Simulation of Acid Gas Removal Unit using MDEA Amine Solvent

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Abstract: The Acid Gas cleaning process used in gas processing plants deploys gas sweetening process. Due to the inexpensive cost of amine solvent, more than 95 % of Gas processing plants use an acid gas removal unit that utilizes an aqueous amine solvent to remove sour gas components such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S). The gas needs to be treated for safety considerations and environmental regulations for H_2S toxicity (H_2S present in sales gas). The heating value of sales gas and CO_2 content needs to be reduced. The acid gas dissolved in water to form acids which causes corrosion, and the equipment needs to be protected. The acid gas needs to be treated to meet the the environmental regulations to reduce SO_2 emissions also called acid rain. The present investigation addresses the performance of using MDEA to determine the absorption capacity of CO_2 & H_2S using Aspen HYSYS software

Keywords: Aspen Hysys V12, Amine, Acid Gas (CO_2& H_2S) Removal, Absorption

INTRODUCTION

Acid gas removal involves the removal of carbon dioxide (CO_2) and/or hydrogen sulfide (H_2S) from vapor streams. Vapor streams containing acid gases enter and are put in contact with a lean solvent in an absorber column. The lean solvent absorbs the acid gases and exits the bottom of the column as a rich solution, which is then sent to a regenerator column to strip the acid gases from the solvent so it can be recycled. Many industries, including oil refining, ammonia plants, natural gas plants, LNG, and hydrogen plants require these processes. For property packages three acid gas cleaning packages are available. Acid gas chemical solvents

The acid gas chemical solvents package is used to simulate typical acid gas removal through absorption into amine solvents. It uses Electrolyte nonrandom two liquid model for thermodynamics. It used Peng Robinson equation of state for vapor phase properties.

- Acid gas physical solvents

The acid gas physical solvents property package is designed to use in systems for removal using dimethyl ether of polyethylene glycol (DEPG). Physical solvents have low solvent regeneration requirements but higher association with hydrocarbons. Physical solvents are favorable for bulk removal of acid gases at high pressure. The Perturbed Chain - Statistical Associating Fluid Theory (PC SAFT) Equation of state is used to model the interactions of DEPG with other components.

- Acid gas liquid treating.

The acid gas liquid treating is designed for bulk removal of acid gases at high pressures. Liquid treating occurs at low temperatures and high pressure. A liquid liquid extractor is used instead of an absorber column. The property package used Electrolyte Non-Random Two Liquid (ENRTL) model for thermodynamics. It uses Peng Robinson equation of state for vapor phase properties. Selection of acid gas property package will automatically add selection of reactions to Aspen hysys model. These reactions are made to emulate chemistry that occurs between amines, water and acid gas. Reaction set 1 covers reaction in Absorber, Reaction set 2 covers reaction in Regenerator. Reaction set 3 is used for reaction equilibria. The kinetic reaction model is represented by

$K = A*e^{(-E/RT)}*T^B$

Where, A- frequency factor

E- Activation Energy, B- Extended rate reaction constant

On an industrial scale, chemical solvents are used for the separation of CO2 which is based on the amine scrubbing technique. The aqueous solution of the amine-based scrubbing technique is a highly mature and mostly practiced technique in the CO2 capture process on an industrial scale. Amines are further divided into three different categories; primary, secondary, and tertiary amines, depending upon their one, two, or three hydrogen atoms which are replaced by the alkyl functional group. Monoethanolamine (MEA), diethanolamine (DEA), N-methyl diethanolamine (MDEA), diglycolamine (DGA), diisopropanolamine (DIPA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ) are some of the most commonly utilized aqueous alkanolamines in the absorption process.

Even though alkanolamines have numerous applications industrially, and are frequently used solvent, still have many demerits, which includes low loading of CO2, high loss of vapors, corrosion of equipment, and consumption of high energy, thermal and oxidative degradation. According to the stoichiometric analysis, the loading capacity of primary and secondary amines (MEA and DEA) is restricted to 0.5 moles of CO2 per mole of amine. The tertiary amines MDEA and TEA have recently become very important amines because it is selective and more ideal for H2S but having the high capacity to remove CO2, loss of low vapors, enthalpy of reaction with CO2 is very low, high thermal stability, low vapors loss, and low enthalpy of reaction with CO2, the most vital property in the regeneration of amines.

This study aims to investigate the capture of both CO2 and H2S using a novel amine blend to find out the solubility of CO2 and H2S. MDEA is selected as the main amine in this study. The concentration of H2S and CO2 in sweet gas using MDEA at 25 ºC to 50 ºC and at pressure of 57 bar was investigated by using the Aspen HYSYS V12 simulator.

METHODOLGY

The present work was completed by using Aspen HYSYS V12.1, a commonly used software for acid gas removal unit (AGRU) in different oil and gas fields. The Acid Gas (chemical solvent) built-in thermodynamic package was used for this simulation because both solvents are chemical solvents, and the Acid Gas package produces output with lesser deviation.

The Acid Gas – Chemical Solvents package in Acid Gas technology supports solvents including MDEA, DEA, MEA, DGA, DIPA, PZ and TEA. It also supports solvent blends including Sulfolane + DIPA, Sulfolane + MDEA, Sulfolane + MDEA + PZ, MDEA+ MEA + DEA and any two chemical solvents. The Acid Gas - Chemical Solvents package is developed with the Peng-Robinson equation of state for vapor phase and electrolyte NRTL (eNRTL) for electrolyte thermodynamics.

PROCESS DESCRIPTION

A feed stream of natural gas with bulk spec concentration of CO_2 and H_2S containing above specification levels of acid gases (both CO_2 and H_2S) and Lean amine solution of 45wt% MDEA and 55 wt% Water. The absorber is critical unit in acid gas cleaning. It contains 20 trays and operates at high pressure. Th sour feed gas and lean amine enters the column while sweet gas and rich amine exits the column. The temperature in the absorber can range from 15-65ºC.

Higher temperature helps prevent condensation and foaming. Other factors that affect performance can include strength of amine, flowrate and impurity loading in amine.

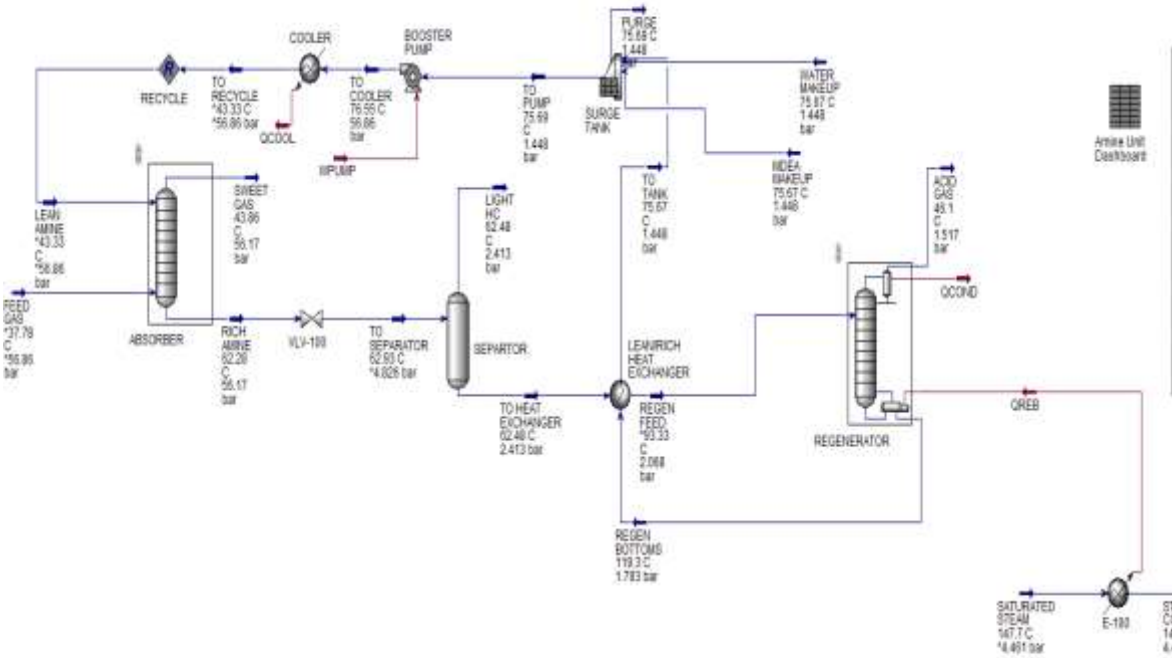
Most of the mass transport occurs in bottom half of the column. A phenomenon called ‘temperature bulge’ can occur due to high heat of absorption generated by mass transfer. Heat is quickly carried by the column by liquid flow so heat travels upwards with the vapor flow. Increase in vapor flow rate will increase temperature bulge.

The separator flashes rich amine to low pressure. It is used to separate dissolved sweet gas. Dissolved hydrocarbons can cause foaming Residence time can be over 20 minutes. Light hydrocarbon liquids are skimmed within the flash tank.

Regenerator allows for reclamation of amine by separation. It is energy intensive process. The heat exchanger preheats the regenerator feed stream with bottoms product stream from absorber. This heat integration controls the temperature profiles in the system and reduces the amount of cooling and heating energy that needs to be used in the process. Passing as much heat as possible from the lean amine to rich amine provides the most favorable heat integration. The regenerator heats the amine solution unbinding the contaminants from amine solution. This takes place at elevated temperatures and low pressures to facilitate the separation. The condenser will not condense CO_2 and H_2S instead only returning water, amine and hydrocarbons. Common reflux ratio range from 1 to 3. The reboilers are major cost center to the Column. A typical Reboiler duty is 6 MMBtu/hr. The lean amine solution from the column leaves through bottom of column and sent to lean/rich heat exchanger.

The Concentrated contaminants stream leaves through top of column for further process. To keep the process at steady state a storage tank is used to provide makeup water and lean amine. This restores the amine solution to its original strength. Replenishing losses due to separation operation or formation of heat stable salts. In addition, a portion of lean amine called the slip stream is diverted to remove contaminants such as iron sulfides. Subsequent pumping and cooling will bring the recycled amine for conditions to required to be used in absorber. This closes the recycle loop for lean amine. Process limits for the sweet gas stream is 4 ppmv H_2S and 2% CO_2 by volume.

Process Simulation of Acid Gas Cleaning Using MDEA



Amine Unit Dashboard		
CO2 Composition(mole %)	0.7385	
H2S Composition(ppm)	0.6392	
Reboiler Duty	1757	kW
Regenerator Steam	2972	kg/h
Lean Amine Loading	4.231e-003	
Rich Amine Loading	0.3837	
Amine Strength (wt%)	45.00	
Amine Recirculation Rate	100.0	USGPM
Regenerator Feed Temperature	93.33	C
Regenerator Reflux Ratio	2.161	
Lean Amine Temperature	110.0	
Feed Gas Flowrate	498.1	kgmole/h
Feed Gas CO2 Mole Fraction	5.000e-002	
Feed Gas H2S Mole Fraction	2.500e-002	

SIMULATION BASIS

The default method for acid gas cleaning is efficiency mode. The calculations in Aspen Hysys assumes the two film Theory assumes the resistance to heat and mass transfer is concentrated in two films one for each phase. In efficiency mode this theory is used to determine mass fluxes and efficiencies for CO_2 and H_2S only. The model does not account for resistance to heat transfer or further discretized the films. It accounts conversion for CO_2, H_2S and amines in fluxes while the other compounds are determined with equilibrium calculations and efficiencies. It is possible to specify efficiencies for these other components. It relies on equilibrium model for material/energy balances. Acid gas in Aspen Hysys is rate-based technology.

Acid Gas in Aspen HYSYS accounts for not only kinetic reaction rate-based modeling, but it also accounts for mass transfer resistance. The Acid Gas technology provides Efficiency Modeling mode and Advanced Modeling mode for different levels of model fidelity. Advanced Modeling mode can be used to identify bulge-pinched and lean-pinched absorber columns. One can plot absorber temperature by stage in Aspen HYSYS and see the corresponding efficacy of the absorption.

One can just plot the partial pressure of H2S or CO2 by stage in the vapor vs. aqueous phases to see if the column is pinched. Efficiency mode accounts for mass-transfer resistance at the vapor-liquid interface to calculate "rate-based" efficiencies for H2S and CO2, and this mode allows the HYSIM I/O algorithm to be used in the column. The Advanced Modeling mode accounts for mass-transfer resistance at the vapor-liquid interface to calculate the flux of all components, and this mode uses the rate-based distillation directly.

PROCESS SIMULATION

This study consists of a liquid-liquid acid gas treating process using MDEA as a chemical solvent at high pressure to remove H_2S and CO_2 from acid feed gas. 9610 kg/hr of acid gas feed (2.5 mol% H_2S and 5 mol% CO_2) is fed to Absorber (57 bar), where the H_2S is removed to < 10 ppm H_2S in the overhead hydrocarbon product (mostly C3). Acid gases are stripped from amine by a regenerator column at low pressure (1.5 bar) and high temperature (119 ^oC) from the MDEA solvent, which is recycled with makeup back to the extractor column. The Feed Gas enters the absorber at 56.86 bar and temperature 38 ^oC where acid gases are absorbed with lean amine and the sweet gas (sales gas) from the top of absorber is achieved with desired spec. The bottom rich amine from absorber at temperature of 63 ^oC is fed to separator where light hydrocarbons are flashed and the outlet is preheated with the bottoms form regenerator at temperature of 93 ^oC fed to Regenerator. In Regenerator the rich amine is stripped of acid gases (H_2S and CO_2) at a reboiling temperature of 147 ^oC and heat duty of 1757 KW. The stripped rich amine from bottom of Regenerator at temperature of 119 ^oC is cooled to 76 ^oC in lean/rich heat exchanger and fed to surge tank for makeup lean amine going to absorber. The desired sakes gas specification of less than 10 ppm H_2S gas and 0.74 mol% (<2 mol%) CO_2 in sweet gas is achieved with MDEA as amine solvent.

Input specification for Aspen Hysys Simulation

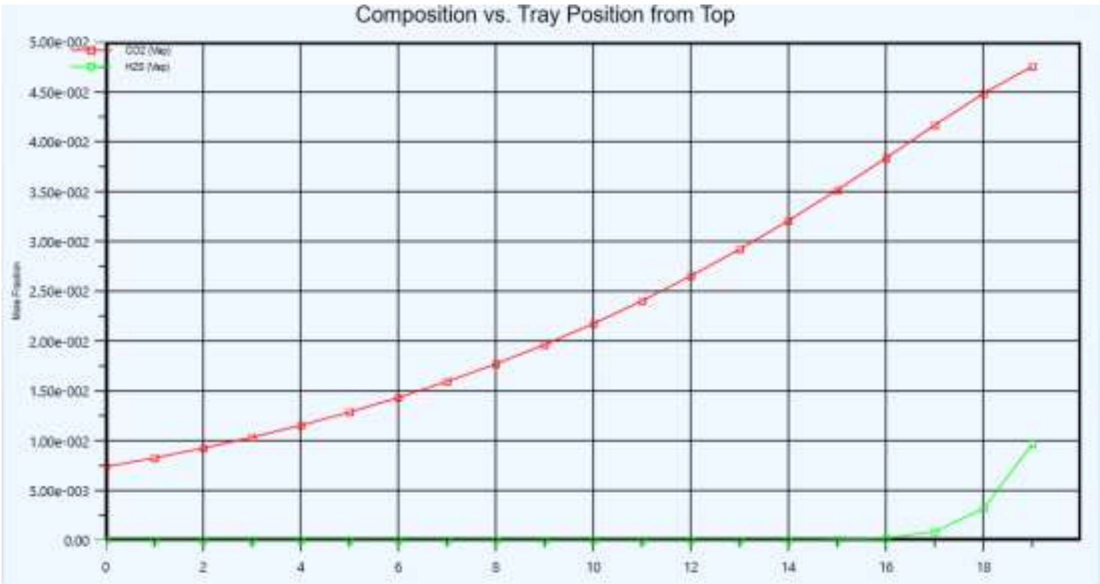
Parameters	
Gas flowrate (kgmole/hr)	498.1
Gas temperature (^oC)	38
Gas pressure (bar)	57
Composition of CO_2 in feed gas (mole fraction)	0.05
Composition of H_2S in feed gas (mole fraction)	0.025
Solvent flowrate (m^3/h)	24
Solvent temperature ^oC	43
solvent pressure (bar)	57

Absorber trays	20
Regenerator trays	10
Condenser temperature °C	46
Reboiler temperature °C	148

RESULT AND DISCUSSION

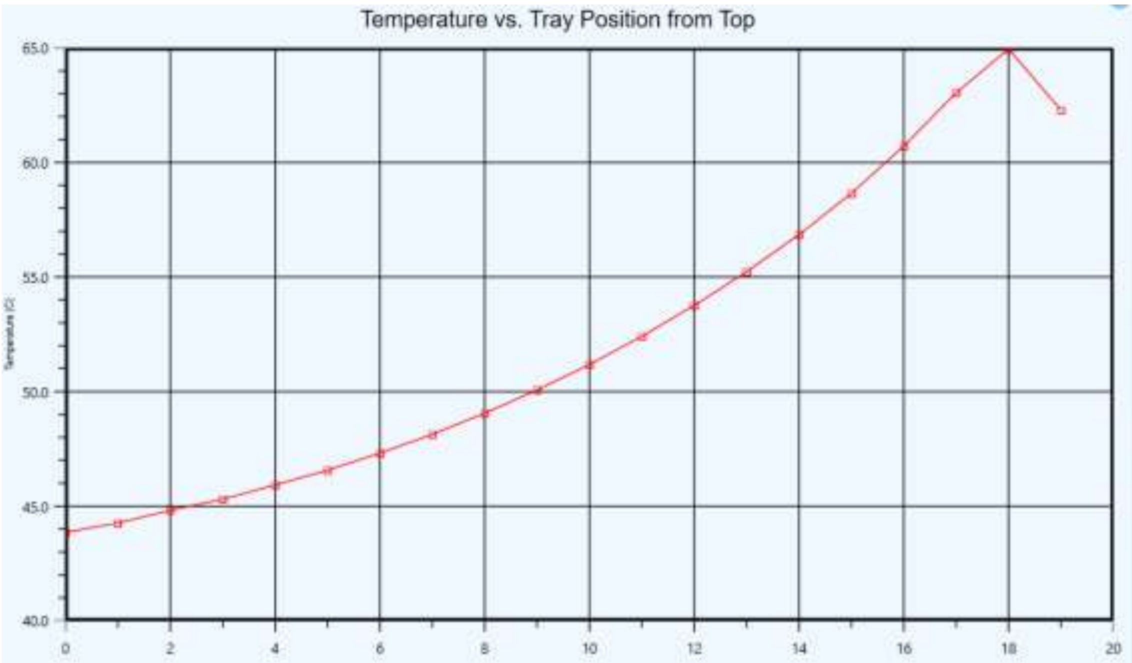
- **Effect of Composition vs Tray Position from Top**

It can be seen from the composition vs the tray position from top curve that as the acid gas rises in the absorber with countercurrent flow of lean MDEA Solution, the H_2S concentration gradually decrease from 2.5 mole % at 20th tray to zero mole % at first tray. Similarly, the CO_2 concentration gradually decrease from 5 mole % at 20th tray to less than 1 mole %. at first tray. This shows that the most of mass transfer from acid gas to lean MDEA solution takes place at the bottom of the Absorber.



- **Effect of Temperature vs Tray Position from Top**

Also, it can be seen that as the acid gas rises to top in the Absorber, Temperature bulge occurs in the column with temperature rising highest at tray eighteen in the bottom of the absorber. This temperature rise is due to high heat of absorption taking place at the maximum mass transfer towards the bottom of the absorber.



CONCLUSION

The overall CO2 and H2S absorption in a MDEA solution was investigated using Aspen HYSYS simulation software. It is investigated that the tertiary amines MDEA have recently become very important amines because it is selective and more ideal for H2S and having the high capacity to remove CO2 using the Acid Gas Cleaning -Chemical Solvent Property Package in Aspen Hysys V12.The effect of composition and Temperature on tray position from top was studied and it is observed that the bulk of mass transfer takes place at the bottom of the Absorber with high temperature in the Rich Amine outlet in the Absorber due to high heat of Absorption.

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