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Acid Gas Removal from Natural Gas with N-Methyldiethanolamine (MDEA): A Case Study

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Abstract

Natural gas is one of the most popular fossil fuel in the current era and future as well. Natural gas impurities like water, CO_2, H_2S, COS, mercury & N_2 have to be removed to meet transport specifications. Amines processes are the developed technology available today for the removal of acid gases (CO_2 & H_2S). In the present study, Siri Island Natural Gas sweetening plant process was investigated. Since the plant started up in 2007, it has employed the MDEA process to purify sour natural gas to ultra sweet specifications before it moves to liquefaction. The process was simulated by Aspen Hysis Program and optimized based on the real field data. The sensitivity of the process to amine temperature and flow rate has been done. Besides the Siri NGL process's relatively high capital and operating costs and high stripping energy, reports of major process concerns of poor CO_2 removal. To overcome this obstacle, other solvents were investigated and analyzed. The results show that the mixture of MDEA with DEA can achieve the economic aspects and operational specification.

Introduction

About 33% of the world's natural gas reserves are discovered in offshore fields and 40 % of the natural gas reserves are sour or acid, containing large quantities of CO2 and H2S and other sulphur compounds. To realize its value it has to be brought onshore, to be processed to the required specification and send to distribution networks. Lack of means to bring stranded natural gas to the market leads to increase of remotely located natural gas reserves, flaring and re-injection of associated gas from offshore fields [1-2].

Flaring of associated gas has become an environmental issue with high degree of focus among approving authorities and oil companies. Handling of associated gas for oil developments has become a more critical issue than before. Therefore, this has led the oil and gas industry to seek solutions that can handle the associated gas in an acceptable manner both economically and environmentally. The Iranian Offshore Oil Company (IOOC) is planning for the expansion of the existing onshore Sirri Island complex located in the South East of Sirri Island in the Persian Gulf, Iran. The Sirri Island Gas Gathering and NGL Recovery Project involves expansion of existing reception facilities and the addition of new gas & condensate transmission lines, gas compression and processing facilities, with associated utilities.

There are several treating processes available for H_2S removal from natural gas. Some of these processes use chemical, physical, and hybrid solvents while few others using physical separation by special membranes. [3]

Among the addressed methods, alkanolamines for sweetening have been employed widely. The alkanolamine aqueous solutions are capable of absorbing impurities such as hydrogen sulphide and carbon dioxide from natural gas. [4]As the degree of the gas acidity increases, the energy required by the process to achieve sweet gas specifications in terms of H2S and CO2 concentrations will increase.[5] This is particularly true for gas sweetening processes using Alkanol-amine solvents such as the primary amine: methyl-ethanolamine (MEA), the secondary amines: diethanolamine (DEA) and di-isopropanolamine (DIPA), and the tertiary amines: tri-ethanolamine (TEA) and methyldiethanolamine (MDEA). Many recent researches have focused on investigating the mixing of different amine solvents. [6-9]

In the past few years, mixed amine solvents for the removal of acid gases have received increased attention. [6] Application of mixtures of alkanolamines, a solution of two or more amines in varying concentration, has been shown to produce absorbents with excellent absorption characteristics Reliable accurate models of gas sweetening processes allows one to optimize operating conditions thus minimizing operational costs. This is a necessity due to inherent seasonal variations in feed stream and temperature. Attempts to develop such models include those that are based basic principles and those that are data-based using input/output plant data [10]. Models based on detailed mass and energy balance equations proved to be very complicated and hard to solve especially when coupled with optimization computer routines [11].

The study aims to simulate the gas sweetening process Siri Island NGL plant by using the latest version of Aspen HYSYS program. The simulation work is adopted amine gas sweetening process by using MDEA solution and its results were compared with real plant data. The simulation work is will be used for process optimization

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by using several amine rate and temperature. In addition, several amine types and blends are compared to select the best solvent.

Experimental

Gas sweetening processes

Numerous processes are available:
- Chemical absorption
- Physical absorption
- Solid bed adsorption

Absorption processes are the most utilized.

Chemical Absorption

In this type of process, the chemical solvent absorbs the acid components present in the feed gas by chemical reaction and releases them by heating at low pressure. A chemical reaction processes mixes a chemical with the gas stream in order to neutralize hydrogen sulphide, or "sweeten" the gas. The most common of these processes is called "amine sweetening". Alkanolamines (or simply, amines) are substances which are weak bases. They react chemically with acid gases like hydrogen sulphide to form salt complexes.

These salt complexes can be broken down so the amines are relieved of acid gases and can be recycled. An acid gas is a gas that forms an acid when combined with water. Examples of acid gases include hydrogen sulphide and carbon dioxide. [9](Figure 1)
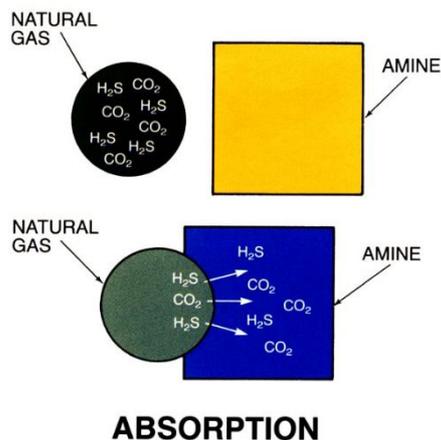

Figure 1: Amine chemical absorption

The main chemical solvents are:
- The Alkanolamines
- MEA (Monoethanolamine)
- DEA (Diethanolamine)
- TEA (Triethanolamine)
- MDEA (Methyldiethanolamine)

Amines properties are listed in table 1.Alkanolamines cannot be used pure for different reasons:
- Close to solid state at ambient conditions
- Low stability at high temperature (heating is needed to extract the absorbed acid gases) with generation of highly corrosive products by decomposition.[10]

Therefore these products are utilized in aqueous solutions with the following concentrations:
- MEA   15 to 20 % weight
- DEA   25 to 35 % weight
- MDEA   30 to 50 % weight

Table 1: Amines properties

PROPERTY	Monoethanol Amine	Diethanol amine	Triethanol amine	Methyldiethanol amine
Formula	HOC2H4NH2	(HOC2H4)2NH	(HOC2H4)3N	(HOC2H4)2NCH3
Molecular Wt	61.08	105.14	148.19	119.17
Boiling Point @ 760 mmHg, °F	338.9	516.2	680	477
Freezing Point, °F	50.9	82.4	72.3	-5.8
Critical Constants Pressure, psia Temperature, °F	868 662	474.7 827.8	355 957.7	562.3 611.6
Density @ 20ºC gr/cc	1.018	1.095	1.124	1.0426
Weight,IB/gal	8.48 @ 60°F	9.09 @60°F	9.37 @68°F	8.69
Specific Gravity 20°C/20°C	1.0179	1.0919	1.1258	1.0418
Specific heat @ 60°, Btu/ Ib°F	0.608 @68°F	0.6	0.7	
Thermal Conductivity @68°F	0.148	0.127		
Heat of Vaporization Btu/lb	355 @ 760 MM Hg	288 @73mmHg	230 @760mmHg	233
Viscosity, Cp	24.1 @68°F	350 @68°F	1013 @68°F	101 @20°C
Flash Point,°F	200	280	395	
Constance for Antoine Equation A B C	8.02401 1921.6 203.3	8.12303 2315.46 173.3	9.6586 4055.05 237.67	16.23 7456.8 311.71

Sour gas (or natural gas with acid gas in it), is subjected to a stream of amines, which absorbs the acid gas, leaving sweet gas (or natural gas without acid in it). The amine solution containing the acid gas then goes through a process of distillation to remove the acid gas. The lean amine is then reused.(Figure 2)

H_2S gas becomes concentrated during the distillation process. Typically, it is burned in a flare stack. If the volume of H_2S is very large, then the H_2S must be converted to sulphur and recovered for environmental reasons. The recovered sulphur can be sold to help offset operating costs.
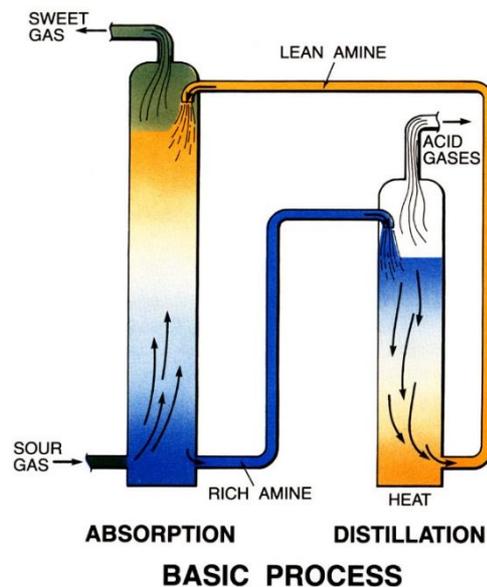

Figure 2: Amine regeneration process

Process description

In the gas processing industry absorption with chemical solvents has been used commercially for the removal of acid gas impurities from natural gas. Alkanolamines are the most commonly used category of chemical solvents for acid gas capture. In Siri Island NGL project, the Acid Gas Removal unit will treat approximately

143.4 to 143.0 MMSCFD (summer and winter cases) of gas containing approximately 4.12% CO2 and up to 240 ppmv of H2S. A generic MDEA solution, at 50 wt% strength, is used to sweeten the gas and reduce the CO2 content to below 2%. Sour gas is first passed through an Inlet Gas Filter/Coalescer to remove any liquid or particulate contamination, before passing through the Amine Contactor. The Inlet Gas Filter/Coalescer is a vertical vessel comprised of upper and lower chambers, separated by a tubesheet. The Gas first enters the lower chamber, for bulk liquid removal, and then the upper chamber, through the tubesheet and the coalescing filter elements. The flow through the coalescing elements is inside out. The coalescing filter elements will remove both solids and liquid droplets that are 0.3 microns and larger. Liquid droplets coalesce and grow in size in the elements, descend via gravity, and are collected and removed, at the bottom of the upper chamber. At the same time, the solid particles removed from the gas are swept out of the element by the downward liquid drainage from the elements.

This plant uses the process of chemisorptions to remove H2S, and other acid gases, such as Carbon Dioxide (CO2), from the raw gas stream. Chemisorption is a two-step process involving both absorption and chemical reaction. An aqueous amine solution, at a concentration of 50 weight percent, is used to sweeten the raw gas. This solution contains water into which the gases dissolve, and formulated solvent, containing the basic tertiary amine, n-methyldiethanolamine (MDEA), with which the acid gases chemically react. Sour raw gas introduced into the bottom of the tower and is passed, counter current to lean amine solvent, through the Amine Contactor. Gas leaving the topmost tray of the Amine Contactor should have less than 2 ppmv H2S and less than 2% CO$_2$ before it proceeds on to the Sweet Gas Cooler.

The Amine Contactor is a trayed absorption column containing single-pass valve trays. The three topmost trays are water-wash trays used to scrub any entrained amine solution from the exiting gas. The lower trays, promote mass transfer between the aqueous amine solution and the sour gas.

The bottom of the tower, directly below the seal pan of the bottommost tray, provides some surge capacity.

Lean amine is fed to top section of the Amine Contactor, and flows down the column to be collected in the surge section. A lower lean amine feed point will increase the amount of CO2 in the sales gas stream, and reduce the amount of stripping energy required. Amine in the surge section is rich and must be regenerated before it is reused.

Demineralized water is fed to the topmost tray, Tray #1, and blends into the amine solution flowing down the column. This sweet gas passes through the Sweet Gas Cooler (11-A-101) , where the temperature is reduced to 55oC .This will condense water from the gas stream prior to entering the molecular sieve dehydration unit and reduce the load on the dehydration system. If the stream is cooled too much some of the hydrocarbons will start to condense and reduce the product recovery. If the temperature is too warm the water loading on the molecular sieve dehydration unit will be increased and water breakthrough could possibly occur.

The 2-phase stream from the Sweet Gas Cooler is separated in the Sweet Gas Scrubber (11-D-101) , to remove the free liquid from the gas stream. The gas flows upward through a wire mesh mist eliminator where liquid droplets greater than 10 microns are removed and flows to the Sweet Gas Filter/Coalescer. The liquid is level controlled and flows to the closed drain tank.

Rich amine is collected, at the bottom of the Amine Contactor, and flashed down to near 6 Bara. The flashed gases and amine enter the Flash Tank (11-D-102), to allow the release of absorbed hydrocarbon gases and the separation of absorbed hydrocarbon liquids. The vapour is back pressure controlled and flows to the acid gas incinerator (19-X-101).

The rich amine flows through a particle filter (11-F-102 A/B) to remove solid impurities before a slip-stream flows through an activated carbon filter (11-F-103) to remove residual hydrocarbons in the rich amine. Before being fed to the top tray of the Amine Regenerator, the stream is preheated in the Rich/Lean Heat Exchanger (11-E-101).

The amine sweetening process involves an acid-base reaction between acid gases and amine. In order to reverse this chemical reaction, pressures are decreased and temperatures are increased, thus liberating the acid gases (H2S and CO2) and regenerating the amine solution. Regeneration is accomplished using the Amine Regenerator (11-C-102), Amine Reboiler (11-E-102), and associated reflux equipment.

The Amine Regenerator is a trayed distillation tower equipped with valve trays. Rich amine enters the tower, flows down through the trays, and is collected in the surge section of the tower, before flowing to the Amine Reboiler. Reflux is returned to the tower, on the topmost tray, Tray #1. Hot vapours, from the reboiler, enter the tower's surge section and flow upward, counter current to the amine, and exit the tower, overhead. During normal operation, the liquid level, in the surge section of the tower, is determined by the weir height in the reboiler and the liquid and vapour hydraulics.

The Amine Reboiler is a horizontal kettle reboiler designed to provide the duty required to drive the stripping in the Amine Regenerator. Amine is fed into the shell side and LP steam flows through the tubes. The shell is divided into two compartments by a weir. In the inlet compartment, heat is transferred from the steam to boil the incoming amine. The boiled vapour is routed back to the surge section of the Amine Regenerator and will travel up through the tower's trays. Lean amine, in equilibrium with the boiled vapour, will overflow the weir, into the reboiler's downstream compartment.

This lean amine will be cooled by the Lean/Rich Amine Heat Exchanger (11-E-101) and sent to the Lean Amine Surge Tank (11-T-101). Temperature control is achieved by changing the flow rate of the heat transfer medium. Pressure, in the Amine Reboiler, is controlled by increasing or decreasing the back pressure on the regeneration system. The amine regeneration reflux circuit consists of: the Amine Reflux Condenser(11-A-102) , the Amine Reflux Accumulator (11-D-103) , and the Amine Reflux Pumps (11-P-103A/B).

The Amine Reflux Condenser is a forced-draft air cooler used to cool the Amine Regenerator overhead vapours. This cooler is equipped with variable pitch fan blades and automatic louvers on the air outlet and for temperature control. The cooled acid gases and condensed water enter the Amine Reflux Accumulator. The water/acid-gas mixture temperature must be controlled near its setpoint. Figure 3 shows Siri Island NGL recovery sweetening unit PFD.

Simulation and Validation

Simulation is done using Amine Package with Kent Eisenberg's thermodynamic Model for Aqueous Amine Solutions and non ideal vapour phase model. The input gas composition for base model can be found in table 2.

To validate the model results, the Top Regeneration was compared by the plant data. The performance of the proposed method is evaluated with statistical concept of mean relative error (MRE). As the figure shows, the simulation result is in good agreement with real data.

$$MRE = \frac{1}{N} \sum \frac{C_R - C_s}{C_R} \tag{1}$$

Where C_R is the component concentration in real data and C_s is concentrations in the simulation case. Mean relative error of the comparison was about 0.02%.

Table 2: Feed Gas Composition for base model

Mole Fraction	Summer%	Mole Fraction	Summer%
MDEA	0	CH4S	0,00040894
Methane	71,2449	COS	9,53E-05
Ethane	11,5462	P-C6*	0,30987
Propane	7,23941	P-C7*	0,14999
Isobutane	1,224	P-C8*	0,0638791
n-Butane	2,1139	P-C9*	0,015633
Isopentane	0,56633	P-C10*	0,0034371
n-Pentane	0,55066	P-C11*	0,00073686
Hexane	0,017739	P-C12*	0,00011709
Water	0,22848	P-C13*	5,81E-05
Nitrogen	0,58282	P-C14*	5,93E-06
Carbon Dioxide	4,1173	P-C15*	6,56E-07
Hydrogen Sulfide	0,024006	P-C16*	9,50E-08

Figure 3: PFD of the Amine Sweetening Unit

Table 3: Simulation vs. Real data for Top Regeneration

Component	Simulation	Real
Methane	0.002655	0.019485
Ethane	3.14E-04	0.002417
Propane	1.13E-04	0.001041
i-Butane	1.20E-07	1.24E-05
n-Butane	1.99E-07	2.06E-05
i-Pentane	9.12E-08	6.71E-06
n-Pentane	8.56E-08	6.32E-06
n-Hexane	4.94E-06	4.68E-05
H2O	0.093672	0.092356
Nitrogen	6.57E-06	8.96E-05
CO2	8.91E-01	0.872346
H2S	1.23E-02	0.012064
M-Mercaptan	6.11E-05	6.03E-05
COS	4.80E-05	4.70E-05
MDEAmine	2.10E-15	1.60E-07

Results and Discussion

Amine Temperature effect

To investigate the effect of the amine temperature on the efficiency of the absorption column, different cases with the same flow rate and pressure but with different temperature were prepared. Figure 4 shows the change in H_2S concentration in the rich amine as function of temperature. Based on the results it is clear that the equilibrium constant in the MDEA protonation reaction gets higher with lower reaction temperature. In other words, decreasing the temperature shifts the equilibrium of the exothermic reaction forward, thus increasing the absorption rate. Based on the figure, decreasing the Amine temperature leads to an increase the rich amine loading, thus a decrease in H_2S concentration in sweet gas.
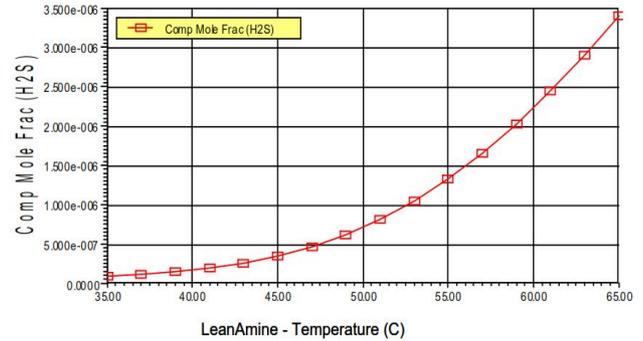

Figure 4: Effect of lean amine temperature on H_2S absorption

Amine flow rate

Several case studies were carried out to verify the lean amine flow rate effects on the absorption column efficiency. The circulation rate in turn is considered one of the most important parameters determining the degree of removal of H_2S and CO_2 as the acid gas impurities. Clearly, a higher circulation rate will results the higher energy costs to regenerate the amine. Increasing the Amine flow rate causes that the plants experience operating difficulties including high solvent losses and contamination of the amine solution. On the other hand, low amine flow rate will results failure to meet sweet gas specification.

The selected temperature can be influential on the selecting proper lean amine flow rate. Improperly selected lean amine temperature results in decreased amine acid gas loading and will results in acid gas content increment in the sweet gas. In this case to ensure the required level of gas sweetening, the process must be forced to increase the amine circulation rate. Rising the circulation rate certainly leads to an increment in energy costs and operating costs overall. Figures 5 and 6 are the proofs for the stated facts.
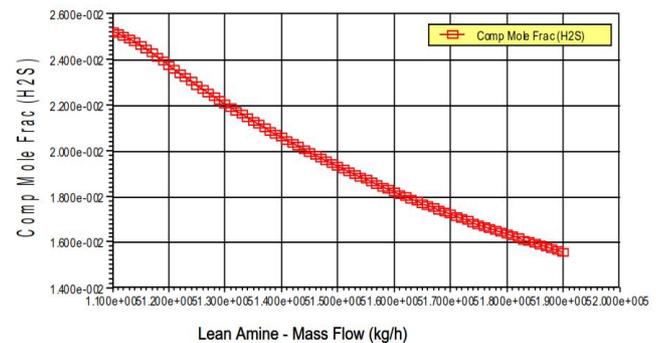

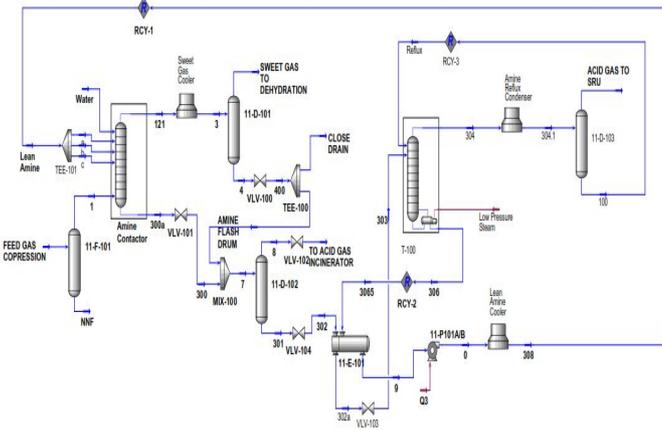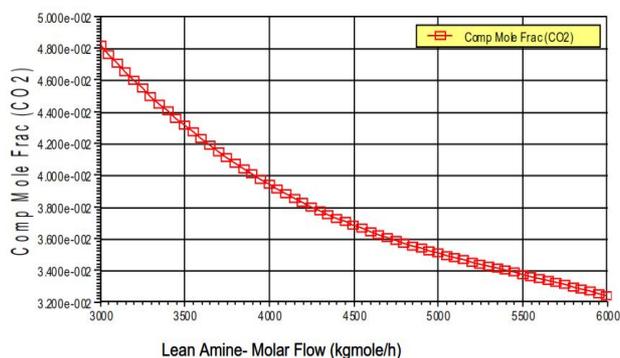**Figure 5**: H_2S content variation with Amine mass flow

Figure 6: CO_2 content variation with Amine mas flow

In addition to the Amine flow rate, Amine concentration is another variable which affects the process behavior. Increasing the amine concentration is not always feasible because of corrosion. High amine concentrations result in rich acid gas loadings which are high enough to results in inverse corrosion problems in the heat exchanger, filters and reboiler. In particular case, increasing the amine concentration may not be a viable option.

Amine Selection

The use of MDEA for selective H_2S removal is based on the fact that unlike DEA, MDEA does not react directly with CO_2. This particularity, which is used to advantage for selective H_2S and controlled CO_2 removal, becomes a difficult situation for complete acid gas removal. In addition, employing MDEA is advantageous only to the extent that it raises the amine concentration and decreases the mixture's heat of absorption. It will be critical when a considerable quantity of CO_2 has to be removed. To surmount on this kinetic obstacle, the mixture of secondary amines which have high speeds of reaction with CO_2 with desirable MDEA solvent are the most prospective solvents.

Since the Siri NGL process's relatively high capital and operating costs and high stripping energy, investigating a new suitable solvent for sweetening plant is necessary. To do so, MDEA added to a 30 wt % DEA solution. H_2S concentrations are not shown since these were well below specification. The circulation rates and all other process variables were held constant. Figure 7 shows the different amine solutions performance. Based on the figure, the mix Amine show better performance in CO_2 removal than the single ones.
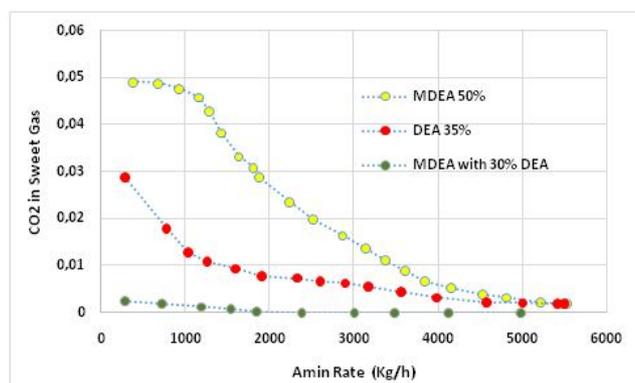

Figure 7: CO_2 content variation with different Amine solutions

Figure 8 shows the acid gas concentration in the sweet gas as a function of lean amine temperature for different solvents. The sweet gas CO2 concentration exhibits a minimum at a lean amine temperature for all the cases. The higher temperature increases the kinetic effect to a greater extent relative to the decrease in

solubility. However, after a certain temperature, the solubility dominates the kinetics. Note that the CO_2 concentration is never higher than the design specification.

Another parameter which must be considered to proper design is water loss of the system. It seems from Figure 9 that the water loss in sweet gas stream is increasing by increasing amine rate for all amine types. However, 35% DEA may show the lowest water losses for almost amine rate. In fact, water losses lead to various technical problems for example, amine losses and low amine concentration as well. Moreover, amine foaming may also be considered as the main responsible about this phenomenon.
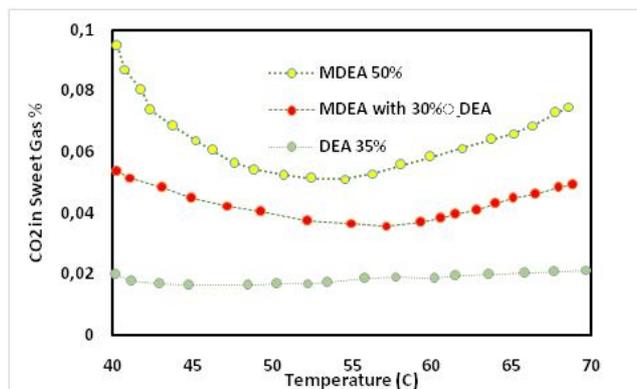

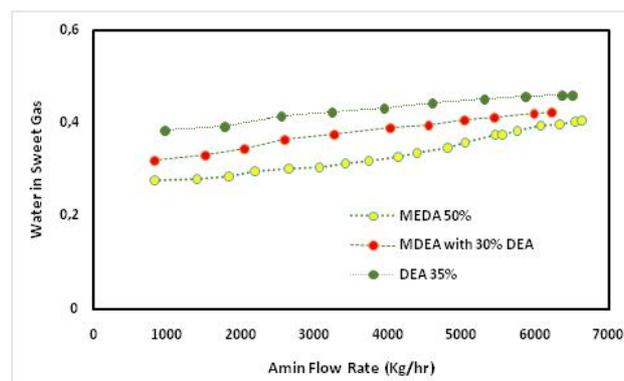**Figure 8**: Effect of lean amines temperature on CO_2 absorption

Figure 9: Water Loss for different types of the solvents

Economic analysis must be done for selecting proper solvent. In process economics, the total expenses on capital and operation of a plant are directly influenced by the design and operating parameters of the process. The circulation rate is considered the most important influence on the economics of gas treating with chemical solvents. Solvent circulation rate influences the size of pumps, lines, heat exchangers, and regeneration tower, and affects the capital cost of gas-treating plants. Circulation rates also influence the energy requirement for solvent regeneration because the reboiler heat duty is associated directly with the liquid rate. Another factor that plays an important role in gas-treating economics is solution corrosivity, which determines the material of construction of units due to the high temperatures and solution acidity. Cost estimates of equipment and other costs related to capital investment play a crucial role in selection among design alternatives. Capital cost estimates combined with process operating cost and other expenses need to be fully considered, since the viability of a proposed change to an existing gas-treating unit depends on them. Figure 10 shows a comparison of the estimated annual cost of power for all the alternatives. It shows that MDEA-DEA alternatives have considerably lower annual costs of power consumption. Replacing the Siri NGL process with

MDEA-DEA alternatives will save up to 48%/year of the expenditure on power.
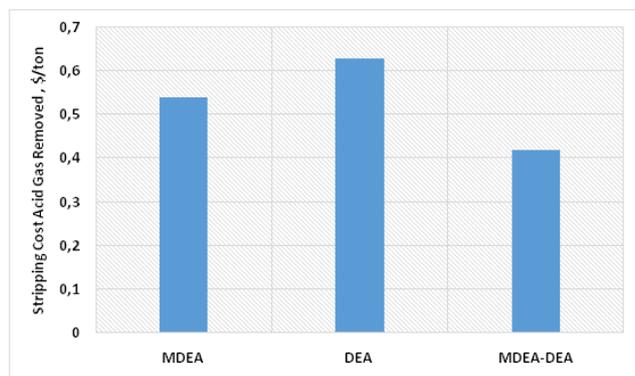

Figure 10: Economic Efficiency on Acid gas stripping

Conclusions

In conclusion, this work-study is achieved Siri Island NGL plant gas sweetening process design calculations and simulates the process by using Aspen HYSYS. The model was verified with real data. The process was optimized and the sensitivity analysis was done on the process. Several process parameters are examined like Lean Amine flow rate and temperature. To investigate another solvent, the mixture of DEA with MDEA was investigated and compared with DEA and MDEA. The results show that its performance for CO_2 absorbing is much better than MDEA and has less stripping cost than the other solvents.

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