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SIMULATION OF AN OPERATIONAL AMINE BASED CO_2 REMOVAL PLANT AS AN EXAMPLE OF CO_2 CAPTURE AT COAL-FIRED POWER PLANTS

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Abstract

Among many understudy CO_2 capture technologies, amine scrubbing is the most promising near term strategy. In this article, Kent/Eisenberg, Lee/ Mather and Electrolyte Non Random Two Liquid model (E-NRTL) models were utilized to simulate an operational unit based on monoethanolamine (MEA) as solvent and 18 % molar CO_2 feed gas. Simulated results are compared to plant data. Important parameters like temperature and pH are traced at absorption and stripping towers and other process equipments. Secondly use of MEA, DGA, MDEA, DEA and DIPA and their mixtures for CO_2 Scrubbing were simulated. Our study shows that diglycolamine (DGA) and DGA/MEA mixtures can outperform MEA in energy consumption, tower diameter and circulation rate for flue gases containing high CO_2 content. The results of our study can help lowering both capital and operational expenses of CO_2 capture.

Key words: CO_2 capture; Amine scrubbing; Process Simulation; Electrolyte NRTL.

1. Introduction

Amine scrubbing [1-2], O_2/CO_2 recycle combustion [3-4], membrane gas absorption [5], photosynthetic bioreactor [6], CO_2 hydrate [7] and mineral trapping [8] are some of under studied technologies for mitigating CO_2 emissions. Among these, amine scrubbing is the most promising near term strategy. It has been decades since amines were first utilized for removal of CO_2 or H_2S in gas refineries or other gas sweetening applications. Many researchers have explored for finest amine for a specified application to obtain better performance [9]. Also different thermodynamic models have been introduced to predict CO_2 solubility in amine solutions. From those, Kent–Eisenberg, Lee/Mather, Pitzer and Electrolyte NRTL are the most important of all [10-18].

Financial studies have shown that CO_2 capture has high operational and capital expenses [3, 19-20]. Desorption of CO_2 from amine solution and flue gas compression are highly energy consuming, which account for CO_2 capture high operational costs. In this situation, computer based process simulations, have been proofed to be highly useful in optimization of the process and selecting an amine to minimize energy demands for power plants CO_2 capture [21-24]. Although simulated assisted studies can be useful, the convergence of the process is not easy to achieve which is due to process nonlinearity and the recycle streams.

Of the fossil fuels, coal is much more carbon intensive than oil or natural gas, resulting in greater volumes of CO_2 emissions per unit of electricity generated (approximately 100 kg CO_2 per GJ produced). In fossil fuel power plants, gas-fired flue gases typically contain 8% CO_2 but coal-fired flue gases can contain up to 20 % CO_2. This high content of CO_2 can make modeling and simulation of the process more challenging because each thermodynamic model and simulator has its own assumptions and limitations.

Although complete sets of data for operating and equipment conditions are not easy to find, we had the opportunity to obtain the plant data for an industrial case. The aim of this

research is to compare simulation results of CO_2 removal unit utilizing different thermodynamic models with plant data. Another goal of the study is to examine whether or not DGA, MDEA, DEA, DIPA and their mixtures can be used for flue gases containing up to 18% CO_2 concentrations and to find their corresponding energy demands, circulation rate, and tower diameters.

2. Process

Fig. 1, illustrates process flow of a typical CO_2 scrubbing unit. In the studied plant, 1184 kmol/hr CO_2 is introduced to the absorber which is analogous to CO_2 emissions of an approximately 150 MW Coal-fired power plant . For absorption of flue gas containing 18 % molar CO_2 (feed gas is H_2S free), 25 % wt. MEA is utilized in two steps of absorption and stripping. The flow sheet is almost same for every industrial amine scrubbing facility. CO_2 enters the absorber and counter currently contacts an aqueous solution of amine. The rich amine stream exits the absorber at the bottom of the column. It is then preheated in E-101 heat exchanger (known as L/R exchanger) by the lean amine stream leaving the stripper and enters the stripper. In the striper, with addition of heat, the reaction is reversed and CO_2 is removed. The lean MEA is then recycled to the absorber. Absorber and stripper design specifications and operating conditions are tabulated in Tables 1.

Table 1 Absorber and stripper design specifications and operating conditions

Feed gas flow (kmol/hr)	1184
Number of absorption tower trays	20
Absorption tower diameter (m)	3.35
Absorption tower spacing (m)	0.61
Feed gas temperature(°C)	63
Number of tripping tower trays	19
Condenser duty (GJ/h)	41
Reboiler duty (GJ/h)	122
Absorber pressure (bar)	27.7
Absorber pressure loss (bar)	0.3

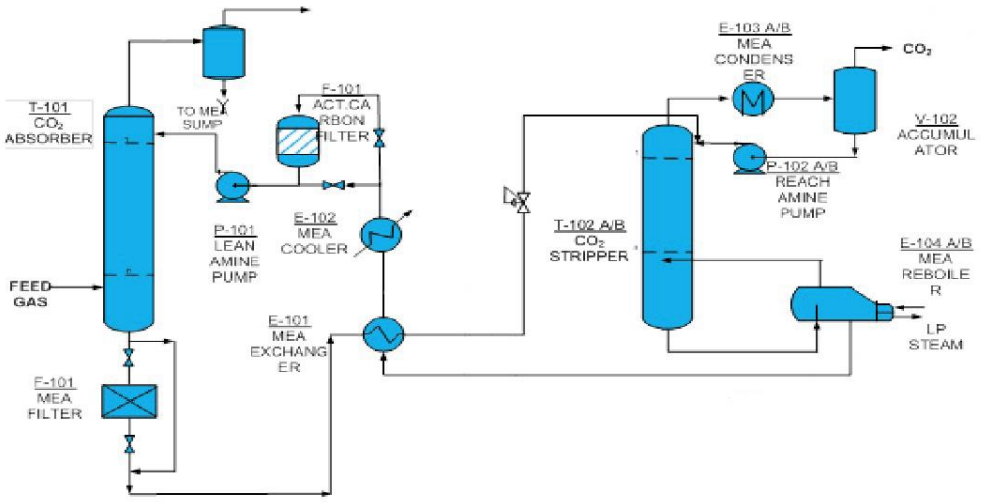

Fig. 1 Amine scrubbing CO_2 removal process flow

3. Models and Simulators

An amine plant simulation can be close to reality if only it is based on both rigorous thermodynamic modeling and understanding of transfer phenomena.

3.1 Modeling [10-18]

Model presented *by Kent –Eisenberg* is based on chemical and phase equilibriums, mass balance and Murphree efficiency. It is noteworthy that AMINE package in ASPEN PLUS perform calculations based on Kent/Eisenberg model. Model presented by *Lee/Mather* is based on liquid/ vapor phase equilibrium and chemical equilibrium of liquid phase. For phase equilibrium The Fugacity coeficient is calculated from Peng Robinson equation of state and activity coeficient is calculated from Pitzer model. *Electrolyte* model is used for the calculation of activity coefficients for aqueous electrolytic systems and several different solvents. Activity coefficients for ions and molecules in solution can be calculated by this model. EL-NRTL model uses infinitely lean aqueous solutions as a reference state for ions. For this reason water must be one of system components. Following simulators are capable of amine calculations:

PRO II (from SIMSCI) has AMSIM 7 package for amine calculations. In this package three models are designated. One drawback for using this software is its anability to perform ion concentration calculation. It is noteworthy that Pro II can only perform amine calculations for MDEA/MEA and MDEA/DEA mixtures. ASPEN HYSYS® has AMSIM package for amine calculations. This package only contains kent/ Eisenberg and Li/Mather models.

PROMAX (from BR&E) is highly used for amine plant calculations though It can not perform ion concentarion calculations. Design II (from WINSIM) utilizes two thermodynamic models 'Mixed Amine' and 'MEA/DEA' for amine calculations. One of the advantage of Design II is that in tower simulations it does not assume thermal equilibruim between gas and liquid phase.

CHEMCAD (from Chemstation) can calculate ion concentrations base on thermodynamic models such as Electrolye NRTL and Pitzer models. Unfortunetly limitations with this simulator are its incapability to perform calcaulations for MEA or amine blends.

ASPEN PLUS® (from AspenTech) has more than ten Thermodynamic model for elctrolyte calculations. It can perform pH calculations for all amine systems and amine blends.

4. Results and discussion

4.1. MEA based simulations

In our study, ASPEN HYSYS V7.3 and ASPEN PLUS V7.3 were utilized for simulation of CO_2 removal unit. First simulations were carried out at designed plant specifications and MEA as solvent.

In ASPEN HYSYS simulations, Kent/Eisenberg and Li/Mather models were used for amine calculations while in simulation using ASPEN PLUS, AMINES and Electrolyte NRTL were utilized. Simulation result using thermodynamic models AMINES, Electrolyte NRTL and collected plant data are summarized in Table 2 and Table 3. Results show that both thermodynamic models predict streams specifications and required duties for condensers and reboilers perfectly well. For real tray calculations stage efficieny must be taken into account.simulators incorporate specilized stage efficiency models to perform efficiency calculations. These models calculate CO_2 component stage Murphree efficiencies based on tray dimensions given and calculated tray conditions. Stage efficiencies are a function of pressure, temperature, phase compositions, flow rates, physical properties, mechanical tray design dimensions, kinetics and mass transfer parameters. ASPEN PLUS predicts absorption tower CO_2 efficiency to be 31%.

In amine package simulations coolers and L/R heat exchanger heat loads are predicted with 4% and 0.90% errors accordingly. In electrolyte NRTL simulations coolers and L/R heat exchanger heat loads are predicted with 0.3% and 1.85% errors. Comparing results of simulations using described models and plant data show that electrolyte NRTL model gives more accurate results. This model also has capability of predicting some important properties of the process such as pH on trays. pH is one of the most important parameters in described CO_2 removal unit, because of major corrosion concerns associated with MEA. Simulated pH profile for both absorption and stripping tower are shown in Fig. 2. Also fig. 3 shows pH at different process locations, at specified operating condition while temperature profile is presented in Fig.4.

Table 2 ASPEN PLUS simulation results for stack and CO_2 streams specifications using thermodynamic models AMINES and EL- NRTL compared to data from operating plant

Description	Absorber overhead,CO_2 free stack				
	Plant data	Amines Model	± %Error	EL-NRTL Model	± %Error
CO_2 molar%	0.5	0.5	0.04	0.5	0.06
Temperature (°C)	46	46	0.00	45.9	0.04
	Stripper overhead,CO_2 stream				
	Plant data	Amines Model	± %Error	EL-NRTL Model	± %Error
Total(kmol/h)	1402.9	1409.6	0.48	1403.1	0.02
Temperature (°C)	60	60.4	0.62	59.9	0.06

Table 3 ASPEN PLUS simulation results for energy consumptions using thermodynamic models AMINES and EL- NRTL compared to data from operating plant

	Plant data	Simulation Results			
		Amines Model	± % Error	EL-NRTL Model	± % Error
Heat Exchanger Duty (E-101), GJ/h	91.7	90.8	1	91.4	0.3
Cooler Duty (E-102), GJ/h	159.2	152.5	4	156.2	1.85
Condenser Duty (E-103), GJ/h	82.6	82.5	0	82.5	0
Reboiler Duty (E-104), GJ/h	237.8	237.8	0	237.8	0

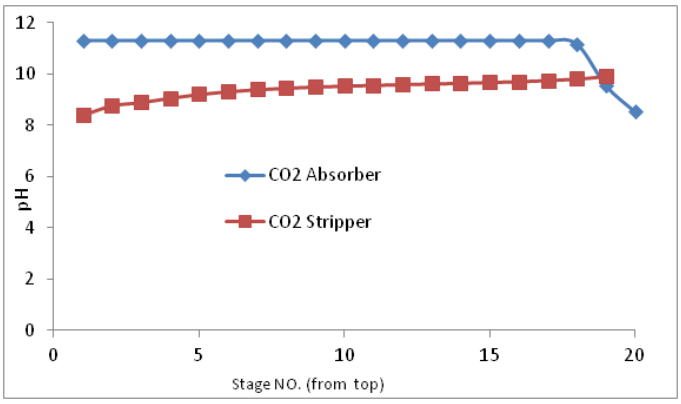

Fig. 2 Simulated pH profile on trays for absorption and stripping towers

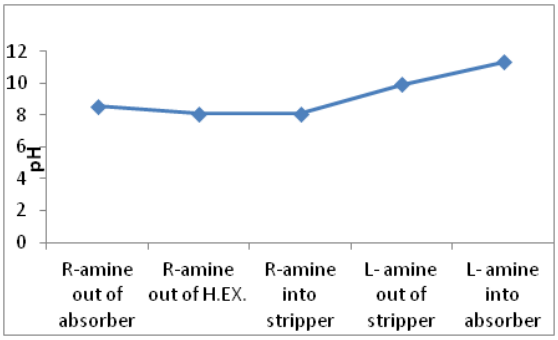

Fig.3 Simulated pH at different process equipments

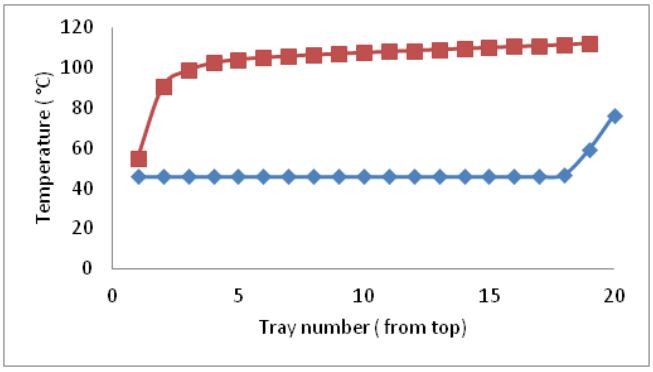

Fig 4 Simulated temperature profile for absorption and stripping towers (□ absorption, ●: stripping)

ASPEN HYSYS incorporate Lee/Mather and Kent-Eisenberg models for amine calculations. Table 4 and Table 5, present simulated results using Kent/Eisenberg and Lee/Mather models,

calculated Murphree tray efficiency is 48%, which is 17% higher than efficiency predicted by ASPEN PLUS.

Table 4 Comparison between plant data and Kent/Eisenberg simulated result

Description	Absorber Overhead Plant data	Absorber Overhead ASPEN HYSYS results
CO_2 molar %	0.54	2.02E-03
Temperature (°c)	46	45.96

Table 5 Comparison between plant data and Lee/Mather simulated results

Description	Absorber Overhead	ASPEN HYSYS results
CO_2 Molar Flow*(kmol/h)*	0.54	2.03E-03
Temperature (°c)	46	46

4.2. Case studies on different amine systems

Different types of amines, used in CO_2 and/or H_2S removal units are as follows:

*MEA (*monoethanolamine*):* MEA is the most common amine. It is highly alkaline, has highest separation capacity and can be recovered easily. Although MEA is suitable in many ways, but due to its corrosive nature, concentration should be low, maximum relative concentration is 25% wt.; although use of corrosion inhibitors can make use of 35 wt% MEA feasible as a result, MEA needs high solvent rate (high pump power consumption) and steam rate in stripping tower.

DEA (Di Ethanol Amine): DEA is a secondary amine. DEA is a weaker amine and can not absorb CO_2 with a rate as high as MEA, but because it is not as corrosive as MEA, concentrations can be up to 35%. DEA circulation rate and demand for steam is relatively lower, but due to higher viscosity, power consumption in pump is higher. This solvent acts selectively in absorption of acid gases and in cases which H_2S and CO_2 are present, absorbs H2S relatively more, thus, is more suitable for natural gas refining purposes.

TEA (Tri Ethanol Amine): TEA is ternary amine. It has a lower absorptive property relative to the both MEA and DEA.

DGA (Di Glycol Amine): DGA is a primary amine, it is highly absorptive. Since it has low corrosion problems and is completely miscible and is used at concentration up to 70% by weight. As a result needs lower circulation and steam rates.

DIPA (Di Iso Propanol Amine): is a secondary amine. It is used at concentration up to 50%.

MDEA (Methyl Di Ethanol Amine): MDEA is tertiary amine, with a low absorption rate, but it has no corrosion problem. This solvent can be used at concentrations up to 50% wt. Demand for energy is low for this solvent. This solvent acts selectively in absorption of acid gases (absorbs H_2S more).

Using ASPEN PLUS simulator and E-NRTL model, diameter of absorption tower and amount of solvent in circulation are simulated for 6 systems of amines and their mixtures. These systems are: 1) DGA 60%, 2) DEA 30%, 3) DIPA 40%, 4) mixture of MDEA/ MEA (45%, 5%), 5) MDEA/ DEA (45%, 5%), 6) MDEA 50%. Same temperature and pressure of lean amine, pressure at the top and bottom of absorption tower and same specifications of feed gas to absorption tower were considered for all solvents. Simulation results are shown in Fig. 5 and Table 6.

Table 6 Diameter of absorption tower for different solvents at same operating conditions

Solvent	60% DGA	25% MEA	45% MDEA + 5% MEA	30% DEA	50% DIPA	45% MDEA+ 5% DEA
Estimated tower diameter(*m)*	3.1	3.6	5	8.3	21	21

Simulation results show that for all solvents, except DGA 60%, considerable higher flow rate and tower diameter are needed. Referring to described simulations, among the alkano-amines, DGA can both lower circulation rates and tower diameters, which account for lowering

both capital and operational expenses of CO_2 capture. Having that in mind, two mixtures of (MEA 20% + DGA 5%) and (MEA 15% + DGA 10%) have been simulated using EL-NRTL model. Table 7, summarize simulation results for MEA system vs. MEA/DGA solutions. Table 8, summarizes energy consumption results for MEA vs. DGA/MEA solutions. It is noteworthy that in case of using MEA/DGA mixtures for CO_2 removal, considerable decrease in reboiler and condenser duties are predicted. Fig. 6, Fig. 7 and Fig. 8 show pH profile in absorption and stripping tower trays and other process equipments .In Fig. 9 and Fig. 10, temperature profile in absorption and stripping towers for three simulated solvent systems are shown.

Table 7 Simulated absorber overhead CO_2 for MEA vs. DGA/MEA solutions

	MEA 25%	MEA 20% + DGA 5%	MEA 15% + DGA 10%
CO_2 Molar %	0.55	0.55	0.57

Table 8 Simulation energy consumption results for MEA vs. DGA/MEA solutions

	25% MEA	20% MEA + 5% DGA	15% MEA + 10% DGA
Condenser Duty (Gcal/hr)	19.66	10.77	10.76
Reboiler Duty (Gcal/hr)	56.63	45.7	43.87

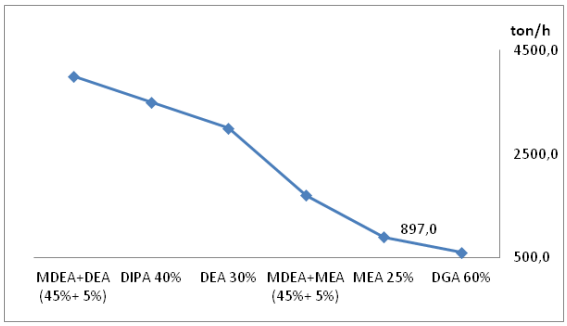

Fig. 5 Solvent circulation rate for different amine systems

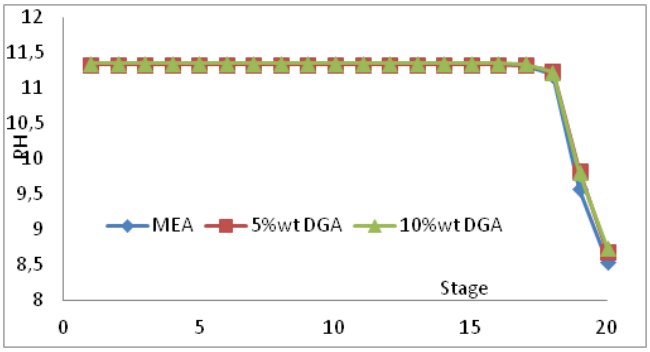

Fig. pH profile in absorption tower trays for (MEA 25%), (MEA 20% + DGA 5%) and (MEA 15% + DGA 10%)

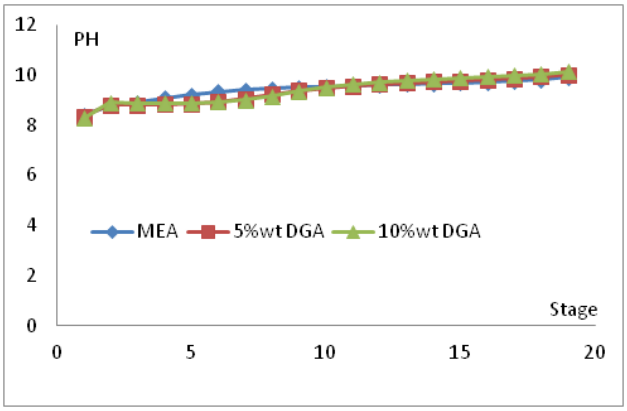

Fig. 7 Simulated pH profile at different stripping tower trays

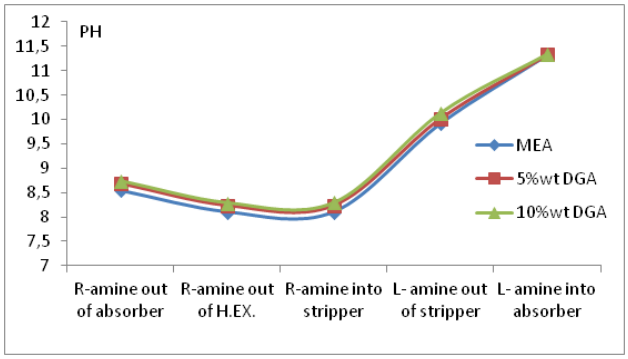

Fig. 8 Simulated pH profile at different process equipments

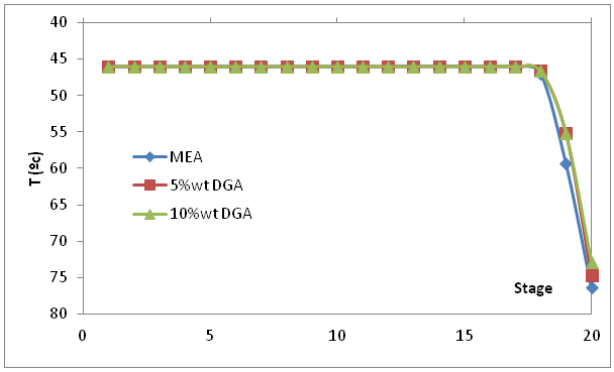

Fig. 9 Simulated temperature profile at different absorption tower trays for different solvents

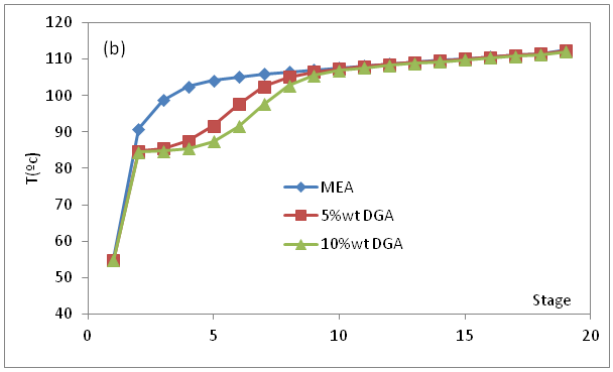

Fig.10 Simulated temperature profile at different stripping tower trays, for different solvents

5. Summary and Conclusions

In this research, thermodynamic models capable of amine calculations were analyzed. These models were incorporated in simulation of CO_2 removal unit using MEA, also six other amines or amine mixtures are simulated. Results of this study show that simulated results using electrolyte NRTL model can most accurately fit plant data for absorber overhead specifications and reboilers and condensers duties. For a 18% CO_2 feed, DGA can outperform MEA in energy consumption, circulation rate and tower diameters. Although DEA, DIPA, MDEA, mixture of MDEA/ MEA, mixture of MDEA/ DEA are utilized as CO_2 scrubbers in many refining applications, for CO_2 capture purposes this solvents require high circulation rates, tower diameter and energy.

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