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Simulation of Loading Capacity of MDEA and DEA for Amine-Based CO_2 Removal Using Hysys

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Abstract: Besides meeting international stringent LNG product specification, this work will address the problem of off-spec product, high operational cost of acid gas (CO_2) removal and pollution-free product, which is currently a huge global challenge. This work studied other ways by which amine unit can best be optimized to produce LNG gas with low CO_2-content and high cost of acid gas removal. MDEA instead of DEA solvent-absorption method was chosen for the optimization using HYSYS 3.1 process simulator to predict the CO_2 removal through the establishment of process operating conditions. A base case of amine-based CO_2 removal process was used to create a steady-state and dynamic simulation using HYSYS 3.1 simulator. The differences between the values of acid gas loading capacity and CO_2 content of the existing DEA operational value and HYSYS simulations were 0.00005 and 4.98 respectively. This established the advantage and accuracy of the HYSYS simulator and the developed models. The simulation results showed that the proposed MDEA had higher CO_2 removal capacity of 89% to 55.02% for DEA and lower CO_2 content of 0.0012 mole of CO_2 in sweet gas to 0.014 mole of CO_2 in DEA. MDEA had higher solvent recovery of 83% to 60% recovery for DEA. The pump size required to recycle MDEA with molar flow rate of 1877 Kg mol/hr. was smaller and less expensive than that required for DEA at 2371 Kg mol./hr. resulting in lower production cost.

Keywords: Absorber, Absorption, DEA, HYSYS, MDEA, Optimization, Regenerator, and Stripping

1. Introduction

The LNG production process plants have undergone tremendous development in process design, plant size and liquefaction method, since its discovery and soon forgotten is the most important component of LNG production which is the acid gas removal unit regarded as a problem zone or cost incurring centre which does not generate “real” income, but a closer look at this unit with all the attendant problems, can indirectly be a source of revenue for the production process plant.

The problem of foaming, plugging by freezing can also be traced to CO_2 content. This study will seek the best means to optimize the unit and changing from cost-incurring unit to profit-generating unit through reduced operational cost using HYSYS software.

The world today is facing huge environmental challenge of greenhouse effect and other global climate changes that are traceable to Ozone layer depletion caused by the continuous emission of large amounts of CO_2 into the atmosphere from the operations of oil and gas production, a crime of which the LNG production plants is also guilty. The high cost of production caused by the incessant production of off-specification (spec) liquefied natural gas (LNG) with high CO_2 content reduces the market value, possible rejection and penalty paid for non-compliance with regards to international and local legislature on allowable limits of CO_2 in LNG, all of which leads to loss of income on the huge investment on the LNG production.

The need to reduce the cost of production via optimization of the purportedly cost-incurring Acid Gas removal unit and production of on-spec LNG product that is environmentally friendly directed the pathway and the necessity for this work. Some works were able to show amine scrubbing as the best among the numerous methods available for post-combustion CO_2 capture [1]. Attempts have been made at increasing the production of clean natural gas with low CO_2 content with the use of a different solvent diethanolamine (DEA), which has also taken prominence over the years as the most popularly used solvent for this scrubbing as against monoethanolamine (MEA) which once enjoyed the spot [2].

The process involves absorption reaction of CO_2 with an amine solution followed by regeneration of the amine. MEA has been the preferred choice due to its high absorption efficiency [3]. However, the energy requirement for MEA regeneration is the highest. Furthermore, MEA is known to be very corrosive. Therefore, there is a considerable incentive for using an alternative solvent such as DEA, which is comparable to MEA in terms of performance and cost. In 2003, comparison of the performances of two different technologies was done by the usage of HYSYS and Aspen Plus simulator in estimating the CO_2 capture costs from a coal based power plant for MEA scrubbing and O_2/CO_2 recycle combustion process [4]. Flow sheet decomposition method for simulating key variables affecting MEA scrubbing process was applied [5]. Their simulation was performed using Aspen Plus. HYSYS simulator was applied to design an MEA-based CO_2 removal from a combined cycle gas power plant [3]. Both the power plant and the MEA process were simulated using the software package. The performances of amine solutions for design of CO_2-capture from refinery gas using their own column model written in MATLAB combined with the equilibrium parameters of CHEMCAD and Aspen Plus were compared [6]. While the process simulators are useful, their capability is limited to predicting the behaviour of the process in response to changes in the process structure or operating variables. This study will advance our knowledge by correcting the notion that the CO_2 gas removal regarded as cost incurring can actually be optimized to serve as indirect revenue generation center through the reduction in its operational cost. It also will give an overview of the attendant gains in the use of a new solvent that hitherto was considered undesirable by the known properties of the MDEA. The work therefore seek alternative way by which the unit can be optimized taking advantage of the use of engineering software that reduces the downtime that would have been experienced in stoppage of production and further costly construction of pilot plants to determine or test the efficacy of the developed model.

2. Methodology

2.1. Amine-Based Acid Gas Removal Unit

Extensive laboratory researches earlier conducted on alkanolamines CO_2-absorption reactions were relied on. Laboratory experiments conducted to determine the solubility and reactivity of CO_2 with amines was used to explain and determine the possible removal mechanism and kinetics of reactions of the selected MDEA (a new amine) [7], [8]. and [9]. Their reactivity, compatibility with existing amine plant, availability at low cost, lower corrosive property and high heat of reaction made MDEA achieve a peak position in our list of choice for the replacement of the existing DEA solvent. There are two possible reaction mechanisms for the CO_2 absorption, while one of the reaction proceeds very fast in the formation of bicarbonate, the other reaction is much slower with the formation of carbonic acid. The principle of absorption of CO_2 by amine solvents is governed by the following equations; for instance the reaction of DEA with CO_2 is:

Formation of Carbonate Bicarbonate

$$2R_2NH_2 + H_2O + CO_2 \rightleftarrows (RNH_3)_2CO_3 \quad (1)$$

$$(RNH_3)_2CO_3 + H_2O + CO_2 \rightleftarrows 2RNH_3HCO_3 \quad (2)$$

Formation of carbamate

$$2R_2NH_2 + CO_2 \rightleftarrows RNHCOONH_3R \quad (3)$$

The reactions above proceed to the right at low temperature and allow CO_2 absorption to the left at a higher temperature favours stripping which is a reverse reaction with the formation of carbonate salt and on decomposition release the acid gas absorbed. Reactions (1) and (2) are usually slow because carbon dioxide must form carbonic acid with water (slow reaction) before reacting with amine[10]. Reaction (3) which predominates when DEA is involved is relatively fast, and that is why elimination of selectivity of hydrogen sulfide is impossible.

2.2. Process Description of Amine Units

The general process flow for an amine sweetening plant can be seen in Figure 1 below there are different varieties of the units without much variation in units and accessories irrespective of the type of amine solvent employed for the sweetening process. The main equipment of major importance is the contactor and stripper column together with the associated piping, heat exchanger, and other separation equipment.

The sour gas with its CO_2 should always enter the plant through a scrubber to remove any free liquids and /or entrained solids, the sour gas then enters the bottom of the contactor and flows upward through the column in intimate counter-current contact with the aqueous amine solution Sweetened gas leaves the top of the contactor and flows to a dehydration unit before being considered ready for sale.

Lean amine solution from the bottom of the stripper column (still) is pumped through an amine, amine heat exchanger and then through a water or air-cooled exchanger before being introduced to the top tray of the contactor. The amine moves downward through the contactor counter-current to the sour gas, and removes acid gas constituents from the gas stream. Rich amine solution flows from the bottom of the contactor through the amine-amine heat exchanger and then to the top of the stripper column.

The amine-amine heat exchanger serves as a heat conservation device and lowers total heat requirements for the process. A part of the acid gases will be flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in counter-current contact with vapor generated in the reboiler. The reboiler vapour (primarily steam) strips the acid gases from the rich solution. The acid gases and the steam leave the top of the stripper and pass overhead through a condenser, where the major portion of the steam is condensed and cooled. The acid gases are separated in a separator and sent to the flare or to processing. The condensed steam is returned to the top of the stripper as reflux.

2.3. Method of Optimization

In other to establish the accuracy and choice of the usage of HYSYS 3.1 Simulator for the optimization of the process, it was used to model the existing DEA acid gas removal unit by inputting the operational values in the HYSYS Software and the HYSYS Simulation DEA result revealed high accuracy with a difference of 0.0005 % mol. of CO_2 in Sweet Gas as the modeled HYSYS result was able to predict 0.01400 CO_2 yield in Sweet Gas (% mol. of CO_2 in Sweet Gas) as against the 0.01395 CO_2 yield in Sweet Gas (% mol. of CO_2 in Sweet Gas) of the existing DEA operational value, good result was also recorded for the acid Gas Loading capacity (% mol. of CO_2 in Amine) for the HYSYS Simulated result which is 55.02 % as against the 60% of the existing operational value with a difference that is less than 5%. This results clearly established the accuracy and choice of the HYSYS 3.1 Software, there is also the advantages of high speed and result accuracy, provision of process alternatives and variable modifications, avoidance of expensive experimentation and pilot plant building, prevention of down time (System shutdown), flexibility of usage and ease of evaluation of result, Clarity of Simulation environment and provision of reliable property package.

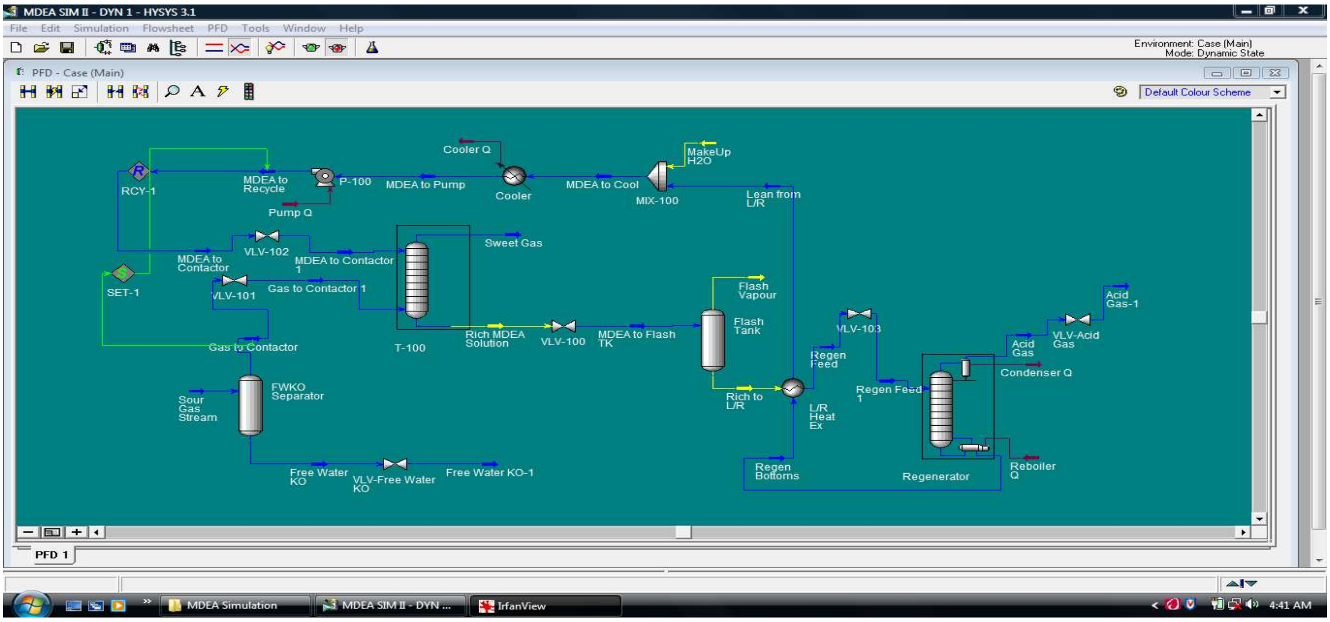

Figure 1. *Complete MDEA Dynamic State Simulation PFD.*

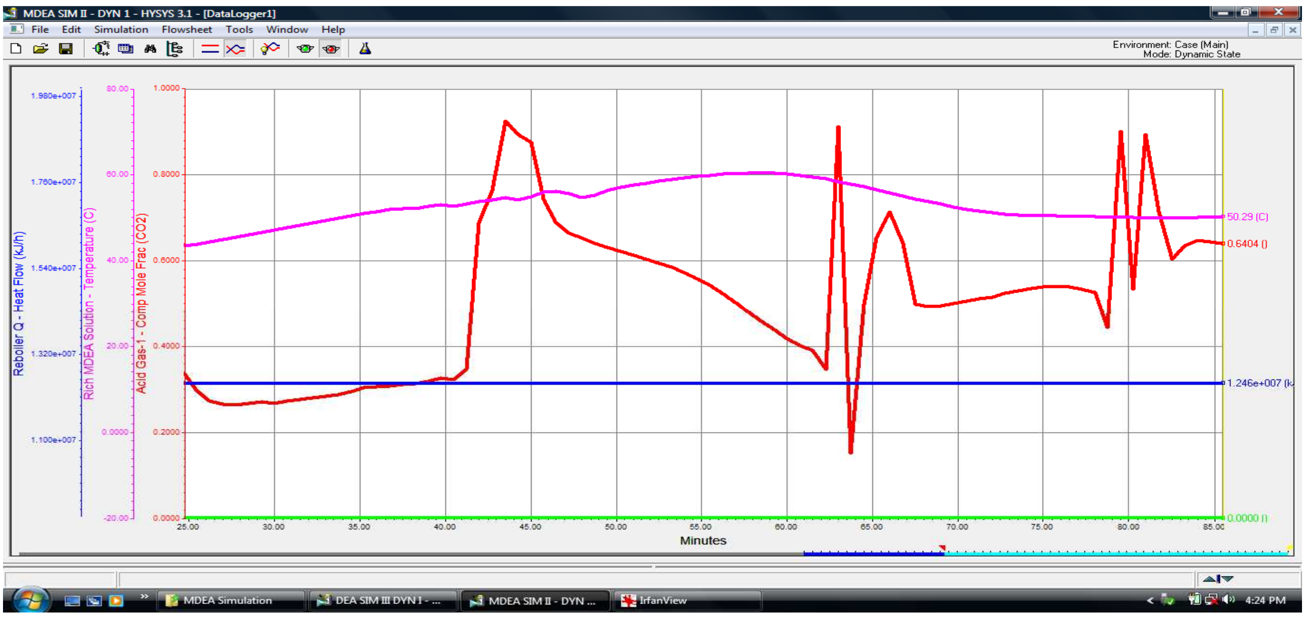

Figure 2. *Strip chart showing real time variables for MDEA Simulation Case.*

3. Results and Discussion

3.1. HYSYS Simulation Results and Comparative Analysis

Through the dynamic mode, we were able to determine the status of numerous variables that defines the optimal operating conditions needed to run the live plant, these variables ranges from temperatures, pressures, flow rates, exchangers heat duties, pump capacities required for the circulation, acid gas loading capacities and CO_2 contents in the individual streams in Fig. 2 which is the strip charts showing updated variables in real time for the MDEA case.

A comparative analysis was carried out using the data from an LNG plant, where diethanol amine (DEA) is in use for CO_2 removal process unit which resulted in a CO_2 yield of 0.01395 % by mole in the sweet gas and peak acid gas loading of about 60%. Aspen HYSYS was used to simulate the process using the same parameters, resulted in acid gas loading of about 55.02 % with a CO_2 yield of 0.01400 % shown in Table 1.

Considering the fact that purity in the sweet gas is needed, Methyl diethanol amine (MDEA) instead of DEA was used in the Aspen HYSYS process simulation as shown in Fig. 1. This resulted to a peak acid gas loading of 89.39 % in the MDEA amine and CO_2 yield of 0.0012% by mole.

The acid gas loading in the amines of the existing LNG operation, HYSYS simulated DEA and MDEA used showed a result the loading capacity of HYSYS simulated MDEA is 89.39 % and higher than that of existing LNG operations DEA which is 60% and that of the HYSYS simulated DEA is 55.02%. The MDEA is a better amine than the DAE.

From Table 2, the amount of MDEA recovered at the regeneration is 83.635% which is about 20% higher and an improvement in amine recovery when compared to the quantity of 63.73% DEA recovered at the regeneration. It is therefore obvious that the use of MDEA solvent led to a high recovery of amine solvent with a minimal loss of solvent compared to that of DEA.

Table 1. *Comparative Analysis of the results from the Simulation cases*

Parameter	NLNG Result	Aspen HYSYS Simulation with DEA	Aspen HYSYS Simulation with MDEA	Remarks
CO_2 Yield in Sweet Gas (% mole)	0.01395	0.01400	0.0012	Difference in types of amine used
CO_2 loading in amine (% mole)	60	55.02	89.39	Temperature and pressure affect CO_2 pick- up rate

Table 2. *Summary of results and comparative analysis between MDEA and DEA*

Parameters	MDEA	DEA	Remarks
% mole CO_2 in Sweet Gas	0.0012	0.01400	MDEA lower CO_2 content meets sales spec as better quality product than existing DEA product
% mole Acid Gas Loading Capacity	89.39	55.02	MDEA has higher CO_2 loading capacity than existing DEA and by extension a better absorber.
% Amine Solvent Recovery	83.62	63.73	% MDEA recovered is higher than DEA meaning less solvent loss, while DEA change out rate will be higher and more expensive to operate due to high solvent loss.
% Regenerator Stripping Capacity	70.78	60.73	MDEA stripping capacity is higher and therefore will be less contaminated when compared to DEA for recycled solvent.
Solvent Flow rate for recirculation. (Kg mol /hr)	1873	2283	Required flow rate recirculation determine the size of pumps and accessories, therefore MDEA will be less expensive to recycle
Optimum Operating Temperature ^{o} C	121.1	125.8	DEA optimum operating temp of 125.8 is too close its boiling point which lead higher solvent loss with frequent and expensive change out
Optimum Operating Pressure KPa	202.4	232.7	DEA will require a compressor of higher duty to meet 232.7 KPa pressures, while MDEA will be less expensive

3.2. Regenerator Column Stripping Capacity

The stripping of CO_2 acid gas from rich MDEA is high and about 70.7879 % with little CO_2 of about 0.1374 % left with the lean MDEA at the regenerator bottoms this show case a high stripping or desorption performance and less possibility of MDEA amine contamination, while in the DEA regenerator, the stripping value of the acid gas from the rich DEA is 60.7345 % and the amount left at the bottom of the regenerator after stripping was a bit low.

The recirculation of MDEA solvent at the regenerator is 1877 Kg mol/hr. which means that a smaller pump and piping accessories will be required to re-circulate 1877 Kg mol. of solvent for every one hour, while higher pump size and cost is required for DEA with flow rate of about 2371Kg mol./hr. this circulation rate is higher than that of MDEA.

From the chart below, it can be seen as already discussed that MDEA has higher acid gas loading capacity, amine solvent recovery rate and regenerator CO_2 stripping capacity. The CO_2 content of the sweet gas produced from MDEA simulation is very low when compared with DEA simulation indicating that MDEA produced sweet gas with very high purity level required of international sales gas specification. The low sweet gas CO_2 content from MDEA simulation will also guarantee an environmentally friendly product on combustion and ensure compliance with both local and international regulatory bodies on the acceptable CO_2 emission level into the atmosphere.

Table 3. *Summary of results and comparative analysis between MDEA and DEA*

Parameters	MDEA	DEA	Remarks
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4. Conclusion

The following conclusion can therefore be reached:

- That MDEA produced sweet gas with less CO_2 content than the existing DEA which is compliant with international sales gas specification [11] as a high quality product than DEA sweet gas. Table 4 shows the international specifications as it applies in North America and Europe.
- The acid gas loading capacity (CO_2 removal) of MDEA of 89.3% is almost twice higher than 55..02% DEA, thereby producing a sweet gas stream that is environmentally friendly and on combustion will emit lower and acceptable amount of CO_2 into the atmosphere as low greenhouse contributor
- Use of MDEA is more economical to operate than the DEA unit because of its high recovery rate of 83.62% of MDEA when compared to 63.73% DEA with less money required for incessant change-out due to solvent loss and degradation.
- With the use of HYSYS software it was possible to build models and establish the optimum operating conditions of the MDEA stripper bottoms to be 100-121.1^{o}C and 200 KPa. By the usage of HYSYS, shut down of the unit was avoided and by extension the cost of the expensive shut down was reduced.

Table 4. *International Sales Gas Specifications*

INTERNATIONAL SALES GAS SPECIFICATION S		
Specifications	**North America**	**Europe**
Water Content (North America Water dew point (Europe)	4-7 ibm H2O / mmcsf of gas	10 ^{0}C @ P less than 7000kPa
Hydrocarbon Dew point	14-40 ^{0}F @ specified Pressure	0-5 ^{0}C @ P less than 7000kPa
Carbon dioxide (CO_2)	1-3 mol%	2-3 mol%
Nitrogen (N_2)	2-3 mol%	2-3 mol%
Total Inert	3-5 mol%	N/A
H_2S	0.25 -1.0 grain/100 scf	5 -7 mg/ Nm^3
Total Surphul (S)	0.5 -20 grain/100 scf	120 -150 mg/ Nm^3
Mercaptans	0.25 -1.0 grain/100 scf	6 -15 mg/ Nm^3
Oxygen (O_2)	10 -2000ppm mol	1000 -5000ppm mol
Heating Value	950-1200 Btu/Scf	40-46 Btu/Scf
Wobbe Number	N/A	15-56Mj/ Nm^3

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