secondary source (table first column).
[3] Kinetic reactions only used in the absorber model. The stripper is reported to be modelled with equilibrium reactions.
[4] Standalone absorber simulations reported.
[5] No activity coefficient model. Parameters used in modified correlations for the Henry's law constant.
[6] Standalone stripper results reported.

3.1. Model development

A reliable design tool for modeling this system is called separation Rate-based Aspen. This methodology provides a quantitative evaluation of complex relationships between process variables related to this technology. The advantages of their approach are:

- Package properties including electrolytic, chemical systems and reaction kinetics.
- No need to use lumped approximations as efficiencies or HETPs, which particularly for reactive separation processes do not work properly for the quite noticeable deviation from equilibrium model.
- Adaptable to most absorption equipment dimensions and internals.

Liquid Fase: ENRTL (Electrolyte NRTL The electrolyte-Nonrandom Two-Liquid). Aspen Plus works with the ENRTL model, built to meet the non-ideality in the liquid phase, especially for aqueous electrolyte systems or mixed solvents. The model contains Debye-Huckel terms, Correlations Born to mixed solvents, and terms of local interaction. This assumes that the excess Gibbs free energy in the electrolyte system is the sum of two contributions (Kothandaraman, 2010).

Vapor Phase: Soave equations of state-Redlich-Kwong. The equation of state of Soave-Reidlich-Kwong is applied in this model for the vapor.

3.1.1. Modeling bases with ASPEN RateSep

The rate-based mode of RadFrac allows for the rate-based modeling of absorption and desorption columns. It allows the modeling of mass and heat transfer phenomena as well as the kinetics of chemical reactions.

The various equations that are solved in ASPEN RateSep include:

- Mass and heat balances for the vapor and liquid phases.
- Mass and heat transfer rate models to determine interphase transfer rates.
- Vapor-liquid equilibrium equations for the interphase.
- Estimation of mass and heat transfer coefficients and interfacial areas.
- Enhancement of mass and heat transfer processes by chemical reactions.

Aspen RateSep uses the solution proposed by Alopaeus to solve the Maxwell-Stefan multi-component mass transfer equation. It uses the two-film theory and allows for film discretization which is useful to get an accurate concentration profile in the film for fast reactions. It also combines the film equations with separate balance equations for the liquid and vapor phase, diffusion and reaction kinetics, electrolyte solution chemistry and thermodynamics (Kothandaraman, 2010). The flow models are used to determine the bulk properties that are used in calculating the mass and heat fluxes and the reaction rates. ASPEN RateSep has different flow models available for modeling. In the Mixed Flow Model, the bulk properties for each phase are taken to be the same as the outlet conditions for that phase when it leaves that stage. This is the default flow model in RateSep and is the model adopted in this work.

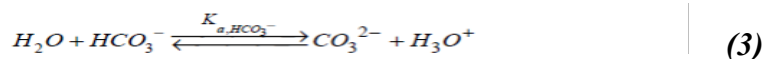### 3.2. Thermodynamic model construction and Chemical Equilibrium

To simulate in Aspen Plus, first we need to define a global system of reactions. Following chemical reactions (Equations 1-7) are taking place when CO_2 is absorbed into an aqueous solution Here are equilibrium reactions, which explain the mechanism of the electrolytes process. The generation of ionic species on the other hand, makes the system highly no ideal.
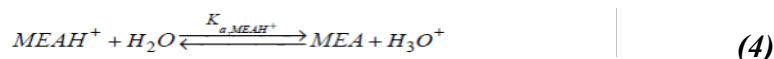
$$MEACOO^- + H_2O \underset{\longleftarrow}{\overset{K_{carb}}{\longrightarrow}} MEA + HCO_3^- \qquad (1)$$
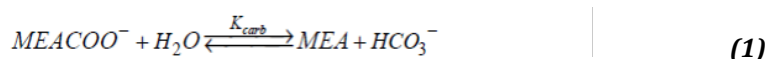
Dissociation of dissolved carbon dioxide:

$$2H_2O + CO_2 \underset{\longleftarrow}{\overset{K_{a,CO_2}}{\longrightarrow}} HCO_3^- + H_3O^+ \qquad (2)$$
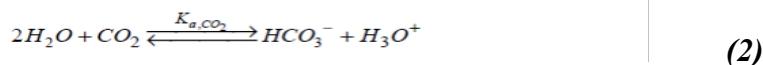
Dissociation of bicarbonate:

$$H_2O + HCO_3^- \underset{\longleftarrow}{\overset{K_{a,HCO_3^-}}{\longrightarrow}} CO_3^{2-} + H_3O^+ \qquad (3)$$

Dissociation of protonated MEA:

$$MEAH^+ + H_2O \underset{\longleftarrow}{\overset{K_{a,MEAH^+}}{\longrightarrow}} MEA + H_3O^+ \qquad (4)$$

Ionization of water:

$$2H_2O \underset{\longleftarrow}{\overset{K_{H_2O}}{\longrightarrow}} H_3O^+ + OH^- \qquad (5)$$

In addition to these main reactions, following two reactions are taking place when a sulphur compound exists in the flue gas system (coal fired flue gas).

Hydrogen sulfide:

$$H_2O + H_2S \leftrightarrow HS^- + H_3O^+ \qquad (6)$$

$$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+ \qquad (7)$$

3.2.1. Equilibrium data

The mole fractions of every single component in the liquid and vapor phase are calculated by solving above equations. The equilibrium constant is calculated using following rate equation (Equation 8).

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \qquad (8)$$

The equilibrium constant data which is imported from Freguia (2002) is considered for mathematical model development and tabulated in Table 2.

Table 2. Constant values of equilibrium constant equations (Freguia, 2002).

| Parameter	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6	Reaction7
A_j	-0.52	231.46	216.05	-3.038	132.89	214.58	-9.74
B_j	-2545.53	-12092.1	-12431.7	-7008.3	-13445.9	-12995.4	-8585.47
C_j	0	-36.78	-35.48	0	-22.47	-33.55	0
D_j	0	0	0	-0.00313	0	0	0

3.2.2. Rate kinetic data

Rate kinetic data are important to understand for reacting system. In addition to diffusion limitations also the kinetics of the reactions between CO_2 and MEA (Eq. (9)) and between CO_2 and OH- (Eq. (10)) must be taken into account, since the equilibrium conditions chemical are not reached. The reactions considered are:

Absorber tower, the first two reactions of the overall system is replaced by the following irreversible reaction kinetics:

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{9}$$

$$MEA + CO_2 + H_2O \rightarrow MEACOO^- + H_3O^+ \tag{10}$$
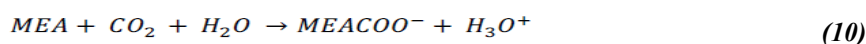
The system corresponding to the **regenerating tower** reactions, the first two reactions of the overall system are replaced by the following irreversible reaction kinetics:

$$HCO_3^- \rightarrow CO_2 + OH^- \tag{11}$$

$$MEACOO^- + H_3O^+ \rightarrow MEA + CO_2 + H_2O \tag{12}$$
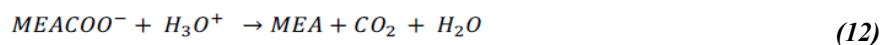
The values of the constants and kinetic parameters were obtained from the database Aspen Plus. The rate constants are expressed according to the Arrhenius relationship Eq.13:

$$r_j = k_j \left(\frac{T}{T_O} \right)^{n_j} exp \left[-\frac{E_j}{R} \left(\frac{1}{T} - \frac{1}{T_O} \right) \right] \tag{13}$$

And values are tabulated in Table 3:

Table 3. Constant and kinetic Values.

Parameter	Reaction 9	Reaction 10	Reaction 11	Reaction 12
k_j	4.32e+13	9.77e+10	2.38e+17	2.7963e+20
n_j	0	0	0	0
E_j (cal/mol)	13249	9855.80	29450.89	17229.79
T_O (K)	298	298	298	298

3.3. Bases consideration for simulation

To build the simulation process, we have some preliminary considerations for better approach, making more viable processes, and reducing the time in the simulation.

3.3.1. Flue Gas Stream

Prior to CO_2 removal, flue gases (usually at near atmospheric pressure and temperatures above 100°C) from power plant are cooled down to the temperature levels required for absorption, and treated for contaminants. To chemical absorption with MEA, the combustion gas concerned to remove NO_x, SO_x and similar impurities. The presence of both in the flue gas is undesirable,

because they react irreversibly with amine solvent to form stable salts to heat, which cannot be removed. NO_2 level less than 20 ppmv and less than 111PPV SO_X is recommended. Most modern plants produce a flue gas containing NO_2 below this and therefore, this does not suppose too much trouble. The gas from a coal fired power plant to be treated has the composition mentioned in the Table 4.

Table 4. Composition of combustion gas.

FLUEGAS	
Molar fraction	
H_2O	0.0818
CO_2	0.1500
N_2	0.7465
O_2	0.0212
H_2S	0.0005
Density gm/cc	0.00119
PM Fluegas g/Mol	29.68

3.3.2. Model Separation Rate-based Aspen Plus

The model used for the Absorber and stripper has present in the Table 5.

Table 5. Aspen Plus Rate-based model: absorption and stripper.

Parameter	Absorber	Stripper
Properties methods	ELECNRTL	ELECNRTL
Chemical- Electrolytic ID	MEA	MEA
Film Resistance Liquid Vapour	Discrxn with 5 discretisation points. Film	Discrxn with 5 discretisation points. Film
Flow model	Mixed	Mixed
Number of iterations	200	**100**

3.3.3. Loading definitions

The loading is defined on a mole basis as given by:

$$Loading = \frac{Moles\ of\ all\ CO_2\ carrying\ species}{Moles\ of\ all\ MEA\ carrying\ species}$$

$$Loading = \frac{[CO_2]+[HCO_3^-]+[CO_3^{2-}]+[MEACOO^-]}{[MEA]+[MEA^+]+[MEACOO^-]}$$

The lean amine comes in a loading between 0.2- 0.4 and leaves at a loading close to 0.5.

3.3.4. Capture of CO_2 Capacity and purity

From numerous studies (see the Table 1), the purity of CO_2 are between 80% and 99%.The 90% is recommended as standard, which is a value we set in the simulations.

3.3.5. Summary of Operating Parameters

The Table 6 has shown the summary of Operating Parameter for the simulation.

Table 6. Operating Parameters for simulation.

Parameters	Assumptions
Loading absorption [moles CO_2/moles MEA]	Around to 0.2 - 0.3
Loading Stripper [moles CO_2 /moles MEA]	Around to 0.5
Head Duty Reboiler	3.0-4.5MJ / CO_2kg
MEA % weight	30%
% Purity CO_2 product.	90%
Fixed capture level of CO_2	90%
Max. Degradation Temperature of MEA	120 °C
Concentration NO_X	< 20 ppmv
Concentration SO_X	< 111ppv

4. The Optimizing process operating conditions

The flow sheet is modeled as a simulation open loop since this would allow and facilitate convergence multiple runs conducting quickly. However, the design specifications were put in place to ensure that the simulation converge in closed form as well. Developed flow diagram shown in Figure 5.
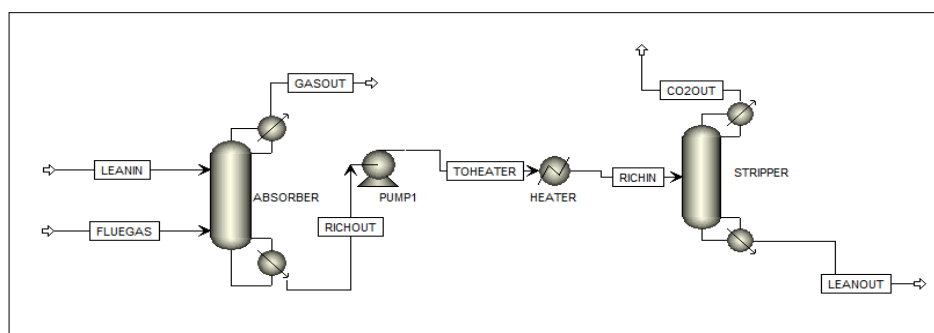
Figure 5. Flow sheet of the study System.

For the optimization process, these parameters were changed and assessed due to the effect on the reboiler duty of stripper (see Table 7).

Table 7. List of the Parameters to Optimize with Sensitivity Analysis.

Absorber	Stripper
Flow inlet LEANIN	
Flow inlet FLUEGAS	
Temperature of LEANIN	Pressure of the equipment
Temperature of FLUEGAS	

4.1. Parameters Effect on the re-boiler Duty

We used the sensitivity analysis, plus Aspen tool, in order to obtain the effect of each particular change in the energy efficiency; also it defines the optimally conditions.

4.1.1. FLUEGAS & LEANIN flow-rate at inlet

The simulation is carried to pilot plant level, considering gas flows (15% CO_2) to be treated are between 500-700Kg / hr. The MEA solution inlet has 30% of weight fraction, also a lithe concentration of CO_2 (0.05%wt) is included since the solvent recycle in the process. The Flow of MEA inlet was calculated assumed the Loading as 0.2; then the Molar Flow CO_2 is 1, 7-2,4Kmol/hr. And the Molar Flow MEA = 8.5 to 12 Kmol/hr. Then, the MEA 30% wt will be between 1728 to 2440kg/ hr.

The simulated process was first running with the optimal liquid flow-rate due to the less heat duty in the reboiler, as shown in the following analysis:

4.1.2. Optimization of FLUEGAS flow-rate

Initially considering Dugas parameters simulation:
$P_{absorber}$ & $P_{Stripper}$ = 1 atm
$T_{fluegas\ \&\ solvent}$ = 313 K

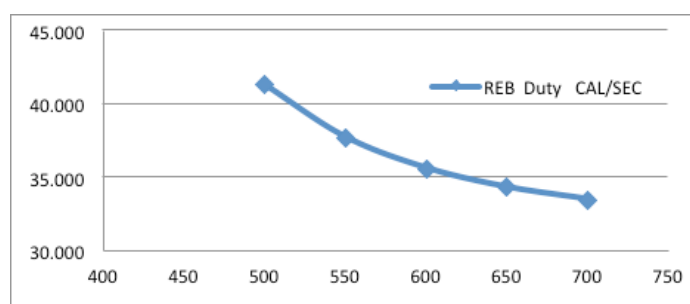| VARY FLUEGAS		
Flow KG/HR	REB Duty CAL/SEC	Mass KG/HR
500	41340.429	93.141
550	37766.816	93.133
600	35637.859	93.127
650	34329.714	93.122
700	33499.135	93.118

Figure 6. Variation of reboiler duty with loading for FLUEGAS from 90% CO_2 Capture.

According to the Fig.6, for a value of 1880 kg / hr of MEA solution, the optimal fluegas flow is around 650 kg/hr, as it predicted not very high reboiler duty.

4.1.3. Optimization of LEANIN flow-rate (solvent MEA)

From Figure 7, the optimal MEA flow is around to 1800 kg/hr, as it predicted not very high duty.

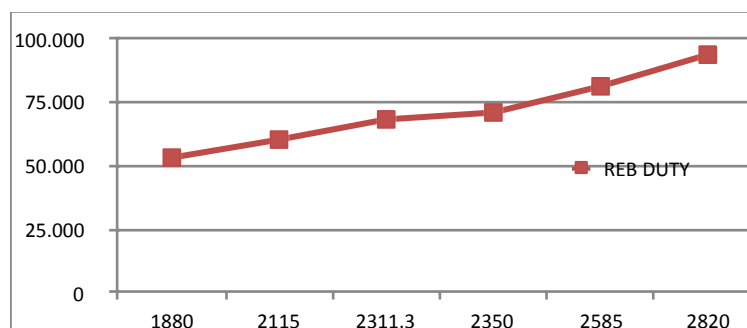| VARY LEANIN	
Flow KG/HR	REB Duty CAL/SEC
1880	53207.732
2115	60318.448
2311.3	68283.597
2350	70006.246
2585	81332.943
2820	93811.946

Figure 7. Variation of reboiler duty with loading for LEANIN from 90% CO_2 Capture.

4.2. Optimization of Temperature and Pressure in the equipment and Streams

Keeps the optimal flows got before; we changed the pressure and study the effects on the reboiler duty by Kg of CO_2 distilled. Then, the removal efficiency has analyzed. **Stream Inlet:** The

effects of the temperature in the Fluegas and MEA solution inlet flows on the heat duty are plotted all together in Figure 8. As the temperature decreased in both flows, the head duty shows a downward trend.
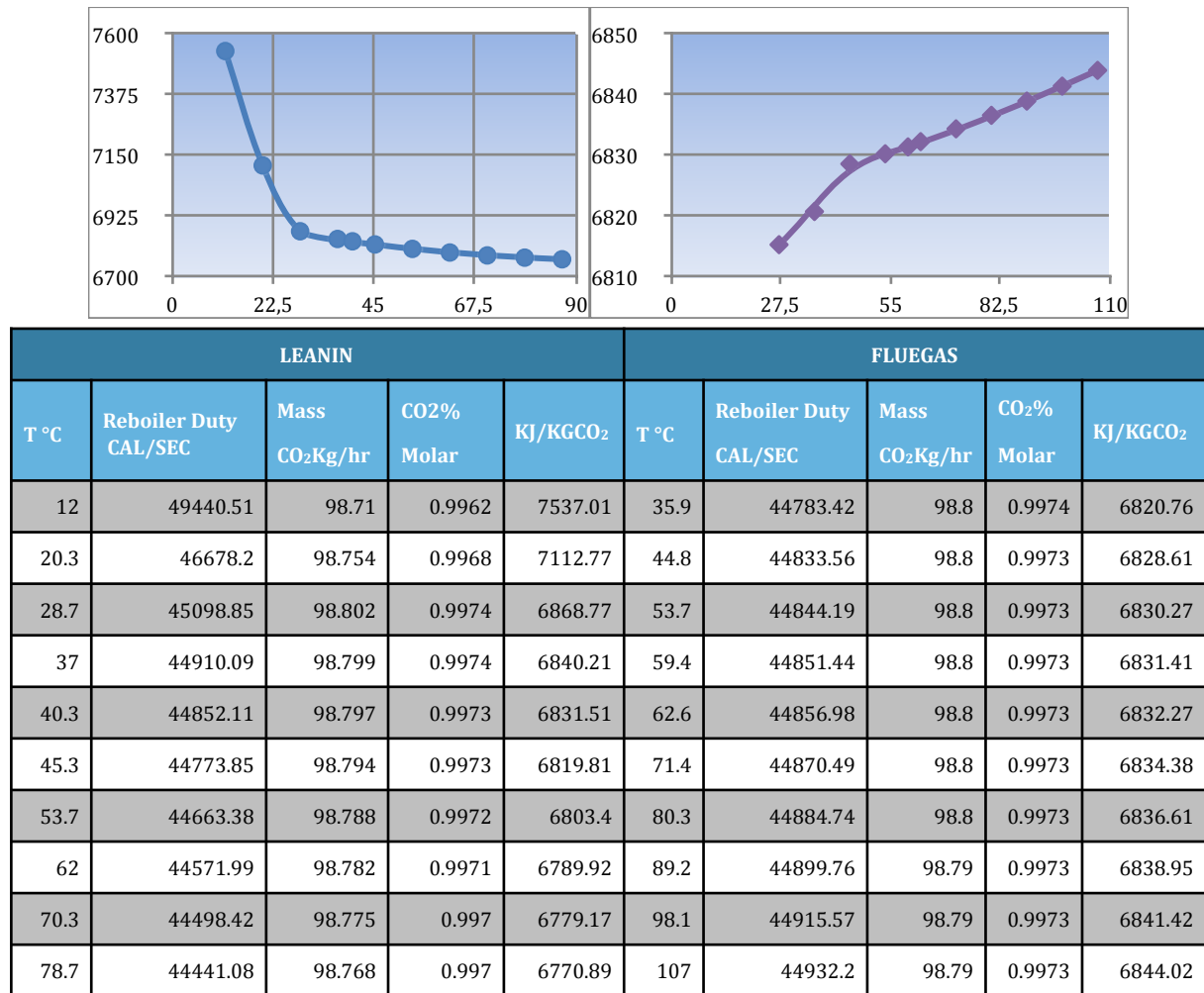

LEANIN					FLUEGAS				
T °C	Reboiler Duty CAL/SEC	Mass CO₂Kg/hr	CO2% Molar	KJ/KGCO₂	T °C	Reboiler Duty CAL/SEC	Mass CO₂Kg/hr	CO2% Molar	KJ/KGCO₂
12	49440.51	98.71	0.9962	7537.01	35.9	44783.42	98.8	0.9974	6820.76
20.3	46678.2	98.754	0.9968	7112.77	44.8	44833.56	98.8	0.9973	6828.61
28.7	45098.85	98.802	0.9974	6868.77	53.7	44844.19	98.8	0.9973	6830.27
37	44910.09	98.799	0.9974	6840.21	59.4	44851.44	98.8	0.9973	6831.41
40.3	44852.11	98.797	0.9973	6831.51	62.6	44856.98	98.8	0.9973	6832.27
45.3	44773.85	98.794	0.9973	6819.81	71.4	44870.49	98.8	0.9973	6834.38
53.7	44663.38	98.788	0.9972	6803.4	80.3	44884.74	98.8	0.9973	6836.61
62	44571.99	98.782	0.9971	6789.92	89.2	44899.76	98.79	0.9973	6838.95
70.3	44498.42	98.775	0.997	6779.17	98.1	44915.57	98.79	0.9973	6841.42
78.7	44441.08	98.768	0.997	6770.89	107	44932.2	98.79	0.9973	6844.02

Figure 8. Variation of the reboiler duty with Temperature of Fluegas & Solvent inlet.

The effect of the pressure in these streams on heat duty has shown in the Figures 9 and 10.

LEANIN	
Pressure Atm	DUTYREB KJ/KgCO₂
1	8658,02
1,5	8658,02
1,68	8658,06
2	8658,02
2,5	8658,03
3	8658,03
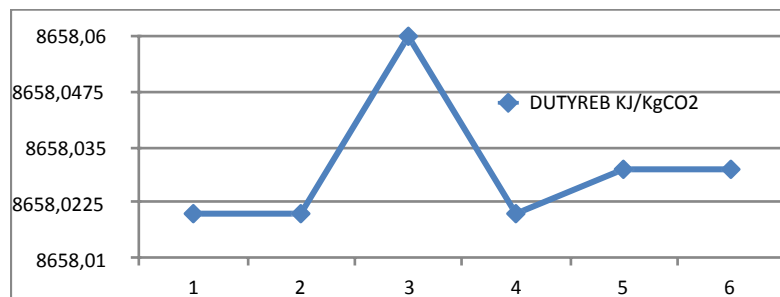
Figure 9. Variation head duty reboiler with the solvent inlet pressure.

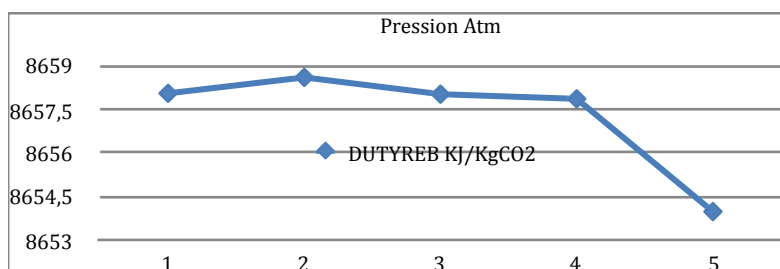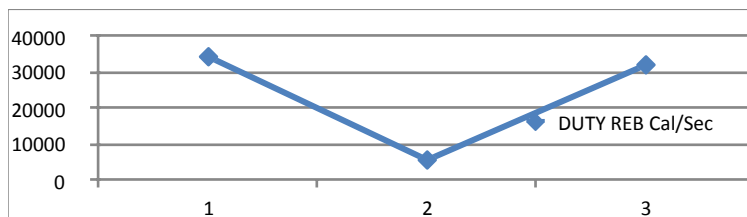| FLUEGAS	
Pressure Atm	DUTYREB KJ/KgCO₂
0,8	8658,04
1,02	8658,59
1,35	8658,01
1,9	8657,85
2,45	8653,96

Figure 10. Variation head duty reboiler with the fluegas inlet pressure.

Equipment: The absorber works with the Pressure 1atm for Dugas. At the Stripper, it was varied; from the Figure 11, the optimum pressure in the stripper should be around 1.6 atm.It evident the significative effect of its variation on the performance of the process.

FLUEGAS	1 Atm			1,5Atm			2Atm		
KG/HR	CAL/SEC	KG/HR	KJ/Kg CO2	CAL/SEC	KG/HR	KJ/Kg CO2	CAL/SEC	KG/HR	KJ/Kg CO2
500	41340.43	93.14	6679.04	31153.73	93.17	5031.84	32731.41	93.20	5284.85
550	37766.82	93.13	6102.16	30311.40	93.17	4895.69	32423.19	93.20	5235.18
600	35637.86	93.13	5758.55	29908.29	93.17	4830.57	32209.37	93.19	5200.79
650	34329.71	93.12	5547.48	29679.92	93.17	4793.75	32061.61	93.19	5177.06
700	33499.14	93.12	5413.53	29538.27	93.17	4770.95	31958.41	93.19	5160.51

Figure 11. Variation head duty reboiler with the pressure.

The optimum streams inlet and equipment parameters have presented in the Table 8.

Table 8. Inlet stream specification for the flue gas and the lean solvent & Specifications of the absorption and stripper columns.

LEANIN		FLUEGAS	
Pressure	1.68 atm	Pressure	1.02 atm
Temperature	313 K	Temperature	313 K
Mass Flow	1800.1 Kg/hr	Mass Flow	643 Kg/hr
Specification		ABSORBER	STRIPPER
Number of stages		20	20
Condenser		NONE	PARTIAL-V
Reboiler		NONE	KETTLE
Top stage Pressure [atm]		1	1.66
Specified Reflux Ratio			1
Specified distillate rate [kmol/h]			98

4.3. Packing Specification

The absorber utilized is typically a random packed column, in which a packing that provides sufficient surface area for the absorption of CO_2, and are easy to transport, storage, and is cheaper. In addition, for packaging Aspen Plus uses the correlation Stichlmair, it requires the void fraction and its surface, as well as three Stichlmair correlation constants for calculations. The correlation parameters Stichlmair, C1, C2, C3 are constant and vary with the type of packaging. In the Stripper, structured packing has a better performance compared to random as they have higher surface areas; but is expensive. See the Table 9.

Regards to correlations and Holdup methods, in the Table 10, they are shown with details. At the Absorber, we consider the specific holdups for rate — controlled reaction are from stage 1 to 20. In the stripper are from 2 to 19 stage, the stage 1 and 20 are in equilibrium, since they are the condenser and the reboiler.

Table 9. Packing specifications: Absorber & Stripper.

Columns	Packing type	Material	Size	Area (m²/m³)	Packed Height (m)	Voids (_ε(%)	C1	C2	C3	Vendor
Absorber	Random IMTP	Metal	38mm	144	6.1	97	1	1	2.65	Norton
Stripper	Structured FLEXIPAC	Metal	1Ycorrugation angle 45	420	6.1	91	5	3	0.45	Koch

Table 10. Correlations and Hold up Methods in the Absorber & Stripper.

Columns	Correlations		Holdups	
Absorver	Mass transfer Coefficient Method	Onda et al. (1968)	Method	Stichlmair et al. (1989)
	Head transfer Coefficient Method	Chilton and Colbum	Liquid Volume	0.0015cum
	Interfacial area Method	Onda et al. (1968)	Scale factor	1
Stripper	Mass transfer Coefficient Method	Bravo et al. (1985)	Method	Bravo et al. (1992)
	Head transfer Coefficient Method	Chilton and Colbum	Liquid Volume	0.002 cum
	Interfacia areal Method	Bravo et al. (1985)	Scale factor	1

The Pump raises the pressure in 1.36atm and the heat exchanger provides temperature to 375.5K. The heat transferred in the exchanger comes from the regenerated stream returns to the absorber to continue the cycle.

5. Simulation in stationary state

When the parametric simulation was performed, the mass & energy balances are in the tolerance between the input and output for each equipment, as can see in the Table11.

Table 11. Mass and Energy Balance in al the Equipments.

Equipment	Mole-flow (Kmol/hr)	Rel.diff.	Enthalpy (Cal/sec)	Rel.diff.
Absorber	In : 95.45	-1.8487	In: -1.57e+06	1.95e-07
	Out : 93.22		Out: -1.57e+06	
Stripper	In : 71.0112	-7.343e-14	In : -1.44677e+06	-0.013889
	Out : 73.1454		Out : -1.42668e+06	
Pump1	In : 70.997	1.73204 e-05	In :-1.4675e+06	-3.488e-05
	Out :70.9958		Out : -1.46751e+06	
Heater	In : 70.9958	-0.000217	In : -1.467e+06	-0.00021
	Out :71.0112		Out :-1.4467e+06	

5.1. Results of the simulation

Table 12 shown the main simulation results for the columns.

Table 12. Results of the simulation Absorber & Stripper.

RESULTS	ABSORBER	STRIPPER
Reboiler pressure [atm]	1.00413	1.66
Reboiler temperature [K]	321.297	390.585
Reboiler heat duty [cal/sec]	0	26577.4
Reboiler duty kJ/kgCO₂		4226.727
Total product stream CO2e flow [kg/hr]	44.9923	94.6209

5.2. Pressure profiles, concentration and temperature in the columns

The process flow diagram is implemented with the optimized parameter for closed loop system. After the simulations, the profile of temperature of the absorber has shown an increase in temperature in some areas, this is due to exothermic reactions occurring peaks and is where the greatest amount of CO_2 is absorbed (see Figure 12).
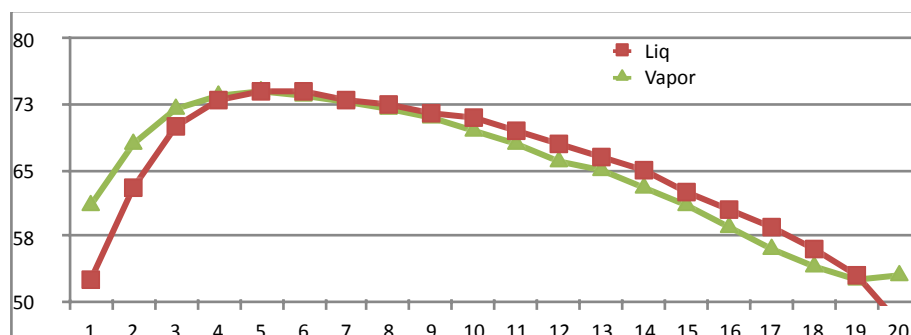

Figure 12. Absorber Temperature profile.

In Figure 13, the removal of CO_2 from the gas is carried out gradually until consumed all of it, being absorbed in the liquid solution as reaction products of the MEA.
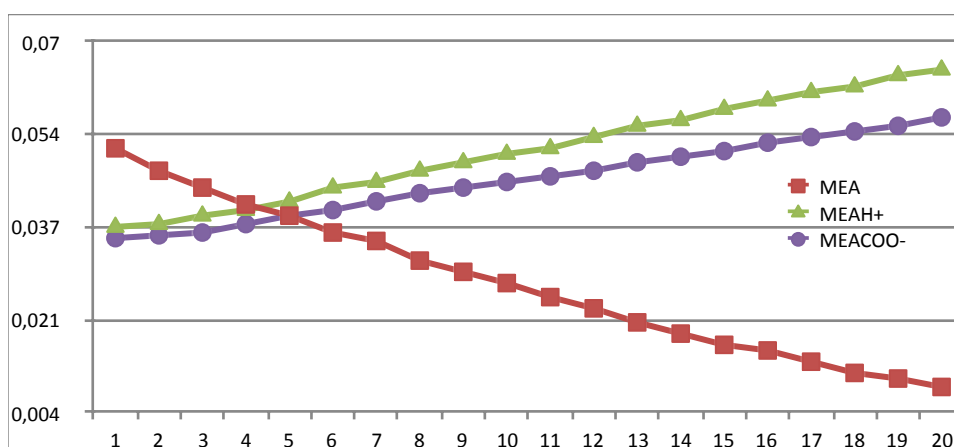

Figure 13. Absorber Concentration profiles of Liquids phase.

In the stripper occurs the removal of CO_2 at high concentrations by the top, while the concentration profile of the liquid phase (Figure 14), showing regeneration of the MEA, after releasing the CO_2. Figure 15 presents the stripper's profile temperature, it is observed that reaches a maximum value of 92°C in the reboiler, that is not higher than 120°C, therefore does not undergo degradation occurs.
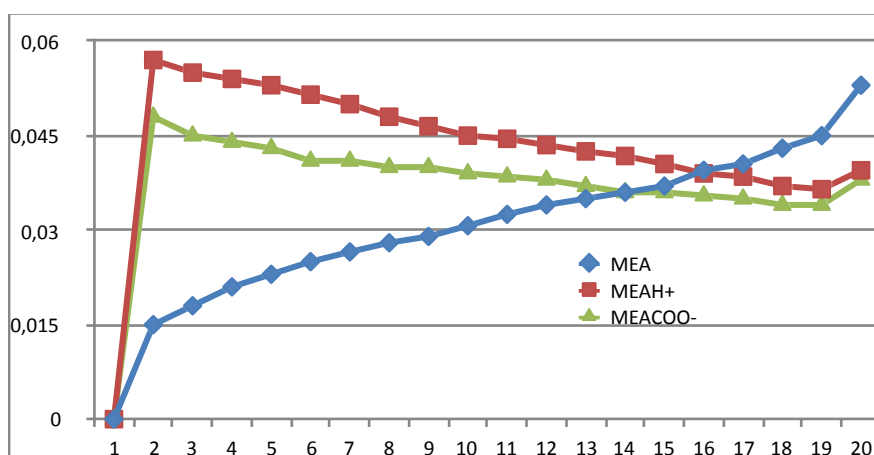

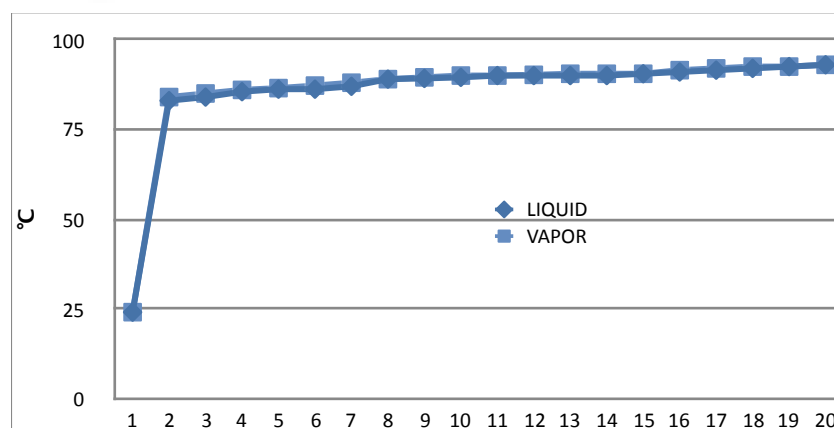**Figure 14.** Stripper Concentration liquids phase Profiles.

Figure 15. Stripper Temperature Profiles.

6. Discussion of Results

This paper presents a description of the CO_2 removal process of 550MW coal fired power plant. The parameters and other operating conditions for Aspen Plus rate based model were selected to achieve 90% of removal.

The absorption of CO_2 into aqueous amines is governed by the reaction between electrolytic species, and an appropriate thermodynamic model is required to predict the amine solution properties. Vapor-liquid equilibrium (VLE) and ionic species distribution are based on the activity coefficient predictions of the ENRTL model, and appropriate interaction parameters are essential to guarantee accurate model results. The main characteristics of the use of amine in CCS were discussed using the conventional flowsheet configuration in order to identify the following key features that have placed MEA as the benchmark capture solvent: reaction kinetics, reaction enthalpy, solvent capacity. Besides, ASPEN Ratesep modeling allows mass and heat transfer phenomena considerations in the process as well.

The main characteristic of the model has been based on simulating an experimental pilot plant (Dugas, 2006). The own variations made to this model were: the stripper's pressure is 1.66 atm , it helped to reduce the heat load in the reboiler.

Regarding the absorption reactions, it has been outlined that the carbonate dissociation and ionization of dissolved CO_2 determine the rate of its absorption into aqueous amine solutions. As a consequence, it is expected that the reaction kinetics are to be included in the modeling approach of this CCS simulation.

MEA solution has a higher absorption with moderately cool temperature, because it increases the physical solubility of CO_2, moving the equilibrium constant absorption reactions, so that more it can remain in solution as carbamate, carbonate and bicarbonate.

Absorptive capacity, predominantly depends on the molar loading ratios of MEA solution and the flue gas, which feed the absorption column, our result is a value of 0.36. Also, the load ratio becomes 0.51, before entering the regeneration process.

The optimization of parameters and specifications, have been obtained with the use of sensitivity analysis. There have been many assessments to different conditions, taking aim to reduce energy demand as low as possible to remove one unit of CO_2. The lowest calculated heat consumption was 4,226 KJ / $KgCO_2$ removed. The research has focused on the effects of the variation of the following parameters: the temperature and the flows of the inlet streams as well as the pressure in the stripper.

The 90% CO_2 removal efficiency was achieved at 40°C for inlet fluegas, at higher temperatures the removal is much lower. It is also important to note from the temperature profile of the stripper has shown a maximum temperature of 96°C, avoiding the decomposition of the amine, which occurs to 120°C.

Regards to the lean amine solution exits from the bottom of the stripper. Few losses of amine occur, since MEA is characterized by low volatility.

Besides, the pre-heat "rich" solvent, demonstrated the reboiler heat duty can be significantly lowered.

7. Conclusion

The main purpose of the simulation was to demonstrate the post combustion technology in conjunction with a coal-fired power plant; with the captured of CO_2 by chemical absorption in MEA solvent. Unfortunately, MEA exhibits many disadvantages, such as high heat of absorption and the necessity of supplying an appropriate amount of energy to break the bonding in the MEA-CO_2 complex in the desorption process.

The flexible process flow sheet simulation, offered high potential for the validation of various improvements, which were designed to reduce the process energy demand, and to increase the CO_2 recovery. The main idea is to develop the model that will help to optimize the process with sensitivity analysis. Improvement their accuracy due to broadening of the scope of measured process variables to include the energy requirements, particularly in the Stripper reboiler.

Our results match very well with the reported results from the Fluor Econamine FGTM process which reports a value of 4200 Kj/Kg CO_2 for coal-fired power plants (Arachchige e Melaeen, 2012).

8. Aknowledgements

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9. References

Arachchige, U. S. P. R., & Melaeen, M. C. (2012). Aspen plus Simulation CO_2 removal from Coal and gas fired power plants. *Energy Procedia*, 391-399.

ASPEN Tchnology (2008). *Aspen Plus manual*, Physical Property Model.

Chavarro Montenegro, H. J. (2011). *Novel Solvents For CO_2 Capture Flowsheet Analysis* (pp.31-32)*. Manchester: University of Manchester.

Colin F. Alie (2004). *CO_2 Capture with MEA: Integrating the Absorption Process and Steam Cycle of an Existing Coal-Fired Power Plant*. Master Thesis: Ontario, Canada.

Dugas, R. E., (2006). *Pilot Plant Study of Carbon Dioxide Capture by Aqueous Monoethanolamine*. Austin [Texas] USA: The University of Texas.

EPA (2008). *Air Emissions Inventories*. Recupered of http://www.epa.gov/ttn/chief/net/2008inventory.html;2008 [accessed 18.07.12].

Freguia, S. (2002). *Modeling of CO_2 removal from Flue Gas with Mono-ethanolamine*. Master Thesis, University of Texas, USA.

Global CCS Institute (2013). *The Global Status of CCS: 2013*. Melbourne, Australia.

Kohl A., Nielson R.(1997). *Gas Purification* (5th Edition). Houston [TX] USA: Guft Publishing Company.

Kothandaraman, A. (2010). Monoethanolamine System. Carbon Dioxide. In: *Chemical Absorpion: A solvent compartion study* (Charpter 3). USA: Massachusetts Institute of Technology.

Krótki, Aleksander (2008). Laboratory Studies of Post-combustion CO_2. In *Absorption with MEA and AMP Solvents* (-z. pp. 371-378). Recovered DOI 10.1007/s13369-015-2008.

Manepalli, J. (2010). Green Energy Technology, Economics and Policy. In *Ways of "greening the economy'* (pp. 293–307). Vienna: CRC Press Inc.

Mirfendereski, Y. M. (2008). *Techno-Economic Assessment of Carbon Capture and Sequestration Technologies in the Fossil Fuel-based Power Sector of the Global Energy-Economy System*. Master Thesis, Berlin Technical University, Berlin, Germany.

MIT — Massachusetts Institute of Technology (2007) "The future of coal — options for carbon constrained world 2007".

OECD/IEA (2013). *Redrawing The Energy-Climate Map World Energy Outlook Special Report, 2013*, International Energy Agency, Paris, France.

Stefania Moioli, L. A. (2013). Regeneration Section of CO_2 Capture Plan by MEA Scrubbing with Rate Based model. *The Italian Association of Chemical Engineering Journal, 32*, 1849-1854.