Available online at www.asric.org ASRIC Journal on Engineering Sciences 1 (2023) 11-18



Dynamic Design Simulation of Acidic Natural Gas Sweetening Analysis and the Utilization of Hybrid Amine Membrane

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Received 9 July 2022; revised 31 July 2022; accepted 23 August 2022

Abstract

In order to remove acid gases, chemical absorption by solvents is the most often used sweetening gas strategy. While this method is well-known and tested, it may be difficult to implement, expensive, and wasteful when used to extract very acidic gas. But novel polymeric membranes have been used to remove large amounts of H_2S from natural gas, even at high levels of H_2S . Recent advancements in this field might lead to the production of unconventionally high acidity gas or the retrofitting of existing facilities. For example, the membrane system might be used to lower the bulk concentration of H_2S and CO_2 in the input gas. An amine-based method might be used to sequentially meet the ultimate sweet gas product criteria. It is thus possible to reduce capital and operational costs by using this sort of hybrid design. Using a simulation-based approach, this research evaluates the sweetening of extremely acidic gas with 15% H_2S (i.e., over 20% of H_2S and CO_2 combined). ProMax® v3.2 was used to model the suggested hybrid procedure. According to the simulation findings, a hybrid system approach to the sweetening process might cut operational and utility costs (instead of a stand-alone amine system).

Keywords: Water, Sweetening, CO₂, Acidic Gas, Hybrid, Simulation, Amine, ProMax® v3.2

1.0 INTRODUCTION

Increased concerns about achieving future natural gas needs and export obligations have been voiced recently by a rising number of nations. Due to rising electricity and desalinated water needs, rising living standards, and gas injection for enhanced oil recovery (EOR) operations to extend the life of existing oil fields, this trend is especially visible in the Middle East area [1]. In order to fulfill rising demand for natural gas, companies have been compelled to tap previously uneconomical acidic gas reserves. Sulfur concentration in natural gas poses a significant technological and economic issue [2]. The most frequent method for removing acidic gases from natural gas is absorption using amines. An aqueous solution of alkanolamines (e.g., MEA, DEA, DGA, and MDEA) is used in a tray-packed tower to contact the acidic gas As a result, the process is very energy-intensive because of the high temperature needs for solvent regeneration. Acid gas concentration and natural gas supply flowrate are directly related to the matching energy needs. New approaches like hybrid systems may help overcome the problems and significant operating expenses associated with handling very acidic gas. As a first step, a membrane module may be able to reduce the acid content in the feed gas, while a subsequent stage of gas absorption might match the

ultimate product purity requirements. Experimenting with new technology is another benefit of handling very acidic gas. These new technologies have the potential to reduce costs while also bringing about technological benefits. However, in gas absorption and permeate membrane modules, chemical interactions that take place between solvents and acid gases are what drive this separation process, rather than a pressure differential. The advantages of using membrane separation are inexpensive capital costs, no extra facilities (e.g., solvent storage), simple installation, space efficiency, and low operating costs compared to absorption units. The high H₂S concentrations in this study promote partial pressure difference-based processes, and H₂S selective materials help minimize operating costs as a result of the hybrid method presented in this paper.

2.0 A MODEL FOR ECONOMIC ANALYSIS AND METHODOLOGY

Figure 1 shows the suggested hybrid system for treating extremely acidic natural gas in this research. The hybrid system was modeled using ProMax® simulation software. A single membrane step (pretreatment) is followed by an absorption stage in the hybrid system. Hydrogen Sulfide (H₂S) is removed from the crude natural gas supply by using the membrane module. Afterwards, the gas absorption unit must meet the final pipeline criteria (e.g., 1 mole percent CO2 and less than 4 ppm H₂S). Retentate and permeate streams are created by the membrane module, which divides the incoming feed gas into two distinct streams (acid gas rich). It is preferable to reinject the membrane's permeate gas underground and utilize it in EOR operations. This hybrid method might save money in both capital and operational expenditures.

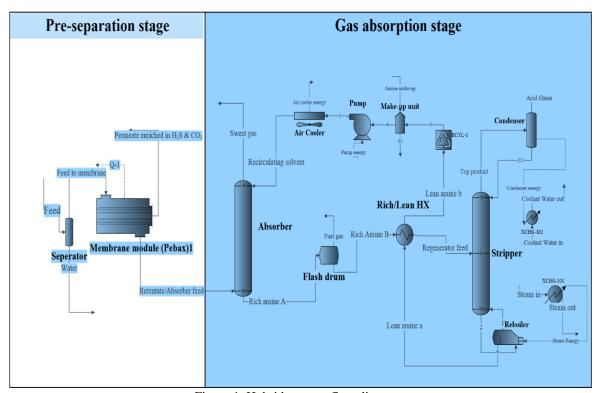


Figure 1. Hybrid process flow diagram.

During the pre-treatment step, commercial PebaxTM [3-5] was used as the membrane material. It is thought that Pebax grades are suitable polymers for acid gas removal because of their strong H₂S/CH₄ selectivity and high permeability. Table 1 lists the membrane's permeability and selectivity. H₂S, CO₂, and CH₄ are merely three of the gases that may pass through the membrane module. Natural gas mixtures include a lot of methane, which is the most important component, while H₂S and CO₂ need to be separated.

Table 1. Pebax membrane properties [6].

Property	Value
Permeability of CH ₄ (stdcm ³ /cm ² .s.cm Hg)	1.8
Components	Selectivity with respect to CH ₄
H_2S	77.78
CO_2	17.22

The membrane module utilized in this work is a technique of selective separation. Solution-diffusion transports the gas across the nonporous (dense) polymer membrane. When the gas dissolves in the membrane high-pressure side of the polymer, it then diffuses through the polymer phase and evaporates at the lower pressure side. In order to assess the membrane's performance, the flow equations for each component may be used:

Assuming that P1 and P2 are the feed and permeate side pressures,

$$J_i = Q_i(P1_{xi} - P2_{yi}) \tag{1}$$

Macab [7] has further information on the calculation of membrane performance. The membrane module calculations were made using the ProMax® embedded membrane tool. Methane leakage occurs at the membrane step due to suboptimal acid gas selectivity. As a result of the procedure of sweetening, the methane losses were determined. The "TSWEET Kinetics" model is used to simulate how the absorber works. This model takes into consideration the differing absorption rates of the various acid gases, notably CO2's kinetically constrained absorption.

The hybrid system's running expenses were used to analyze the gas sweetening process's profitability. There may be potential cost savings by adding a membrane module to the conventional stand-alone absorption process. It is thus necessary to compare both stand-alone and hybrid gas absorption methods in order to assess if the additional pre-separation step is technically and economically viable. The cost of replacing the membrane parts, which must be done on a regular basis, was included in the operational expenses. It is also necessary to include in hybrid system running costs the potential cost of permeate CH4 losses [8]. The economic assessment of the separation process is strongly dependent on the technique of analysis and the values of the economic parameters. Details of the strategy used in this study may be found in [8, 9].

For the membrane module, which includes a pressure vessel, membrane element, and other components, the cost was supposed to be \$180/m2 [10, 11]. For the membrane elements, the cost was assumed to be \$90/m2 [10, 11], which is half of the cost of the membrane module. It was estimated that the membrane capital recovery cost would equal the membrane capital cost divided by the membrane life time, which is generally three years. Because all process configurations examined were similar and labor costs rely on the number of unit operations, the present research did not include operational labor costs. As a result, the price element may be omitted from the comparison as a whole. The membrane's module expenses are considered capital investments since they are one-time expenditures. However, the absorption unit's initial investment was overlooked for a variety of reasons:

- 1. amine sweetening units have a longer service life than membrane modules (e.g., the membrane life time is approximately 3 years while the amine sweetening unit can reach up to 35 years).
- 2. The goal of this study is to examine processes that use comparable equipment and are almost identical in terms of scale. Therefore, omitting the amine sweetening unit will not have a substantial impact on the final output.
- 3. Adding a membrane module to existing amine sweetening facilities is one of the study's primary goals.

It is the primary goal of this research to determine which process variables should be set at their optimal levels. Even more importantly, the H₂S concentration in the membrane's retentate stream (that is, the gas

absorber) is a critical independent variable that considerably impacts the total cost of hybrid systems. Specifically, Economic analysis procedures, costs, and techno-economic assumptions are summarized in Table 2.

Table 2. Economic parameters and assumptions.

Table 2. Economic	c parai	neters and assumptions.					
Cost analysis for		Membrane Capital Co	ost, MCC (\$/y	r) [8]: \$180/m ² of membrane.			
membrane module.		Membrane Replacement Cost, MRC (\$/yr) [8]: \$90/m² of membrane.					
		Membrane Hydrocarbon Losses, MHL (\$/yr) [12]: \$ 19.19/MWh.					
		Membrane Capital Recovery Cost, CRC (\$/yr):					
		MCC					
		CRC=		(2)			
		Membranelifetime					
		Membrane Operating Cost, MOC (\$/yr):					
		MOC=MRC+MHL+CRC (3)					
Cost analysis	gas	Utility Cost(\$/yr).					
of		Electricity Cost, EC [12]: 0.06 \$/kWh.					
absorption unit.		Total power load = Pump power + Air Cooler power.					
		Steam Cost, SC [12]: \$ 29.29 /1,000 kg.					
		Coolant Water Cost, CC [12]: \$ 14.8/1000 m ³ .					
		Total Utility Cost,					
		TUC=EC+SC+CC (4)					
		Absorption stage Hydrocarbon Losses Cost, AHL [12]: \$ 19.19/MWh.					
		Amine Losses Cost	, ALC (\$/yr).				
		Solvents Prices [13]	•				
		Solvent type	(\$/kg)				
		MEA	0.5				
		DEA	3.8				
		MDEA	2.6				
		DGA	4.1				
		Absorption Stage operating cost, AOC (\$/yr).					
		AOC=ALC+AHL+TUC	(5)	•			
Total Separation		Total Separation Cost, TSC (\$/yr).					
Cost.		TSC=AOC+MOC (6)					
Other Assumptions.		Stream Factor: number of working days per year = 300 day. Membrane					
		life time = 3 yr.					

3.0 HYBRID PROCESS ANALYSIS

The suggested hybrid system method is compared to the stand-alone absorption system, and the best performing amine in terms of running expenses is selected. Each alkanolamine (MEA, DEA, DGA, and MDEA) was simulated in the stand-alone absorption system to evaluate its individual performance for treating extremely acidic gas. To ensure that carbon steel may be safely utilized as industrial equipment, the simulations employed high loading and solvent concentration values [14]. An additional factor affecting all of these variables the natural gas reservoir's capacity. As a result, data from the literature (detailed in Table 3) was used to determine the very acidic gas feed conditions in the current study [15].

Table 3. Highly acidic gas feed assumed operating conditions [15].

Operating Conditions	Value
Feed pressure	70 bar
Feed temperature	40 °C
Feed standard flow	250 MMSCFD
Sweet gas specification	4 ppm H_2S ; $CO_2 < 1\%$ mole
Main components	Mole (%)
CO_2	5
H_2S	15
CH ₄	64
Ethane	10
C ₃ +	4
Methyl Mercaptan	1
Ethyl Mercaptan	1

The performance of the four alkanolamine-based stand-alone absorption systems was evaluated using their corresponding total operating expenses. As a result, the total operating cost of single absorption systems using four distinct kinds of alkanolamines (MEA, DEA, DGA, and MDEA) for the treatment of extremely acidic gas is presented in Table 4.

Table 4. Total operation cost for single absorption systems using different types of alkanolamines.

Variable	Type of	Type of amine		
	MEA	DEA	MDEA	DGA
Total operating cost (MM \$/yr)	164	96	72	86

MDEA and DGA are the best performing solvents for use in the absorption unit under the present stipulated extremely acidic feed gas conditions, as indicated in Table 4. As a result, both amines were chosen for techno-economic study of the hybrid system. Additionally, as a first treatment step, a pre-separation stage was inserted into the system before the absorption unit (see Figure 1). The pre-separation step consists of a membrane module with Pebax membrane components. ProMax® was used to simulate the resultant hybrid system in order to compare its performance while treating extremely acidic gas to that of standard stand-alone absorption systems. Numerous possibilities were examined throughout the study. Each scenario analyzes a degree of H₂S removal in the membrane module in conjunction with an absorption unit that utilizes one of the specified amines.

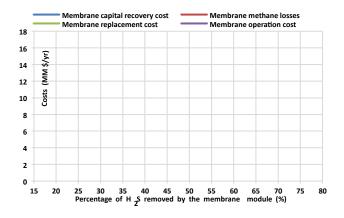


Figure 2. Total and individual expenditures associated with the membrane stage as a function of the amount of H_2S eliminated.

The yearly running expenses of the pre-separation stage are shown in Figure 2 as a function of the percentage of H₂S extracted by the membrane module. The chart indicates that the primary expense of the module is the methane losses via the membrane. Methane losses will undoubtedly occur as a consequence of the membrane's permeability (see Table 1). Methane losses contribute for around 85 percent of the membrane module's overall operating expenses, while capital and replacement expenditures account for approximately 15%. Additionally, the cost of the membrane module is proportional to the amount of acid gases eliminated by the membrane module. For example, when the rate of acid gas removal increases, the required membrane area increases, resulting in increased methane losses.

Regarding the absorption stage, Figure 3 shows the single and total annual operating costs for the absorption stage. From the figure it is worth pointing out that the H_2S content in the absorber's feed has no significant effects on MDEA and DGA losses. On the other hand, the hydrocarbon losses in the absorption stage are inversely proportional to the H_2S fraction removed by the membrane module. Furthermore, over 95% of the absorber's operating costs are utility expenses.

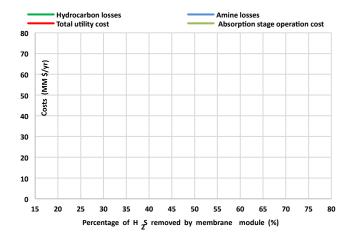


Figure 3. Total and individual absorption stage operating expenses as a function of H2S eliminated for MDEA (continuous line) and DGA (dashed line).

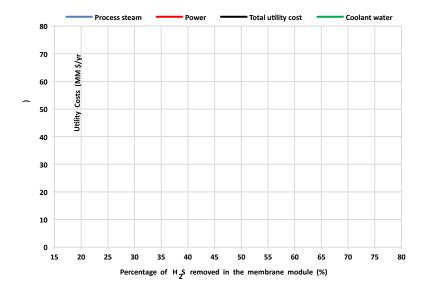


Figure 4. Total and individual utility expenses for the absorption stage as a function of H2S eliminated in the membrane stage utilizing MDEA (solid line) and DGA (dashed line) as solvents.

Figure 4 displays the absorption unit's single and total utility expenses. The need for absorber utilities decreases as the quantity of H2S extracted in the membrane stage grows. This is due to the fact that the absorber will have to remove a less amount of acid gases. As a result, the hybrid system's recirculating solvent flow rate lowers for both MDEA and DGA solvents. This results in a reduction in the amount of electricity needed to cool and pump solvent back into the absorber, and also in the amount of steam needed to renew the alkanolamines. In the absorption stage, the bulk of utility costs are borne by steam and electricity.

Using a membrane module with varying H_2S removal levels, Figure 5 shows overall costs for hybrid systems and stage expenses (pre-separation and absorption). The more H_2S the membrane module removes, the cheaper the whole hybrid system's cost can be shown in the figure. The running expenses of the membrane module grow as the removal rate of H_2S increases. Larger membrane areas are required to remove more H_2S , which results in greater methane losses (see Figure 2). Membranes can remove only so much H_2S before they break down. Reduced H_2S concentration in the natural gas to ppm levels would need large membrane areas and considerable methane losses in order to achieve this goal, so (e.g., making the process unprofitable).

It has been shown that operational expenses are lower in hybrid systems than in stand-alone systems (see Figure 5). Hybrid absorption systems may possibly outperform standard absorption units in treating extremely acidic natural gas.

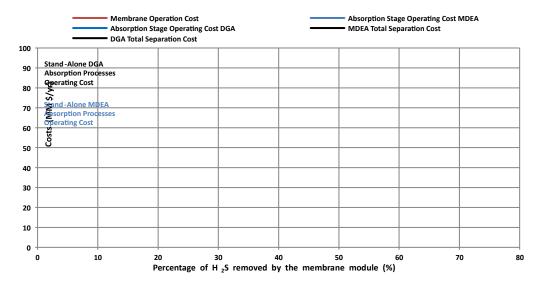


Figure 5. Costs of the hybrid system (using MDEA and DGA) as a function of the amount of H2S extracted by the membrane module.

For existing amine units, the composition and operating parameters of the gas supply might change over time. Because of this, considerable alterations to the current amine units may be required to deal with these changes. It is, however, possible to increase the amine absorption unit's capacity and acid gas concentrations by introducing a membrane separation step before the amine absorption unit. The membrane capacity of hybrid processes may be readily enhanced by adding new parts to existing modules or by installing incremental modules. This provides investment flexibility. Retrofitted hybrid plants, on the other hand, might have economics that vary from those found in this research since they must take into account many more variables. Furthermore, the permeability of higher hydrocarbons across the membrane module was not taken into account in this investigation. Different amounts of higher hydrocarbons condense during membrane separation. Condensation may be avoided by heating the input stream, which is undesired. However, this would mean more equipment, which would raise the price of the hybrid system in terms of both capital and operational expenses.

4.0 CONCLUSION

An amine-based absorption unit and a single membrane module are presented in this work as a hybrid system. Stand-alone absorption units using DGA and MDEA as solvents were determined to be the most energy-efficient procedures for sweetening extremely acidic gas, according to a preliminary simulation analysis and literature material. DGA and MDEA were chosen for the suggested hybrid system analysis since they are both solvents.

When compared to a standard stand-alone absorption process, the hybrid system's economics indicated that it might be more cost- and energy-effective. It is thus possible to save money by using hybrid system principles, which may reduce the usage of steam and electricity. Due to their improved energy efficiency, hybrid systems may also be better for the environment.

In terms of operability, hybrid processes are more adaptable. Retrofitting gas facilities using membrane modules for bulk removal of H₂S might minimize sweetening costs while increasing operational flexibility for treatment input flow rates and composition variations. H₂S removal using membrane modules can only go so far; consequently, depending only on membranes to decrease acid gases concentration into ppm levels is infeasible because of methane losses and the large membrane area requirements. The membrane module's operational costs are heavily influenced by methane leakage. Because of the decreased methane recovery rates, this is one of the key issues and obstacles of using membrane modules.

5.0 ACKNOWLEDGEMENTS

The authors are thankful to, the Imo State University, Owerri, Nigeria for enabling the research project.

REFERENCES

Gierman M., et al., (2014), Acidic-To-Acid concept for acidic gas fields, in Sulphur, BCInsight Ltd: London, UK. p. 62-65.

U.S. Energy Information Administration, United Arab Emirates in International energy data and analysis, (2015).

Vaughn J.T. and Koros W.J., (2014), Analysis of feed stream acid gas concentration effects on the transport properties and separation performance of polymeric membranes for natural gas sweetening: A comparison between a glassy and rubbery polymer. Journal of Membrane Science, 465: p. 107-116.

Kraftschik B., et al., (2013), Dense film polyimide membranes for aggressive acidic gas feed separations. Journal of Membrane Science, 428: p. 608-619.

George G., et al., (2016), Polymer membranes for acid gas removal from natural gas. Separation and Purification Technology, 158: p. 333-356.

Bryan Research & Engineering, Inc., ProMax software, Built-in values (2013).

Mccabe W.L., Smith J.C., Harriott P., (1993), Unit operations of chemical engineering. 5th ed. *No publisher information*.

Bhide B.D., Voskericyan A. and Stern S.A., (1998), Hybrid processes for the removal of acid gases from natural gas. Journal of Membrane Science, 140(1): p. 27-49.

Hao J., Rice P.A. and Stern S.A., (2008), Upgrading low-quality natural gas with H₂S- and CO₂selective polymer membranes: Part II. Process design, economics, and sensitivity study of membrane stages with recycle streams. Journal of Membrane Science, 320(1–2): p. 108-122.

Niu M.W. and Rangaiah G.P., (2014), Retrofitting amine absorption process for natural gas sweetening via hybridization with membrane separation, International Journal of Greenhouse Gas Control, 29: p. 221230.

Hao J., Rice P.A. and Stern S.A., (2002), Upgrading low-quality natural gas with H₂S- and CO₂selective polymer membranes: Part I. Process design and economics of membrane stages without recycle streams. Journal of Membrane Science, 209(1): p. 177-206.

Turton R, Bailie R., Wallace B. W., Joseph A. S., Debangsu B., (2009), Analysis, Synthesis and Design of Chemical Process. 3rd ed. *No publisher information*.

Ochienga R., Berrouka A. S., Petersa C. J., Slagleb. J.,(2013), Amine-based gas-sweetening processes prove economically more viable than the Benfield HiPure process, in Bryan Research & Engineering, https://www.bre.com/Support-Technical-Articles.

Bryan Research & Engineering, Inc., (2015), Level 2 Training: Acidic Gas Processing Removing Undesirable Components from Gases and Liquids.

Slagle, J.C., (2013), Highly Acidic Amine Sweetening Process Study for Conditions Common in the Middle East, in The Abu Dhabi International Petroleum Exhibition and Conference 2013: Abu Dhabi, UAE.