

Simulation of the Benfield HiPure Process of Natural Gas Sweetening for LNG Production and Evaluation of Alternatives

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ABSTRACT

Achieving specifications given by customers, including pipeline-operating companies, LNG storage facilities, and gas-processing plants requires the removal of CO₂ and H₂S from natural gas. It is also becoming more important to meet environmental regulations set by national and local governments. This paper summarizes a study which compares the Benfield HiPure–LNG Train of Abu Dhabi Gas Liquefaction Company Limited (ADGAS) sweetening plant to other sweetening processes using the modeling software ProMax®. Natural gas from the gas reservoirs, containing about 6-7 mole% acid gas, first comes into contact with hot potassium carbonate (30 wt% K₂CO₃) promoted with diethanolamine solution (3 wt% DEA), and finally with 20 wt% DEA solution. The simulation proved to predict the plant operating data accurately. Subsequently, additional alternatives to the Benfield HiPure process were investigated as potential options for replacement, including MDEA, MDEA/piperazine, and MDEA/DEA mixtures. The activated MDEA (50wt% MDEA + 3wt% PZ) with a two-stage flash is the best alternative, with a 36% decrease in the reboiler duty. This paper shows the possibility of shutting down the potassium carbonate section of the sweetening train and swapping the DEA solution in the immediate downstream unit for a mixed amine in order to reduce operating costs while continuing to meet the treated gas specifications. Preliminary results are presented here.

Keywords: Simulation, Benfield HiPure, Activated MDEA, ProMax®, Gas Sweetening, LNG

1. INTRODUCTION

There are many processes available for removal of acid gases from natural gas; the selection of these processes is based on economic feasibility and cleanup ability. These processes include chemical solvents, physical solvents, hybrid solvents, adsorption processes, and physical separation (e.g. membrane systems) [1]. Chemical and physical solvents, or a combination of the two, have been used extensively in many existing LNG facilities. The removal of both H₂S and CO₂ from natural gas before liquefaction is done primarily to meet the LNG product specifications, prevent corrosion of process equipment, and meet environmental performance standards. The recommended specifications for LNG are typically less than 1 ppmv H₂S and 50 ppmv CO₂ in the sweet gas [1-4].

Solvent cost, equipment costs, and energy requirements for regeneration are the most important factors to be considered in selecting an appropriate process [2, 17].

Depending on the process requirements, several options for alkanolamine based chemical solvents may be proposed [1, 5]. Apart from alkanolamine based processes, other methods for removal of H₂S and CO₂ include alkaline salts such as sodium or potassium carbonate (with or without an amine activator) and physical solvents such as DEPG or methanol.

The HiPure process used currently in the ADGAS plant and described by Benson and Parrish [6] uses two independent but compatible circulating solutions in series, specifically, hot potassium carbonate (K₂CO₃) promoted with DEA followed by DEA to achieve high purity at high efficiency.

The hot potassium carbonate process introduces major process concerns of corrosion, erosion, and column instability which affect the capital and maintenance costs in the form of design and operation [5]. If CO₂ is not present, it becomes difficult to regenerate potassium bisulfide; therefore, potassium carbonate is not a suitable option for H₂S only cases [5]. A drawback of diethanolamine is the possible need for vacuum distillation while reclaiming contaminated solutions. DEA also undergoes numerous irreversible reactions with CO₂ forming corrosive

degradation products. For that reason, DEA may not be the optimum choice for treating high CO₂ content gases [1].

The use of blended amines in gas treating can bring about a significant improvement in the absorption capacity, absorption rate, and also savings in solvent regeneration energy requirements [7-10]. This approach could dramatically reduce capital and operating costs while providing more flexibility in achieving specific purity requirements. For a given economic analysis, choosing a process with low initial installation cost might not be the best option since the operating cost may be high, making the breakeven point unattainable.

In most cases, amine mixtures contain MDEA as the base amine with the addition of one or two more reactive amines such as MEA, Piperazine, or DEA. These amine mixtures are also known as formulated amines, activated MDEA, promoted MDEA, and MDEA based amines.

Piperazine activated MDEA has a higher energy requirement than the physical solvent processes, but has lower hydrocarbon solubility. Compared to MDEA with other activators, the Piperazine activated MDEA has a low energy requirement due to its ability to liberate the bulk acid gases in a simple flash. For the two-stage absorption process, only a portion of the semi-lean solution is regenerated. This reduces capital cost and energy requirements.

MDEA based processes have commercial advantages over the current Benfield HiPure Process in that MDEA is less corrosive to carbon steel, the solution is stable, and it is not as susceptible to degradation. Since MDEA is not very corrosive, higher concentrations of up to 50% can be used without any significant effects on the process equipment [2].

Process industries widely recognize process simulators as an essential predictive tool. Providing predictive models provide many benefits: studying process alternatives, assessing feasibility, performing preliminary economics, interpreting pilot-plant data, optimizing process design hardware, estimating equipment, calculating operating costs, investigating feedstock flexibility, and optimizing plant operations to reduce energy use, increase yield and improve pollution control [2].

This study uses the process simulator ProMax® to investigate the use of amine mixtures employing methyldiethanolamine (MDEA), diethanolamine (DEA) and piperazine (PZ) as alternatives to the Benfield HiPure process unit currently in use by ADGAS.

Comparison between the Benfield Process and four others will be based on the net energy requirement and the sales gas specification. The absorber and stripper design of the DEA unit in the HiPure process is considered for all the amine alternatives. The MDEA/piperazine mixture was modeled using both the split flow scheme with a two-stage flash and the conventional amine flow scheme.

1.1 PROCESS CHEMISTRY

The basic reaction chemistry for aqueous hot potassium carbonate solution and CO₂ or H₂S is represented by the following reversible reactions:



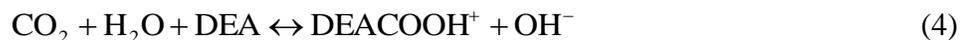
Addition of small amounts of amine promoters provide a faster transfer of CO₂ into the bulk liquid through the formation of a carbamate ion [1, 5, 11, 12, 17]:



In the bulk liquid, subsequent establishment regenerates the free amine by the reverse reaction (3) and the regenerated CO₂ reacts with carbonate and water as in equation (1).

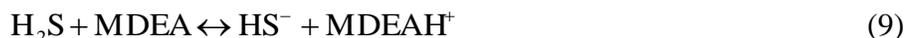
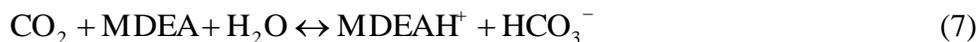
DEA System

The following are the most prevalent chemical reactions that occur in an aqueous DEA solution when CO₂ and H₂S are present:



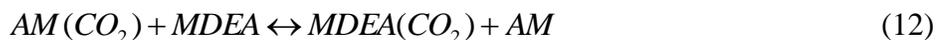
MDEA System

The following chemical reactions occur in an aqueous MDEA solution when CO₂ and H₂S are present:



Mixed MDEA System with PZ or DEA

The mechanism of CO₂ reaction with aqueous solution of MDEA blended with PZ or DEA can be explained by a homogenous activation mechanism [13-15, 17].



AM corresponds to piperazine (PZ) or diethanolamine (DEA). It is also important to note that while the model rigorously calculates the reaction intermediaries, the reactions shown above are simplified.

1.2 PROCESS DESCRIPTION

In the Benfield HiPure process commissioned by ADGAS, the sour gas is contacted with hot potassium carbonate solution [16, 17] followed by contact with DEA. Final acid gas cleanup occurs in the DEA absorber to accomplish the desired purification at reduced temperatures compared to the potassium carbonate absorber. The potassium carbonate and DEA units of this process are shown in Figures 1 and 2, respectively. Figure 3 describes the conventional amine unit flow scheme for the mixed amine solutions. The activated MDEA process with a two-stage flash system is shown in Figure 4. A typical activated MDEA solvent contains up to 7wt % Piperazine in 40 to 54 wt% MDEA [18].

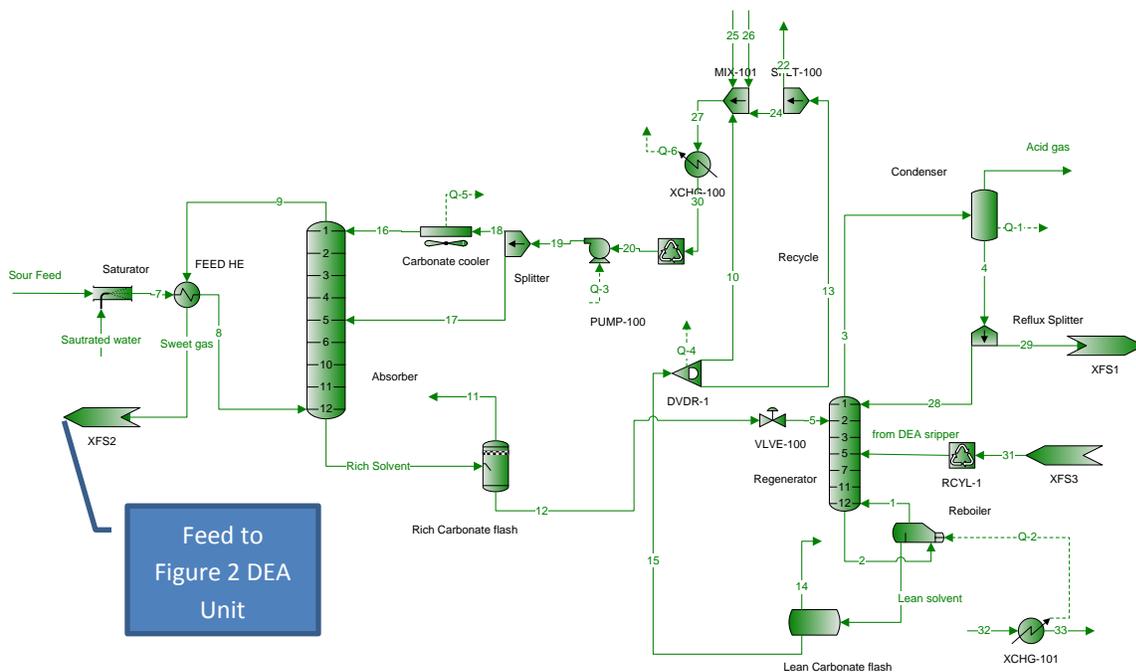


Figure 1: Schematic of Hot Potassium Carbonate Unit of the Benfield HiPure Process

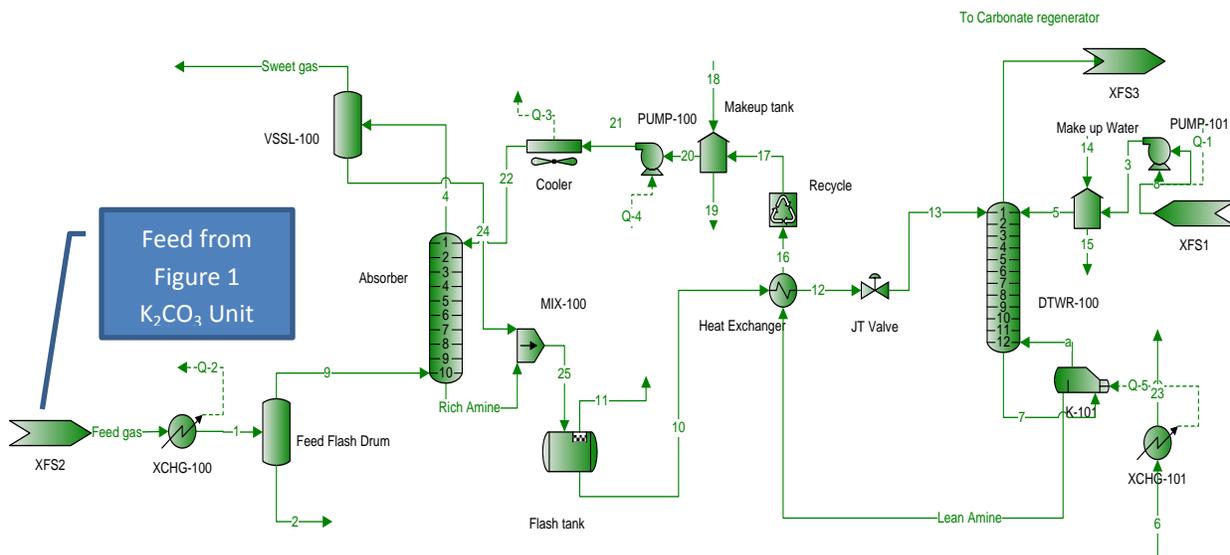


Figure 2: Schematic of the DEA Amine Unit of the Benfield HiPure Process

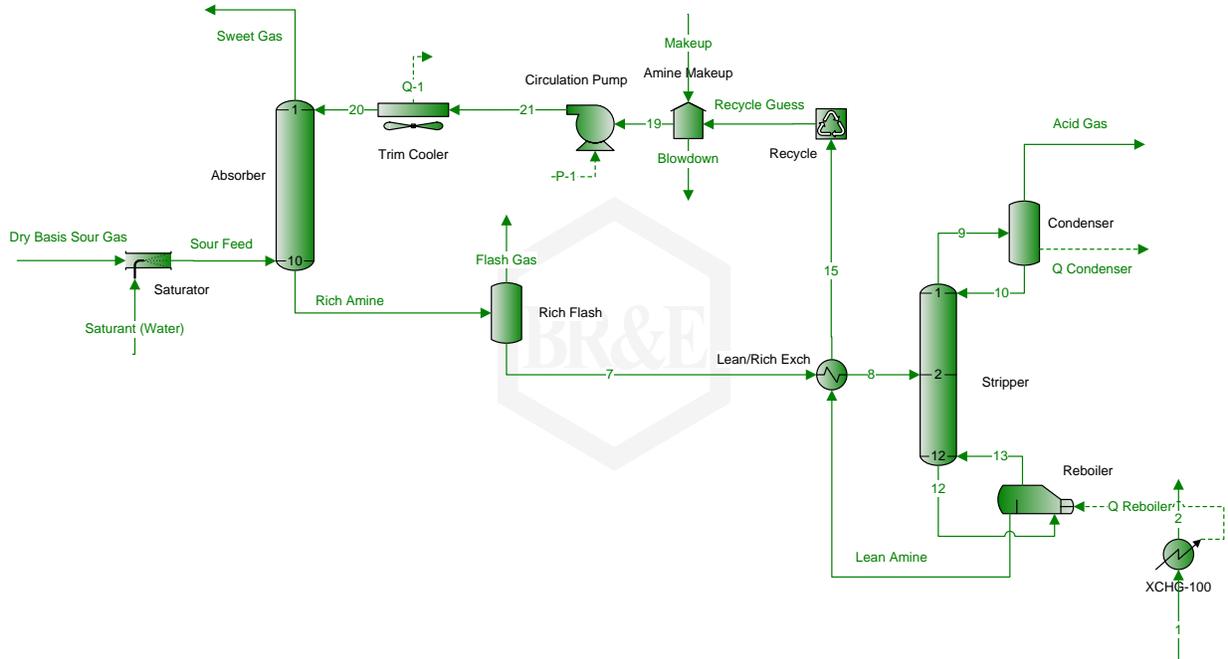


Figure 3: Conventional Amine Flow Scheme for MDEA/DEA, MDEA/PZ (Single Stage Flash) and MDEA

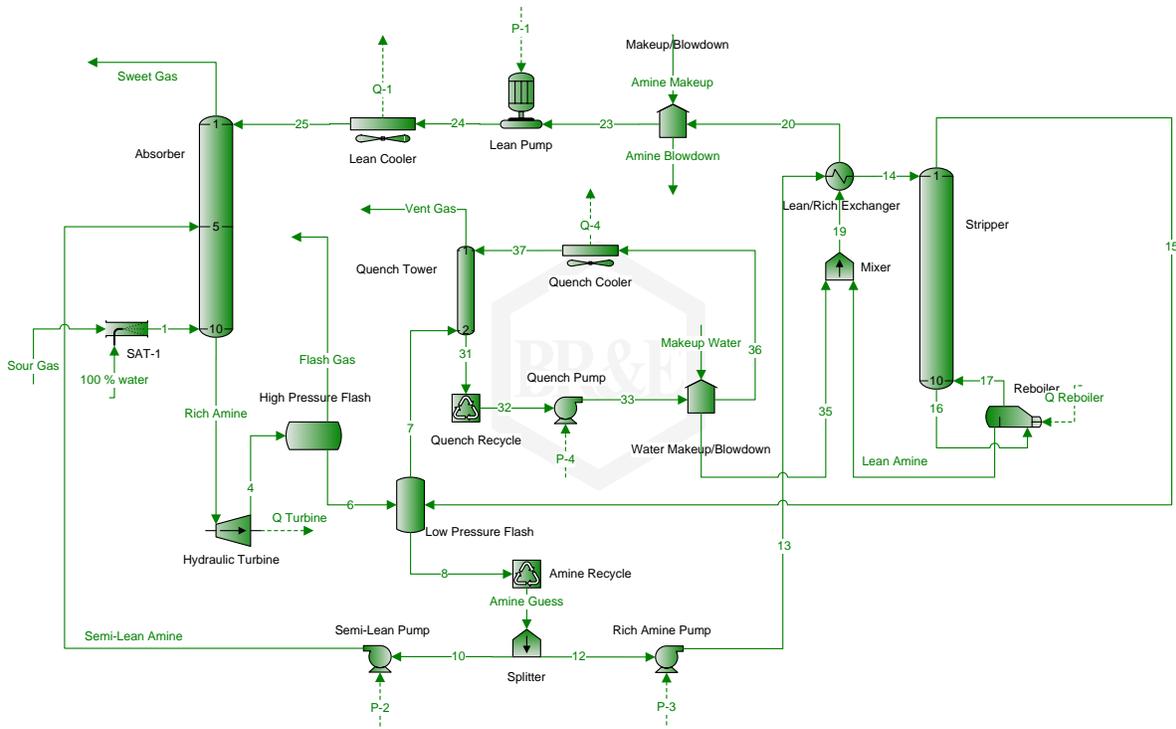


Figure 4: Piperazine Activated MDEA Flow Scheme with a Two-Stage Flash

1.3 PROCESS OPERATING DATA

The operating data and absorber specifications of the Benfield HiPure columns are given in Tables I and II.

**TABLE I: ABSORBER SPECIFICATIONS FOR THE BENFIELD HIPURE SECTION OF TRAIN 3
AT THE DAS ISLAND ADGAS PLANT**

Carbonate Absorber	
Top section	
Column Diameter (m)	3.581
Packing Height (m)	9.144
Bed 1 Packing Type	#2.5 S.S Mini Rings
Bottom Section	
Column Diameter (m)	4.724
Packing Height (m)	9.144
Bed 2 Packing Type	#3 S.S Mini Rings
Amine Absorber	
Column Diameter (m)	2.972
Packing Height (m)	15.24
Packing Type	#3 S.S Mini Rings

**TABLE II: TYPICAL OPERATING DATA FOR THE BENFIELD HIPURE SECTION OF TRAIN 3
AT THE DAS ISLAND ADGAS PLANT**

Parameter	Value
Feed Gas Flow Rate (MMSCFD)	476.93
Feed Gas Temperature (°C)	25.03
Feed Gas Pressure (barg)	52.08
H ₂ S Feed Gas Composition (%)	4.67
CO ₂ Feed Gas Composition (%)	2.11
Hot Potassium Carbonate Unit	
Circulation Rate (m ³ /hr)	Main: 343.50
	Split: 1292.20
Lean Solvent Temperature (°C)	Main: 81.84
	Split: 117
Lean Solvent Pressure (barg)	51.4
K ₂ CO ₃ Concentration (wt %)	30
Promoter Concentration (DEA) (wt %)	3
Amine Unit	
Circulation Rate (m ³ /hr)	109.8
Lean Solvent Temperature (°C)	49.94
Lean Solvent Pressure (barg)	53.71
DEA Concentration (wt %)	20

1.3 PROCESS CALCULATIONS

An electrolytic property package was used to predict the H₂S and CO₂ absorption in both the Hot Potassium Carbonate Unit (Figure 1) and DEA Unit (Figure 2) of the Benfield HiPure Process. Figures 3 and 4 describe the conventional single stage flash and the two-stage flash amine flow schemes, respectively.

The TSWEET kinetics model in ProMax was used to predict the CO₂-amine kinetic reactions taking place in all absorbers. TSWEET kinetics was developed by Bryan Research and Engineering for the purpose of accurately calculating the relatively slow absorption of CO₂ by amine solutions. It is also used to calculate kinetics of CO₂ absorption in Potassium Carbonate and Caustic Units.

2. SIMULATION RESULTS

Table III shows a comparison of ProMax® simulation results to plant data. The regeneration efficiency and the net energy requirement for ADGAS's process are also described in Table IV.

TABLE III: COMPARISON OF OPERATING DATA AND SIMULATION RESULTS FOR THE BENFIELD HIPURE SECTION OF TRAIN 3 AT THE DAS ISLAND ADGAS PLANT

Components	Sour gas	Feed Gas to DEA (ppmv)		Sweet Gas (ppmv)	
	(Mole %)	Simulation	Plant data	Simulation	Plant data
CO ₂	4.7	570	574	25	19
H ₂ S	2.1	683	707	0.40	0.41

TABLE IV: SIMULATION CALCULATIONS FOR THE BENFIELD HIPURE SECTION OF TRAIN 3 AT THE DAS ISLAND ADGAS PLANT

Potassium Carbonate Unit, Reboiler Duty	44 [Gcal/hr]
DEA Unit, Reboiler Duty	15 [Gcal/hr]
H ₂ S Loading Mole/Mole DEA	0.06
CO ₂ Loading Mole/Mole DEA	0.085

2.1 POTASSIUM CARBONATE UNIT

The temperature profile of the potassium carbonate absorber is described in Figure 5 from bottom to top. The profile consists of two maxima: one at the bottom of the column where the sour gas feed is located and also at the midway of the column where the split lean solvent is fed to the absorber. Generally, the temperature profile decreases with increasing height of the column.

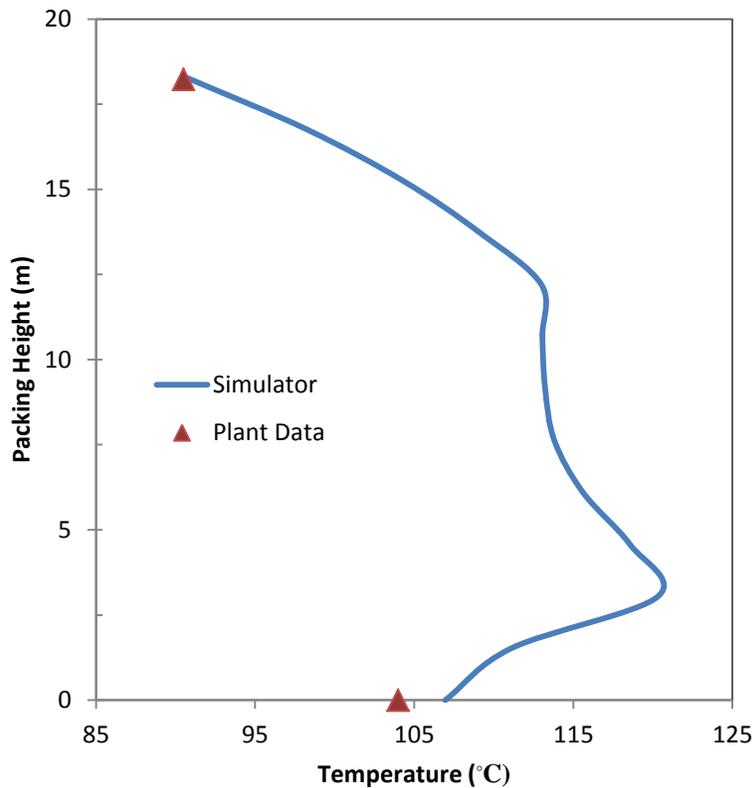


Figure 5: Column Temperature Profile in the Potassium Carbonate Absorber of Train 3 at the Das Island ADGAS Plant

Figure 6 below describes the change in composition of the acid gases with respect to the height of the potassium carbonate absorber. From the figure, it is observed that nearly all the acid gas is absorbed in the bottom (first) quarter of the column. This implies that reducing the absorber height may not have a significant effect on the acid gas absorption in the potassium carbonate section. This figure also shows that both H_2S and CO_2 have fast kinetic interactions with

promoted hot potassium carbonate solution. The effect of residence time may not be significant in the potassium carbonate absorber.

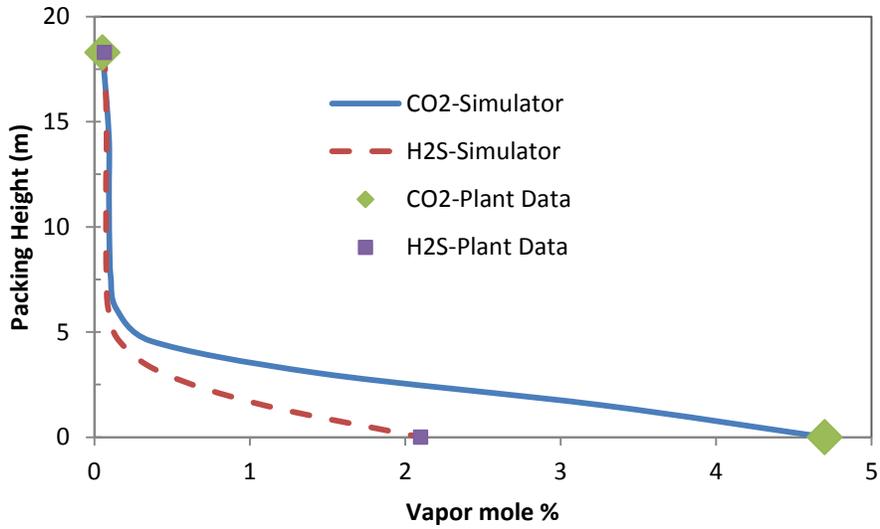


Figure 6: Acid Gas Vapor Composition Through the Potassium Carbonate Absorber of Train 3 at the Das Island ADGAS Plant

2.3 DEA AMINE UNIT

For the DEA absorber, the temperature increases from the bottom to the top as depicted in Figure 7 below. This can seem odd to those familiar with the exothermic reactions that take place in amine units. However, the DEA rich loading is low, about 0.15 moles of acid gas/ mole of DEA, indicating little reaction takes place.

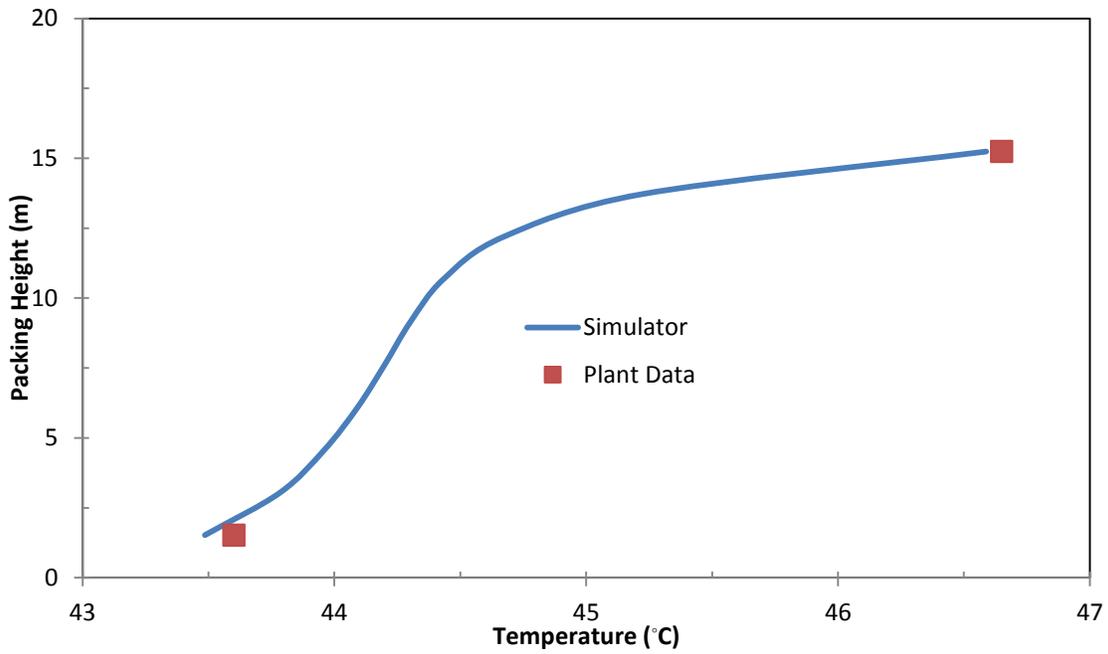


Figure 7: Temperature profile in the DEA Absorber of Train 3 at the Das Island ADGAS Plant

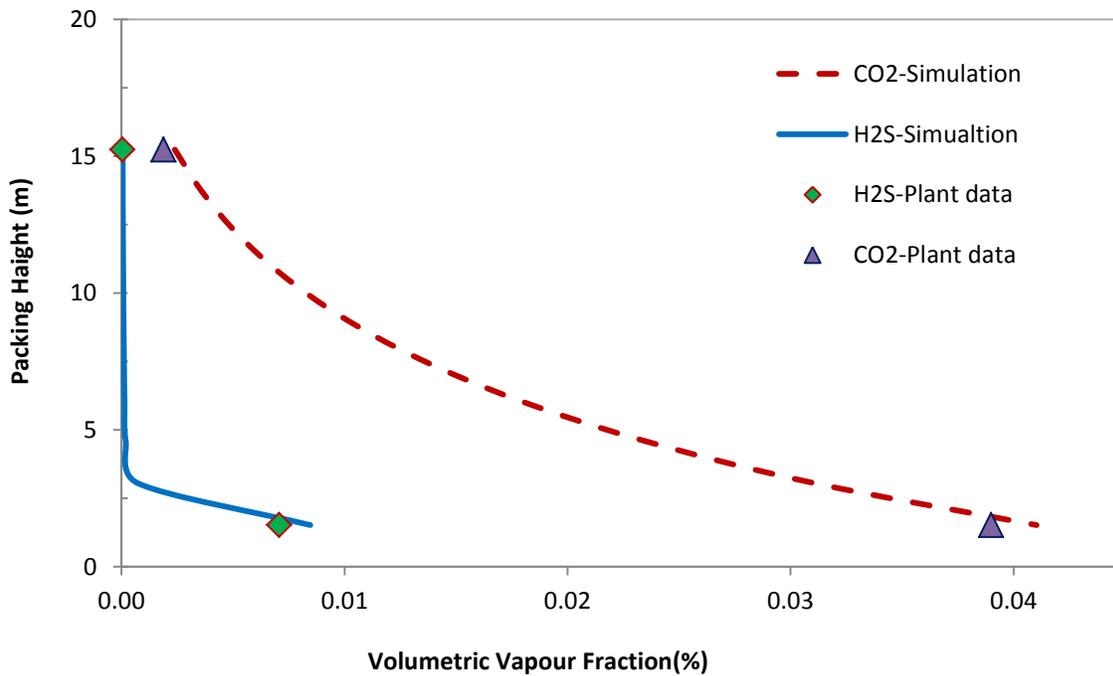


Figure 8: Acid Gas Vapor Composition Through the DEA Absorber of Train 3 at the Das Island ADGAS Plant

Figure 8 shows that all the H₂S is absorbed in the first quarter of the packing. However, CO₂ is absorbed gradually. This is due to the faster reaction kinetics of H₂S with the amine solvents as compared to CO₂.

3. EVALUATION OF ALTERNATIVES

Comparison of MDEA/piperazine, MDEA/DEA, and MDEA processes to the Benfield HiPure Process is described in Table V below. MDEA at 50 wt.% was considered in all the processes along with 3 wt.% concentration of the activator, either DEA or piperazine. Both single stage (conventional) and two-stage flash systems as the amine flow scheme were considered for the MDEA/piperazine mixture.

The steam conditions were assumed to be 50 psig and 147°C.

TABLE V: COMPARISON OF ALTERNATIVES TO THE BENFIELD HIPURE PROCESS CURRENTLY IN OPERATION IN TRAIN 3 OF THE DAS ISLAND ADGAS PLANT

Process design	Solvent (wt %)	Circulation Rate (m³/hr)	Reboiler Duty (Gcal/hr)	H₂S (ppmv)	CO₂ (ppmv)
Benfield HiPure	30% K ₂ CO ₃ + 3% DEA 20% DEA	1635.7 109.8	59	0.45	23
MDEA (Conventional)	50% MDEA	800	72	0.98	5786
Activated MDEA (Two-Stage Flash)	50% MDEA + 3 %PZ	700	38	0.95	9.8
Activated MDEA (Single Stage Flash)	50% MDEA + 3% PZ	700	72	0.82	8.7
MDEA/DEA Mixture (Conventional)	50 % MDEA+ 3% DEA	800	53	0.99	25

The conventional MDEA system does not meet the CO₂ requirement, but the other systems with increased kinetics, are able to achieve both the H₂S and CO₂ specifications. The data also shows that MDEA systems are able to run at about 50% of the flow rate of the Benfield HiPure system.

The table shows that the systems have very different energy requirements. The conventional activated MDEA and pure MDEA systems both require the most energy. The best MDEA system showing energy benefits when compared to the Benfield HiPure system is the two-stage flash activated MDEA system. This system requires 36% less energy and is also able to remove substantially more CO₂ while meeting the 1 ppmv H₂S specification.

In Figure 9 below, MDEA/PZ(1) corresponds to the activated MDEA single stage flash system (conventional amine flow scheme design in Figure 3) and MDEA/PZ(2) is the activated MDEA two-stage flash system in Figure 4 above.

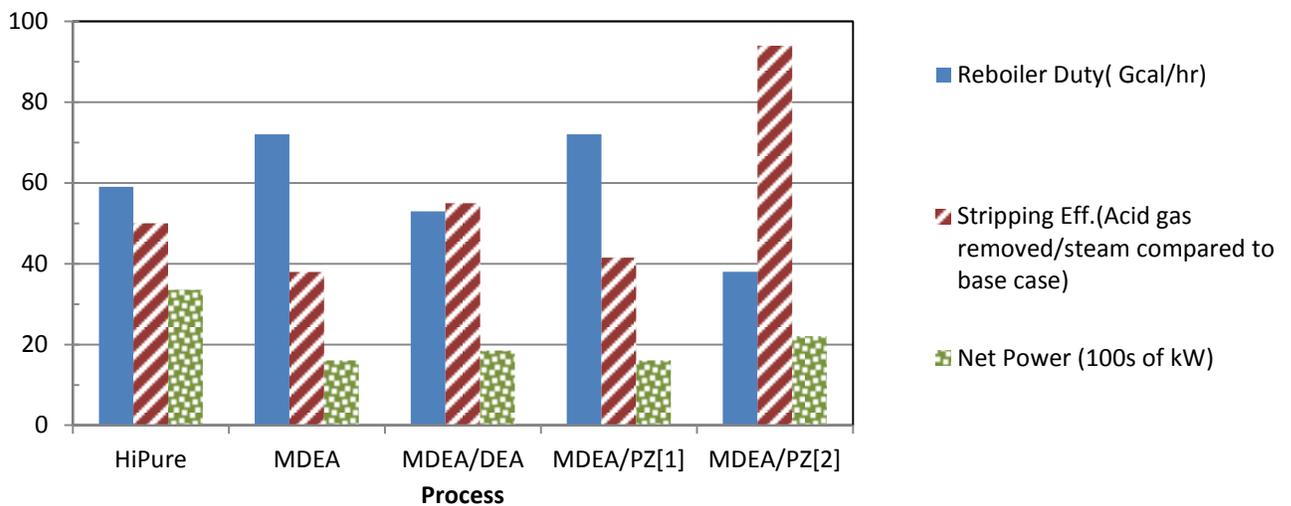


Figure 9: Comparison of Reboiler Duty, Stripping Efficiency and Electrical Power of the Four Amine Based Alternatives to the HiPure Process

The piperazine activated MDEA system with a two-stage flash has the lowest energy requirement, with a 36% reduction in reboiler duty and a 34% reduction in the electrical power requirement. The activated MDEA with a two-stage flash increases the steam stripping efficiency by 91%.

4. CONCLUSIONS

The existing plant operation can be accurately modeled using the process simulator ProMax®. Optimization of the Benfield HiPure Process Plant is essential when evaluating potential improvements or replacement.

This study shows clear possibilities for replacing the current units with a single amine based unit. Activated MDEA with a two-stage flash appears to be the most cost-effective alternative, with a 36% decrease in the energy requirement for this preliminary study. Therefore, the Benfield HiPure process may be replaced by the mixed MDEA solutions which are economically attractive in terms of operating costs. All additional studies need to incorporate feasibility reports focused on using the current DEA unit equipment for any process improvements. The prospect of shutting down the potassium carbonate section completely, switching the DEA solvent to a mixed amine and using the same equipment as the current DEA unit is very real. If that scenario is successful, ADGAS will see a notable decrease in operating costs and, possibly, additional capacity.

It is recommended that a follow up to this paper is prepared to study the piperazine activated MDEA with the two-stage flash case, as these results are preliminary. Additional optimization may be performed. It would also be valuable to generate an economic analysis comparing the optimized Benfield HiPure process to the optimized piperazine activated MDEA with two-stage flash process and the optimized MDEA/DEA case.

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