

Removal of Carbon Dioxide and Hydrogen Sulfide from Natural Gas Using a Hybrid Solvent of Monoethanolamine and *N*-Methyl 2-Pyrrolidone

Abid Salam Farooqi, Raihan Mahirah Ramli,* Serene Sow Mun Lock, Ahmad Salam Farooqi, Muhammad Zubair Shahid, Syed Muhammad Wajahat ul Hasnain, Noor e Hira, and Bawadi Abdullah



conventional chemical solvent MEA. The primary purpose is to meet product requirements while consuming the least energy possible, which is in line with any process plant's efficiency goals.

1. INTRODUCTION

In the coming decades, tackling climate change and reducing its impact will be paramount. The worldwide emission of carbon dioxide (CO_2) has grown at an average rate of 2.7% per year, resulting in values that are 60% higher than those recorded 30 years ago.¹ Electric power generation plants and burning fossil fuels are the primary sources of greenhouse gas emissions. Electric power generation alone accounts for approximately 25% of all greenhouse gas emissions. Therefore, implementing an efficient carbon capture process from power plant flue gases, followed by either sequestration (CCS) or utilization (CCU), can significantly contribute to reducing global warming.²

One of the most environmentally friendly energy sources with a high capacity for converting energy into electricity is natural gas (NG), predominantly composed of methane (CH₄). NG is a vital commodity for generating power, providing heat and fuel for stationary engines and transportation and being a raw material for chemical production.³ The depletion of traditional NG reserves has prompted many oil and gas firms to investigate CO₂-rich NG deposits globally. In Indonesia, the unexplored Natuna gas field has been shown to have CO₂ concentrations as high as 71%, while in Malaysia, the concentration of CO₂ can range up to 87%.⁴

NG is relatively clean compared to other fossil fuels, such as coal and oil. However, it is crucial to eliminate all impurities to ensure that the NG is environmentally safe and usable and meets sales gas requirements. Unprocessed NG contains large amounts of methane and other heavier hydrocarbons such as ethane, propane, isobutane, and *n*-butane, as well as significant quantities of CO_2 and H_2S . Before it can be sold or used, the CO_2 must be reduced to a safe level, as it is highly corrosive in the presence of moisture, causing quick damage to valuable pipeline space.^{5,6} Impurities could result in various problems, such as corrosion, erosion, and clogging, and pose health and environmental risks. The maximum permissible concentration of CO_2 and H_2S in NG is less than 1% and 4 ppm, respectively.^{7,8}

Chemical solvents are widely used techniques for removing impurities from NG, accounting for over 95% of all methods employed. Various solvents, including amines, carbonates, and

Received:November 15, 2023Revised:March 9, 2024Accepted:March 15, 2024Published:June 7, 2024







Figure 1. Process flow diagram of the acid gas removal unit.

specialized chemical solvents, can be utilized in this process. However, amine solvents are the most prevalent in NG treating units.⁹ Solvents are employed to eliminate acid gases, such as $\rm CO_2$ and $\rm H_2S$, from gas streams through absorption. Chemical and physical solvents are the two significant solvents utilized.¹⁰ Chemical solvents typically consist of an aqueous solution of an alkanolamine that chemically reacts with acid gases. Chemical solvents have the advantage of effectively removing acid gases at low partial pressures, minimal losses, and the high solubility of hydrocarbons. Amine solutions, weak organic bases, can absorb gas impurities at room temperature. Alkanolamines are nitrogenous organic compounds derived from combining specific organic materials with ammonia ($\rm NH_3$), and they are classified based on the organic groups connected to nitrogen.¹¹

Primary amines include monoethanolamine (MEA) and diglycolamine (DGA), while diethanolamine (DEA) and diisopropanolamine (DIPA) are examples of secondary amines. Triethanolamine (TEA) and *N*-methyl diethanolamine (MDEA) are known as tertiary amines.¹² Primary amines exhibit stronger basicity than secondary amines and possess greater affinity toward reacting with H_2S and CO_2 to form a strong bond with acidic gases; hence, they require high regeneration energy in the stripping column to break the bond. Generally, primary amines demonstrate higher alkalinity and reactivity than secondary amines exhibit greater alkalinity and reactivity than tertiary amines.^{13,14} Due to its cost-effectiveness and efficient absorption rate, MEA remains the primary solvent in aqueous alkanolamine-based capture processes. However, despite its

advantages, MEA requires substantial amounts of energy for stripping due to its high heat of reaction with CO_2 .¹⁵

According to stoichiometric studies, the loading capacities of primary and secondary amines, such as monoethanolamine (MEA) and diethanolamine (DEA), are limited to 0.5 mol of CO₂ per mole of amine.¹⁶ Tertiary amines, including MDEA, have recently gained popularity due to their higher CO₂ equilibrium loading capacity of up to 1.0 mol of CO₂ per mol of amine.¹⁷ In contrast, physical solvents are organic compounds with a strong affinity for acid gases without a chemical reaction. Dissimilar to chemical solvents, physical absorptions depend on pressure variations and the ability of gases to dissolve in physical solvents selectively. Using noncorrosive physical solvents for absorbing acidic gases has no limit in stoichiometry.¹⁸ Moreover, the heating energy required for regenerating a physically absorbing solution is lower than that of a chemical solution.¹⁹ CO₂ and H₂S can be absorbed using physical solvents such as dimethyl ether poly(ethylene glycols), methanol, propylene carbonate, Nmethyl 2-pyrrolidone, and sulfolane.²⁰

Hybrid solvents, a mixture of chemical and physical solvents, could provide the best of both in one solution. Hybrid solution that effectively removes acidic gases by utilizing the advantages of physical or chemical solvents in various ways.²¹ These advantages include the ability to absorb CO_2 without being limited by stoichiometry, the ability to yield a higher purity for treated gas, lower circulation flow rate and energy requirements for regenerating the solution, reduced costs of gas pressure amplification by avoiding hydrate formation at low

temperatures, and control of corrosion and contaminant dispersion within permissible limits.^{22–24}

Despite the numerous studies conducted on the mass transfer, kinetics, and mechanism of MEA aqueous solution, many unexplored areas still need to be explored in using hybrid solvents containing MEA.²⁵ Therefore, this study aims to provide further insight into how the performance of the commonly used aqueous MEA can be improved by incorporating it with a physical solvent. The research was conducted to evaluate the performance of each physical solvent separately to assess its capacity to absorb CO₂ independently. Among the physical solvents, NMP was chosen for this study based on the following factors: (a) With low viscosity and complete miscibility with water, pumping could be made more efficient and require less power.²⁶ (b) NMP can tolerate and remove H₂S, making it a suitable option for treating highpressure gases with high concentrations of sour gas at an ambient temperature. This makes it particularly useful for offshore applications with significant amounts of H_2S .²⁷ (c) NMP has a high maximum operating temperature of 200°C, which allows it to function over a wide temperature range.²⁶

This study uses the Aspen HYSYS V12.1 software package to develop a model for gas sweetening using a hybrid solvent of MEA + NMP. The model is initially validated using actual plant data to ensure its accuracy and reliability. Subsequently, a parametric sensitivity analysis is conducted on the key variables to assess their impact on the overall process performance.

2. PROCESS DESCRIPTION

The capture site for separating CO_2 and H_2S receives a feed gas available at a high pressure. The gas sweetening unit in the NG processing industry employs a typical absorber-stripper setup to capture CO_2 and H_2S .²⁸ The feed gas is introduced into the absorber column at the bottom and comes into contact with a lean solvent. The hybrid solvent MEA+NMP is used in this study to remove acid gases. The gas free of H₂S and CO₂, referred to as sweet gas, exits at the top of the column and is directed to the next unit. The rich amine solution leaves at the bottom of the column. It undergoes a pressure decrease through a valve before being flashed in a flash drum to remove any dissolved hydrocarbons.²⁹ This step reduces the ionic load on the stripper. The rich amine solution is then heated with the lean amine solution in a heat exchanger before being sent to the regenerator column. Steam is supplied into the reboiler in the regenerator to strip absorbed CO₂ and H_2S from the rich amine solution. The acid gases exit from the top while lean amine leaves from the bottom of the stripping column. Finally, the cooled and regenerated lean solvents are recycled back to the absorber column for an uninterrupted acid gas removal unit (AGRU) process.³⁰ Figure 1 shows an overall process flow diagram of AGRU.

3. REACTION MECHANISM

The reactions between CO_2 and MEA solution have been described in the literature by the zwitterion mechanism introduced by Danckwerts et al.³¹ and the termolecular mechanism introduced by Crooks and Donnellan³² The zwitterion mechanism forms a zwitterion complex, followed by a base's deprotonation of the zwitterion.³³ Reactions 1–10 may occur when CO_2 absorbs and reacts with aqueous MEA. All the species represented are in aqueous solution.

Ionization of water

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$
(1)

Dissociation of dissolved CO₂ through carbonic acid:

$$CO_2 + H_2O \leftrightarrow HCO_3 + H_3O^+$$
 (2)

Dissociation of bicarbonate:

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-}$$
(3)

Zwitterion formation from MEA and the CO₂ reaction:

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^-$$
 (4)

Carbamate formation by deprotonation of the zwitterion:

$$RNH_2^+COO^- + RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$
(5)

$$RNH_{2}^{+}COO^{-} + OH^{-} \leftrightarrow H_{2}O + RNHCOO^{-}$$
 (6)

$$RNH_{2}^{+}COO^{-} + H_{2}O \leftrightarrow H_{2}O^{+} + RNHCOO^{-}$$
(7)

Carbamate reversion to bicarbonates:

$$H_2O + RNHCOO \leftrightarrow RNH_2 + HCO_3$$
 (8)

Dissociation of protonated MEA:

$$RNH_3^+ + H_2O \leftrightarrow H_3O^+ + RNH_2 \tag{9}$$

Bicarbonate formation:

$$CO_2 + OH^- \leftrightarrow HCO_3^-$$
 (10)

Regarding mass transfer, the reaction between H_2S and MEA can be considered an instantaneous equilibrium reaction. It only entails the transfer of one proton from H_2S to MEA, and highly high reaction rate constants roughly represent it. Proton amine and sulfide ions are produced when deprotonated hydrogen sulfide combines with MEA.^{34,35}

 $H_2S + MEA \leftrightarrow HS^- + MEAH^+$ (11)

$$HS^{-} + MEA \leftrightarrow S^{2-} + MEAH^{+}$$
(12)

4. SIMULATION BASIS

Aspen HYSYS V12.1, a popular simulation software in the oil and gas industry, is used to conduct the simulation. The UNIQUAC (UNIversal QUAsi Chemical) thermodynamic property package is employed to calculate all equilibrium and kinetic reactions accurately. This thermodynamic package is an integrated feature of the Aspen HYSYS V12.1. The UNIQUAC property package is chosen to determine physical properties of the system. This package is widely used to model liquid–liquid equilibrium (LLE) and vapor–liquid equilibrium (VLE) systems.³⁶ In the past, different researchers used the UNIQUAC thermodynamic package for the capture of CO₂ and H₂S.^{37,38}

In the gas sweetening process, the absorber and regenerator columns are crucial pieces of equipment that require a reasonable modeling approach in the process simulator. The equilibrium-stage and rate-based models are two popular methods for column modeling. The equilibrium-based model usually needs empirical parameter revisions for accuracy since it assumes that the liquid and vapor exiting each column level are in equilibrium. Theoretical stages are used in this modeling, assuming that the liquid and vapor phases are in equilibrium at each stage. The models include vapor—liquid equilibrium computations together with formulas for material and heat balances.^{31,39,40} However, rate-based models investigate mass

and heat transfer events by considering the tray geometry, concentration gradients between the interacting phases, and transport characteristics. As a result, rate-based models provide outcomes highly consistent with empirical data, making it possible to forecast process parameters over a wide range of operating conditions.^{23,41}

The sour feed gas at 35 °C was introduced into the bottom of the absorber and encountered the lean hybrid solvent mixture countercurrently. The absorber, which had 17 trays numbered sequentially from top to bottom, was used in the current study. The lean amine solvent was introduced at 42 °C from the first tray, and the rich amine exited the bottom of the absorber at 44.14°C.

The rich amine transferred its heat to the lean amine solvent after flowing through the flash tank, increasing the temperature of the solvent to approximately 90 °C before entering the stripper column. The stripper column, which had 13 stages and contained an overhead condenser and a reboiler at the bottom, was used in the simulation study. The absorber and stripper specifications employed in the simulation are listed in Table 1.

Table 1. Specification Used in Simulation of the Acid Gas Removal Unit

sour gas specification	
methane (mol %)	73.20
$H_2S \pmod{\%}$	1
CO ₂ (mol %)	17
ethane (mol %)	4.4
propane (mol %)	2.86
butane (mol %)	1.54
column diameter (m)	1.098
weir length (m)	1
absorber	
number of trays	17
solvent temperature (°C)	42
solvent pressure (kPa)	3180
sour gas flow rate (kg mol/h)	2100
sour gas pressure (kPa)	3140
sour gas temperature (°C)	35
MEA concentration (wt %)	50
stripper	
number of trays	13
rich amine temperature (°C)	109
column top pressure (kPa)	196.3
weir height (mm)	41.2
column diameter	1
column bottom pressure (kPa)	206.3

The stripped H_2S and CO_2 gas was left from the regenerator column top at 93 °C, and the lean amine solution was left from the bottom at approximately 109 °C. The lean amine was

Table 2. Validation of Re	al Plant Data wit	h Simulation	Data
---------------------------	-------------------	--------------	------

cooled before being returned to the absorber to complete the efficient process.

5. RESULTS AND DISCUSSION

5.1. Plant Data Validation. Model validation aimed to demonstrate the precision of the simulated data generated by an Aspen HYSYS 12.1. The collected data's authenticity was assessed by evaluating the Mean Absolute Percentage Error (MAPE), whereby a lower MAPE indicates a higher level of accuracy in the data. To validate the acid gas removal unit, experimental data obtained from Zahid et al.³ was utilized, and the validation was carried out using the 'acid gas' thermodynamic package that comes as an in-built feature in the software. First, the model is validated using DGA solvent with the acid gas package with an error of less than 5%. The same conditions and solvent were used with UNIQUAC and ENRTL; the results show that UNIQUAC is better than ENRTL. The AGRU model was validated using chemical solvents in previous studies because most simulation studies were conducted on chemical solvents or case studies of the actual plants.^{14,42} Recently, one study was conducted on hybrid solvents to remove acid gases from NG, which uses an MDEA system to validate hybrid solvents.

This study utilized a combination of hybrid solvents to remove acid gases from NG. However, the available acid gas package did not contain provisions for hybrid mixtures. As a result, the actual plant data were validated against the acid gas using UNIQUAC and ENRTL thermodynamic package. A comprehensive comparison between the data sets has been presented in Table 2. The analysis indicated that the UNIQUAC package was more effective than the ENRTL thermodynamic packages in accurately estimating the sweet gas stream parameters and the corresponding duties. The standard error difference between the actual and simulated data was less than 5%; therefore, the model is said to be validated.

5.2. Energy Analysis. In postcombustion capture (PCC) based on chemical absorption, solvent regeneration accounts for 60-80% of the total energy consumption required for AGRU.^{43,44} Energy analyses were conducted to understand the power consumption of the acid gas removal plant. The findings indicate that stripper duty is the most energy-intensive in acid gas cleaning. Figure 2 compares the energy contribution of the major equipment used in the process using a single chemical solvent, MEA, and a hybrid solvent MEA + NMP. A 13.2% reduction in the reboiler duty was observed when a hybrid solvent was applied instead of a single chemical solvent. The second highest energy usage in the process is attributed to the lean solvent cooler. A 7.2% reduction in cooling utility was observed when a hybrid solvent was employed compared to a chemical solvent. The reason might be that the temperature leaving the bottom of the regeneration column was less when the hybrid solvent was used than the solvent leaving the

parar	neters	plant data	amine package	error (%)	UNIQUAC	error (%)	ENRTL	error (%)
condenser d	luty (GJ/h)	73.9	72.3	2.16	73.9	0	76.7	3.78
reboiler dut	y (GJ/h)	208	207	0.48	204	1.92	213	2.4
sweet gas te	emp (°C)	45	43.8	2.66	44.6	0.44	48.2	7.1
sweet gas P	ressure (kPa)	5962	5941	0.35	5958	0.06	5988	0.43
acid gas ten	np (°C)	60	58.3	2.83	59.7	0.5	63.1	5.1
acid gas pre	ssure (kPa)	190.9	187.5	1.78	190.6	0.15	194.7	1.99

25707



Figure 2. Major units energy requirement in an acid gas capture plant.

bottom when a single chemical solvent was applied. The Condenser consumes around 15% of the plant's total energy, while the pump contributes around 2%. The energy requirements resemble what has been reported in the literature.^{22,45} Overall, the result shows hybrid solvents required less reboiler, cooler, and pump energy than single chemical solvents. The lower energy requirement is because a physical solvent does not require extra heat in the stripping section to break the bond between amine and acid gases.⁴⁶

5.3. Effect of Lean Amine Temperature. The temperature and reaction kinetics of the absorber column can be controlled by adjusting the feed gas and lean amine temperature, which enter the column at the bottom and top, respectively. While reducing the temperature of the absorber column can improve its performance, it is often challenging to manipulate the temperature of the feed gas. As a result, the temperature of the lean amine is the only variable used to control the temperature of the absorber column. Maintaining a 5 °C temperature difference between the feed gas and the lean amine is advised to prevent the condensation of hydrocarbons in the column.⁴⁷

A sensitivity analysis was conducted to evaluate the impact of the lean amine temperature on the concentration of sweet gas and the reboiler duty. The results indicate that by increasing the temperature of the lean amine from 30 to 60 °C, CO₂ and H₂S content gradually rise in the sweet gas, as shown in Figure 3a,b. The diminished absorption effect is due to the decreased gas molecule diffusion caused by the absorption of CO₂ in the amine solution. An exothermic reaction can cause the equilibrium to shift backward at higher temperatures. Another contributing factor could be that higher lean amine temperatures increase the partial pressures of H_2S and CO_{24} resulting in a decreased solubility in alkanolamine solutions, which lowers their removal efficiency. On the other hand, reboiler duty experiences a slight decrease as the temperature of the lean amine decreases. This can be attributed to the CO_2 and H₂S slips in the sweet gas at higher temperatures, reducing the reboiler load and its duty.⁴⁸

5.4. Effect of Regenerator Inlet Temperature. The temperature of the rich amine stream entering the regeneration



Figure 3. Effect of lean amine temperature on acid gases and reboiler duty (a) of the CO_2 content in sweet gas (b) of the H_2S content in sweet gas.

column from the lean/rich exchanger can be altered to enhance the process performance. Various sources, including operational plants and literature, have reported a temperature of 99 °C with minor variations.^{49,50} However, the base case for this study involves an inlet temperature of 90 °C in the regenerator column. Due to the endothermic nature of the reactions in the stripper, a sensitivity analysis was carried out to examine the influence of the regenerator inlet temperature on the acid gas content in the sweet gas and the reboiler duty. The findings presented in Figure 4a,b demonstrate the impact of the rich amine temperature on the levels of CO₂ and H₂S in



Figure 4. Effect of regenerator inlet temperature on acid gases and reboiler duty (a) CO_2 content in sweet gas (b) H_2S content in sweet gas.

the sweet gas and the reboiler duty. Lower inlet temperatures for the rich amine result in substantial decreases in the CO_2 and H_2S contents in the sweet gas but require more energy in the reboiler. Conversely, increasing the rich amine inlet temperature increases the CO_2 and H_2S slippage in the sweet gas, but the reboiler duty decreases linearly.

5.5. Effect of Amine Flow Rate. One manipulated variable to achieve the desired sweet gas specification is the circulation rate of amine.³⁶ By increasing solvent circulation, more CO₂ and H₂S can be extracted from the feed gas, resulting in a lower content of acid gases in the sweet gas. A higher solvent circulation rate increases the contact time between the gaseous CO₂ and H₂S, improving solubility.⁵¹ Figure 5a,b shows that as the solvent flow rate was increased, CO_2 and H_2S content in the sweet gas was decreased. The concentration of Lean amine is an additional factor that can be employed in conjunction with the circulation rate of the solvent to manage the levels of CO₂ and H₂S present in the sweet gas. The results revealed that as the concentration of physical solvent was increased in amine solvent, a lower flow rate was required to achieve the desired specification of H₂S and CO₂ in sweet gas. On the other hand, when 50 wt % MEA, a chemical solvent, was used, it requires a large amount of flow rate to remove acid gases up to a specific limit, which reduces the reboiler duty of the acid gas removal unit. The same trend was observed in previous studies, which confirms that adding physical solvent has a beneficial effect on AGRU.^{48,52}

The stoichiometry of the chemical reaction limits the capacity of chemical solvents to absorb CO_2 and H_2S . In contrast, physical solvents do not have such constraints and



Figure 5. Effect of amine flow rate (a) CO_2 content in sweet gas (b) H_2S content in sweet gas (c) Reboiler duty.

their absorption ability is directly proportional to the partial pressure of CO_2 and H_2S . Physical solvents are preferred when large amounts of acid gases must be removed and can absorb sulfur compounds such as methyl-mercaptan, dimethyl-sulfide, and ethyl-mercaptan. In contrast, amine solvents have weaker mercaptan absorption abilities. Hybrid solvents containing physical solvents can enhance the absorption capacity of chemical solvents, resulting in lower flow rates than aqueous chemical solvents.²²

Figure 5c shows that the reboiler duty was observed at different flow rates using different amine concentrations. The results were obtained using different MEA+NMP, Single NMP, and MEA concentrations. The total amine concentration was kept at 50 wt %. It was observed here that when a single MEA chemical solvent was employed, it required a higher flow rate and reboiler duty to achieve the desired acid gas specification. On the other hand, it was noted that as the physical solvent was increased in the amine solvent the reboiler duty was less than the chemical solvent. The reason might be that fewer chemical reactions occur in high physical solvent concent

trations. Less energy was required to break the bond between acid gases and amines in the stripping column.^{53,54}

5.6. Effect of Absorber Pressure. A sensitivity analysis was conducted to evaluate the effect of absorber pressure on the sweet gas CO_2 and H_2S contents and the reboiler duty. The impact of changing absorber pressure on the slippage of CO_2 and H_2S in the sweet gas is shown in Figure 6a,b. If the



Figure 6. Effect of absorber pressure on acid gases and reboiler duty (a) CO_2 content in sweet gas and (b) H_2S content in sweet gas.

absorber pressure declines due to gas reservoir pressure reduction or other reasons, the CO₂ and H₂S concentration in the sweet gas increases since the CO₂ partial pressure in the feed stream decreases. The findings were consistent with Henry's law, which posits that increasing gas pressure theoretically enhances gas solubility. The hybrid solvents' improved loading capacity may be attributed to two factors: the solubility of acid gases CO₂ and H₂S increases as pressure rises, reducing their content in sweet gas. Second, physical diffusion occurs at higher pressures, further boosting loading capacity. The reboiler duty of the stripper remains constant regardless of absorber pressure changes. For instance, Vaidya et al.⁵⁵ found that NMP improved the solubility of CO_2 in a hybrid solution based on the solubility investigation for partial pressures of CO₂ up to 0.005 MPa. Additionally, it was concluded that the reaction between MEA and water was unaffected by the addition of NMP. However, the more significant CO₂ intake capacity trend was only seen for the MEA hybrid solution at 5 MPa when some water was replaced with NMP. It was found that the MEA aqueous solution appeared to have a better CO2 removal performance than the MEA hybrid solution at 0.1 and 1 MPa. This revealed that a separate absorption mechanism might work for the hybrid

solution under high-pressure conditions. In this study, Tan et al.²⁵ also demonstrate that at high pressures of 5 MPa, MEA +NMP outclasses the aqueous chemical solvent MEA.

However, if the absorber pressure drops, then an increment in the solvent circulation rate was observed to meet the sweet gas specifications, increasing reboiler duty. The result complies with the previous studies, which show that after adding a physical solvent to a chemical solvent, a drastic increase in the capture of acid gases was observed at high pressure.²²

5.7. Effect of Feed Gas Temperature. In the base case simulation, the sour feed gas temperature is set at 35 °C. However, this temperature can fluctuate by up to 20% depending on the season, even at the exact location. A simulated model was tested to evaluate the effect of varying feed gas temperatures on the process performance. The model incorporated temperatures above and below the base case temperature to determine the impact on CO_2 and H_2S content in sweet gas and their effect on reboiler duty. The feed gas temperature affects the sweet gas CO_2 and H_2S content, as illustrated in Figure 7a,b. The results indicate that increasing



Figure 7. Effect of feed gas temperature on acid gases and reboiler duty (a) CO_2 content in sweet gas and (b) H_2S content in sweet gas.

the feed gas temperature results in more significant CO_2 and H_2S slippage in the sweet gas due to the lower solubility of acid gas at higher temperatures. However, the variation in the input gas temperature has an insignificant effect on the reboiler duty.

5.8. Reboiler Operating Parameters. Increasing the reboiler temperature through additional heating can quickly determine the reboiler duty. This increase in the temperature can have a significant effect on the lean loading, which ultimately affects the performance of the absorber. As per the GPSA Engineering Data Book,⁵⁶ the recommended temperature range for the solvent stripper reboiler is 105–115 °C.

The plant's reboiler duty accurately corresponds to the anticipated reboiler temperature in the simulation model base case.

A sensitivity analysis assessed how the reboiler temperature affects the CO_2 and H_2S levels in the sweet gas and the reboiler duty, as shown in Figure 8a,b. The results indicate that higher



Figure 8. Effect of reboiler temperature on acid gases and reboiler duty (a) CO_2 content in sweet gas (b) H_2S content in sweet gas.

reboiler temperatures lead to lower CO_2 and H_2S concentrations in sweet gas and leaner amine production. Additionally, the reboiler duty increases linearly as the reboiler temperature rises. When the reboiler temperature was increased from 106 to 114 °C, the reboiler duty increased from 8.15 to 12.97 MW. High temperatures are advantageous due to the endothermic reaction in the regeneration column. However, exceeding the typical operating range at extremely high temperatures may cause solvent thermal deterioration. Modifications in the reboiler temperature impact the temperature distribution of the stripping column, and consequently, every rise in the reboiler temperature results in an increase in both the reboiler and condenser duties to meet the acid gas specification for the top product.

There is a connection between the reboiler pressure and temperature such that any alteration in the reboiler pressure will impact the reboiler temperature. Figure 9 presents the fluctuations in the reboiler temperature in response to changes in the reboiler pressure. Elevating the reboiler pressure results in a corresponding increase in the reboiler temperature.

As previously mentioned, the maximum reboiler temperature is limited due to the amine thermal degradation. The total efficiency of the solvent regeneration process is affected by the stripping pressure. The absorption performance is influenced by the differences in heat between the absorption of



Figure 9. Variation in reboiler pressure with a change in reboiler temperature.

acid gases and the vaporization of water. Solvents with high absorption heat reduce the reboiler heat duty at high pressures, while solvents with a low heat of absorption exhibit the same tendency but at low stripping pressures.

A hybrid solvent is generally known for its low heat of absorption. The effect of reboiler pressure on the CO_2 and H_2S concentration of the sweet gas and reboiler duty is shown in Figure 10a,b. When the reboiler pressure increases, the CO_2



Figure 10. Effect of reboiler pressure on acid gases and reboiler duty (a) CO_2 content in sweet gas and (b) H_2S content in sweet gas.

and H_2S concentration in the sweet gas decreases due to a rise in the reboiler temperature and a leaner amine fed to the absorber. Increasing the reboiler pressure often reduces the reboiler duty when only the CO_2 acid gas is present. However, the opposite effect is observed when a hybrid solvent removes a mixture of acid gases (CO_2 and H_2S) since physical solvents are known for their lower absorption. In this case, the increase in reboiler pressure and temperature affects the process efficiency.

6. CONCLUSIONS

Using an Aspen HYSYS V12.1, the design of a CO₂ and H₂S capture process was simulated in this study. Aspen HYSYS provides the "UNIQUAC" thermodynamic package, which can precisely forecast the CO₂ and H₂S capture process using a hybrid solvent (MEA + NMP) across various operational conditions. A comprehensive sensitivity analysis was carried out to evaluate the effect of different operational parameters on the process performance. The absorption reactions are exothermic and elevate the absorber temperature, but optimal performance can be obtained by operating at low temperatures and high pressure. The absorber performance can be improved by adjusting the lean amine and feed gas temperatures. The sweet gas specification can be controlled by regulating the concentrations of MEA and NMP solvents and their circulation rates. Regeneration reactions are endothermic and necessitate low pressure and high temperature. While elevating the reboiler temperature produces high-quality sweet gas, the temperature should not be raised too high as it can cause the solvent to degrade thermally. The study of future prospects will focus on developing design alternatives to explore various possibilities for energy and cost savings and optimizing the plant.

AUTHOR INFORMATION

Corresponding Author

Raihan Mahirah Ramli – Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia; Centre of Innovative Nanostructures & Nanodevices, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia;
orcid.org/0000-0003-2162-5520; Email: raihan.ramli@ utp.edu.my

Authors

- Abid Salam Farooqi Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia; Centre of Innovative Nanostructures & Nanodevices, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
- Serene Sow Mun Lock Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia; CO₂ Research Center (CO₂RES), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Malaysia; orcid.org/0000-0003-2285-0308
- Ahmad Salam Farooqi Interdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
- Muhammad Zubair Shahid Interdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
- Syed Muhammad Wajahat ul Hasnain Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia; CO₂ Research Center (CO₂RES), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Malaysia
- Noor e Hira Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar,

Perak, Malaysia; CO₂ Research Center (CO₂RES), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Malaysia **Bawadi Abdullah** – Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia; CO₂ Research Center (CO₂RES), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Malaysia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c09100

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to express gratitude to Yayasan Universiti Teknologi PETRONAS (Cost centre: 015LC0-444) and for their technical and financial support through grant number 015LC0-444 and University Internal Research Funding (Cost centre: 015LB0-123) for their technical and financial support.

NOMENCLATURE

MEA	monoethanolamine
NMP	N-methyl 2-pyrrolidone
NG	natural gas
H_2S	hydrogen sulfide
CCS	carbon capture and storage
CO ₂	carbon dioxide
CH ₄	methane
UNIQUAC	UNIversal QUAsi Chemical
LLE	liquid—liquid equilibrium
VLE	vapor—liquid equilibrium

REFERENCES

(1) Gao, W.; Liang, S.; Wang, R.; Jiang, Q.; Zhang, Y.; Zheng, Q.; Xie, B.; Toe, C. Y.; Zhu, X.; Wang, J.; Huang, L.; Gao, Y.; Wang, Z.; Jo, C.; Wang, Q.; Wang, L.; Liu, Y.; Louis, B.; Scott, J.; Roger, A. C.; Amal, R.; He, H.; Park, S. E. Industrial Carbon Dioxide Capture and Utilization: State of the Art and Future Challenges. *Chem. Soc. Rev.* **2020**, 49 (23), 8584–8686.

(2) Qiao, W.; Lu, H.; Zhou, G.; Azimi, M.; Yang, Q.; Tian, W. A Hybrid Algorithm for Carbon Dioxide Emissions Forecasting Based on Improved Lion Swarm Optimizer. *J. Cleaner Prod.* **2020**, *244*, No. 118612.

(3) Zahid, U.; Al Rowaili, F. N.; Ayodeji, M. K.; Ahmed, U. Simulation and Parametric Analysis of CO2 Capture from Natural Gas Using Diglycolamine. *Int. J. Greenhouse Gas Control* **2017**, *57*, 42–51.

(4) Tan, L. S.; Lau, K. K.; Bustam, M. A.; Shariff, A. M. Removal of High Concentration CO2 from Natural Gas at Elevated Pressure via Absorption Process in Packed Column. *J. Nat. Gas Chem.* **2012**, *21* (1), 7–10.

(5) Farooqi, A. S.; Yusuf, M.; Zabidi, N. A. M.; Sanaullah, K.; Abdullah, B.CO2 Conversion Technologies for Clean Fuels Production. In *Carbon Dioxide Capture Convers*; Elsevier, 2022; pp 37–63 DOI: 10.1016/B978-0-323-85585-3.00006-7.

(6) Farooqi, A. S.; Yusuf, M.; Mohd Zabidi, N. A.; Saidur, R.; Sanaullah, K.; Farooqi, A. S.; Khan, A.; Abdullah, B. A Comprehensive Review on Improving the Production of Rich-Hydrogen via Combined Steam and CO2 Reforming of Methane over Ni-Based Catalysts. *Int. J. Hydrogen Energy* **2021**, *46* (60), 31024–31040.

(7) Farooqi, A. S.; Ramli, R. M.; Lock, S. S. M.; Hussein, N.; Shahid, M. Z.; Farooqi, A. S. Simulation of Natural Gas Treatment for Acid Gas Removal Using the Ternary Blend of MDEA, AEEA, and NMP. *Sustainability* **2022**, *14* (17), 10815 DOI: 10.3390/su141710815.

(8) Hira, N.; Lock, S. S. M.; Shoparwe, N. F.; Lock, I. S. M.; Lim, L. G.; Yiin, C. L.; Chan, Y. H.; Hassam, M. Review of Adsorption Studies for Contaminant Removal from Wastewater Using Molecular Simulation. *Sustainability* **2023**, *15* (2), 1510 DOI: 10.3390/su15021510.

(9) Mokhatab, S.; Poe, W. A.; Mak, J. Y.Natural Gas Treating. In *Handbook of Natural Gas Transmission and Processing*; Elsevier, 2019; pp 231–269 DOI: 10.1016/B978-0-12-815817-3.00007-1.

(10) Ban, Z. H.; Keong, L. K.; Shariff, A. M. Physical Absorption of CO2 Capture: A Review. *Adv. Mater. Res.* **2014**, *917*, 134–143.

(11) Schäfer, B.; Mather, A. E.; Marsh, K. N. Enthalpies of Solution of Carbon Dioxide in Mixed Solvents. *Fluid Phase Equilib.* **2002**, *194–197* (197), *929–935*.

(12) Fouad, W. A.; Berrouk, A. S. Using Mixed Tertiary Amines for Gas Sweetening Energy Requirement Reduction. *J. Nat. Gas Sci. Eng.* **2013**, *11*, 12–17.

(13) Abid, S. F.; Raihan, M. B. R.; Serene, S. M. L.; Ahmad, S. F.; Syed, M. W.; Sidra, A. F. Absorption of Acid Gases (CO2, H2S) from Natural Gas Using a Ternary Blend of N-Methyldiethanolamine (MDEA), 2-Amino-2-Methyl-1-Propanol (AMP), and Sulfolane. *Mater. Res. Found.* **2023**, *29*, 9–16.

(14) Banat, F.; Younas, O.; Didarul, I. Energy and Exergical Dissection of a Natural Gas Sweetening Plant Using Methyldiethanol Amine (MDEA) Solution. *J. Nat. Gas Sci. Eng.* **2014**, *16*, 1–7.

(15) Shahid, M. Z.; Maulud, A. S.; Bustam, M. A.; Suleman, H.; Halim, H. N. A.; Shariff, A. M. Rate-Based Modeling for Packed Absorption Column of the MEA-CO2-Water System at High-Pressure and High-CO2 Loading Conditions. *Ind. Eng. Chem. Res.* **2019**, 58 (27), 12235–12246.

(16) Camper, D.; Bara, J. E.; Gin, D. L.; Noble, R. D. Room-Temperature Ionic Liquid-Amine Solutions: Tunable Solvents for Efficient and Reversible Capture of CO2. *Ind. Eng. Chem. Res.* **2008**, 47 (21), 8496–8498.

(17) Paul, S.; Mandal, B. Density and Viscosity of Aqueous Solutions of (N-Methyldiethanolamine + Piperazine) and (2-Amino-2-Methyl-1-Propanol + Piperazine) from (288 to 333) K. J. Chem. Eng. Data **2006**, *51* (5), 1808–1810.

(18) Chuah, C. Y.; Kim, K.; Lee, J.; Koh, D. Y.; Bae, T. H. CO2 Absorption Using Membrane Contactors: Recent Progress and Future Perspective. *Ind. Eng. Chem. Res.* **2020**, 59 (15), 6773–6794.

(19) Farooqi, S. A.; Farooqi, A. S.; Sajjad, S.; Yan, C.; Victor, A. B. Electrochemical Reduction of Carbon Dioxide into Valuable Chemicals: A Review. *Environ. Chem. Lett.* **2023**, *21*, 1515.

(20) Wang, Y.; Liu, X.; Kraslawski, A.; Gao, J.; Cui, P. A Novel Process Design for CO2 Capture and H2S Removal from the Syngas Using Ionic Liquid. *J. Cleaner Prod.* **2019**, *213*, 480–490.

(21) Rochelle, G. T.; Freeman, B. D.; Sanchez, I. C.; Eldridge, R. B.; Svendsen, H. F. A Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for Carbon Dioxide Capture from Flue Gas 2008 https://repositories. lib.utexas.edu/handle/2152/3900 (accessed January 06, 2021).

(22) Angaji, M. T.; Ghanbarabadi, H.; Gohari, F. K. Z. Optimizations of Sulfolane Concentration in Propose Sulfinol-M Solvent Instead of MDEA Solvent in the Refineries of Sarakhs. J. Nat. Gas Sci. Eng. 2013, 15, 22–26.

(23) Kazmi, B.; Taqvi, S. A. A.; Raza, F.; Haider, J.; Naqvi, S. R.; Khan, M. S.; Ali, A. Exergy, Advance Exergy, and Exergo-Environmental Based Assessment of Alkanol Amine- and Piperazine-Based Solvents for Natural Gas Purification. *Chemosphere* **2022**, *307*, No. 136001.

(24) Qasim, A.; Khan, M. S.; Maulud, A. S. Simulation of Hydrate Phase Boundary for Natural Gas Mixture with High CO2Content through Simulation. *Int. J. Eng. Adv. Technol.* **2019**, No. 9, 2249– 8958.

(25) Tan, L. S.; Shariff, A. M.; Lau, K. K.; Bustam, M. A. Impact of High Pressure on High Concentration Carbon Dioxide Capture from Natural Gas by Monoethanolamine/N-Methyl-2-Pyrrolidone Solvent in Absorption Packed Column. *Int. J. Greenhouse Gas Control* **2015**, *34*, 25–30.

(26) Shannon, M. S.; Tedstone, J. M.; Danielsen, S. P. O.; Bara, J. E. Evaluation of Alkylimidazoles as Physical Solvents for CO 2/CH 4 Separation. *Ind. Eng. Chem. Res.* **2012**, *51* (1), 515–522.

(27) Hochgesand, G. Rectisol and Purisol. Ind. Eng. Chem. 1970, 62 (7), 37–43.

(28) Pouladi, B.; Hassankiadeh, M. N.; Behroozshad, F. Dynamic Simulation and Optimization of an Industrial-Scale Absorption Tower For. *Energy Rep.* **2016**, *2*, 54–61.

(29) Pourjazaieri, S.; Zoveidavianpoor, M.; Shadizadeh, S. R. Simulation of an Amine-Based CO2 Recovery Plant. *Pet. Sci. Technol.* **2011**, *29* (1), 39–47.

(30) Lunsford, K. M.; Bullin, J. A. Optimization of Amine Sweetening Units; 2006.

(31) Danckwerts, P. V. The Reaction of CO2 with Ethanolamines. *Chem. Eng. Sci.* **1979**, 34 (4), 443–446.

(32) Crooks, J. E.; Donnellan, J. P. Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution. *J. Chem. Soc. Perkin Trans.* 2 **1989**, No. 4, 331–333.

(33) Blauwhoff, P. M. M.; Versteeg, G. F.; Van Swaaij, W. P. M. A Study on the Reaction between CO2 and Alkanolamines in Aqueous Solutions. *Chem. Eng. Sci.* **1983**, *38* (9), 1411–1429.

(34) Bosch, H.; Kuipers, J. A. M.; van Swaaij, W. P. M.; Versteeg, G. F. Mass Transfer with Complex Chemical Reactions: Simultaneous Absorption of H2S and CO2 in Solutions of Alkanolamines. *Gas Sep. Purif.* **1989**, *3* (2), 75–83.

(35) Faiz, R.; Al-Marzouqi, M. Mathematical Modeling for the Simultaneous Absorption of CO2 and H2S Using MEA in Hollow Fiber Membrane Contactors. *J. Membr. Sci.* **2009**, 342 (1–2), 269–278.

(36) Almoshh, A.; Alobaid, F.; Heinze, C.; Epple, B. Comparison of Equilibrium-Stage and Rate-Based Models of a Packed Column for Tar Absorption Using Vegetable Oil. *Appl. Sci.* **2020**, *10* (7), 2362.

(37) Sadegh, N.; Stenby, E. H.; Thomsen, K. Thermodynamic Modelling of Acid Gas Removal from Natural Gas Using the Extended UNIQUAC Model. *Fluid Phase Equilib.* 2017, 442, 38–43.
(38) Pereira, L. M. C.; Vega, L. F. A Systematic Approach for the Thermodynamic Modelling of CO2-Amine Absorption Process Using Molecular-Based Models. *Appl. Energy* 2018, 232, 273–291.

(39) Lv, B.; Guo, B.; Zhou, Z.; Jing, G. Mechanisms of CO2 Capture into Monoethanolamine Solution with Different CO2 Loading during the Absorption/Desorption Processes. *Environ. Sci. Technol.* **2015**, *49* (17), 10728–10735.

(40) Caplow, M. Kinetics of Carbamate Formation and Breakdown. J. Am. Chem. Soc. **1968**, 90 (24), 6795–6803.

(41) Shahid, M. Z.; Maulud, A. S.; Bustam, M. A.; Suleman, H.; Abdul Halim, H. N.; Shariff, A. M. Packed Column Modelling and Experimental Evaluation for CO2 Absorption Using MDEA Solution at High Pressure and High CO2 Concentrations. *J. Nat. Gas Sci. Eng.* **2021**, *88*, No. 103829.

(42) Roy, P. S.; Amin, M. R. Aspen-HYSYS Simulation of Natural Gas Processing Plant. J. Chem. Eng. 2012, 26 (1), 62–65.

(43) Li, J.; You, C.; Chen, L.; Ye, Y.; Qi, Z.; Sundmacher, K. Dynamics of CO 2 Absorption and Desorption Processes in Alkanolamine with Cosolvent Polyethylene Glycol. *Ind. Eng. Chem. Res.* **2012**, *51* (37), 12081–12088.

(44) Rochelle, G. T. Thermal Degradation of Amines for CO2 Capture. *Curr. Opin. Chem. Eng.* **2012**, *1* (2), 183–190.

(45) Abdul Halim, H. N.; Shariff, A. M.; Tan, L. S.; Bustam, M. A. Mass Transfer Performance of CO2 Absorption from Natural Gas Using Monoethanolamine (MEA) in High Pressure Operations. *Ind. Eng. Chem. Res.* **2015**, *54* (5), 1675–1680.

(46) Xu, H.; Xiao, W.; Wang, Z.; Hu, J.; Shao, G. Self-Consistent Assessment of Li+ Ion Cathodes: Theory vs. Experiments. *J. Energy Chem.* **2021**, *59*, 229–241.

(47) Zahid, U. Simulation of an Acid Gas Removal Unit Using a DGA and MDEA Blend Instead of a Single Amine. *Chem. Prod. Process Model.* **2020**, *15* (4), No. 20190044, DOI: 10.1515/cppm-2019-0044.

(48) Ghanbarabadi, H.; Khoshandam, B.; Wood, D. A. Simulation of CO2 Removal from Ethane with Sulfinol-M+AMP Solvent Instead of DEA Solvent in the South Pars Phases 9 and 10 Gas Processing Facility. *Petroleum* **2019**, 5 (1), 90–101.

(49) Stewart, C.; Hessami, M. A. A Study of Methods of Carbon Dioxide Capture and Sequestration—the Sustainability of a Photosynthetic Bioreactor Approach. *Energy Convers. Manag.* **2005**, *46* (3), 403–420.

(50) Kohl, A. L.; Nielsen, R. Gas Purification - Google Books. https://books.google.com.my/books?hl=en&lr=&id=rpzrIZW-OcEC&oi=fnd&pg=PP1&dq=Kohl+AL,+Nielsen+R. + Gas+purification.

+Houston,+Texas,+USA:+Gulf+Professional+Publishing,+1997&ots= qYzVkrWuVj&sig=lBLhqP2W6K6hhBzGqyqgtzPZLNc&redir_esc= y#v=onepage&q&f=false (accessed March 31, 2022).

(51) Rodríguez, N.; Mussati, S.; Scenna, N. Optimization of Post-Combustion CO2 Process Using DEA–MDEA Mixtures. *Chem. Eng. Res. Des.* **2011**, 89 (9), 1763–1773.

(52) Damanafshan, M.; Mokhtarani, B.; Mirzaei, M.; Sharifi, A. Equilibrium Solubility Measurement of Carbon Dioxide in Hybrid Solvents of Aqueous N-Methyldiethanolamine Blended with 1-Methyl-3-Octyl-Imidazolium Tetrafluoroborate Ionic Liquid at High Pressures. J. Mol. Liq. 2021, 337, No. 116571.

(53) Nozaeim, A. A.; Tavasoli, A.; Mortaheb, H. R.; Mafi, M. CO2 Absorption/Desorption in Aqueous DEEA/MDEA and Their Hybrid Solutions with Sulfolane. *J. Nat. Gas Sci. Eng.* **2020**, *76*, No. 103219.

(54) Farooqi, A. S.; Ramli, R. M.; Lock, S. S. M.; Hussein, N.; Farooqi, A. S.; Wajahat, S. M. Simulation of Acid Gas Removal Unit Using DIPA+TEA Amine Solvent. *IOP Conf. Ser. Mater. Sci. Eng.* **2022**, 1257 (1), No. 012033.

(55) Vaidya, P. D.; Kenig, E. Y. CO2-Alkanolamine Reaction Kinetics: A Review of Recent Studies. *Chem. Eng. Technol.* 2007, 30 (11), 1467–1474.

(56) GPSA. Engineering data book - Google Scholar 2004 https:// scholar.google.com/scholar?cluster=11397995467136987224&hl= e n & a s _ s d t = 2 0 0 5 & s c i o d t = 0 , 5 & s c i o q = GPSA+Engineering+Data+Book (accessed May 01, 2022).