

Performance analysis of natural gas sweetening unit with amine solution and blends

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ABSTRACT

In this study, raw natural gas data from Uch gas field located in Dera-Bugti of Balochistan, Pakistan is simulated for performance analysis over amine absorber unit in Aspen HYSYS V9.0. The primary amine, MDEA was selected to remove bulk CO₂ and reduce H₂S to ppm level, where secondary amines, MEA, DEA and Sulfolane were selected to observe CO₂ levels in sweet gas. The primary amine in isolation and blend with secondary amine was simulated and analysed over absorber performance. The absorber performance is reported as CO₂, H₂S and water content in sweet gas, hydrocarbons in rich amine and its temperature. MDEA in isolation resulted in minimum 14.13 and 12.78 mol% CO₂ in sweet gas and rich amine temperature of 81.11oC and 82.13oC with 24 and 30-Trays, respectively at 2500 m³/h of lean amine recirculation rate. Among the tested blends, MDEA/MEA, MDEA/Sulfolane showed no significant improvement on absorber performance compared to isolated MDEA. However, MDEA/DEA blends indicated that CO₂ in sweet gas can be reduced to 12.07, 3.41, 1.85 mol% with rich amine temperature of 89.05, 111.72 and 124.80oC, respectively. The lowest CO₂ detected of 1.85 mol% was achieved with 40 mol% MDEA and 15 mol% DEA blend at 2500 m³/h recirculation rate and rich amine temperature of 124.80oC. The results indicated that MDEA/DEA blend has the potential to attain CO₂ of less than 2 mol%. The higher rich amine temperature raise concern that can be resolved by using heat stabilized salt.

1. Introduction

World primary energy comes mainly from crude oil and natural gas (NG) fossil fuels. These fuel resources are vital in supporting and sustaining socioeconomic development for many countries. Likewise, Pakistan socioeconomic growth is connected with the supply of fuel resources. Pakistan total primary energy supply

reached to 100750 kilo tonnes of oil equivalent by the end of 2017, an increase of 190% over 2007, where oil shared 27.63%, NG 25.64%, coal 10.67%, bio-fuels and waste 34.31% and hydro-nuclear about 1.75% [1]. The country total proven NG reserves were estimated 12.9 trillion cubic feet with reserves to production ratio of 10.7 years in end-2018 [2]. Industrial and residential sectors remained the dominant consumer of NG [1].

NG is a valuable fuel that can be used directly with fewer processing steps compared to crude oil. NG can also be considered clean-burning fossil fuel which can limit carbon dioxide (CO₂) and other air pollutants compared to crude oil based fuels. NG is a versatile fuel to produce liquefied NG (LNG), floating liquefied NG (FLNG) and gas to high-quality fuel products [3]. NG consists mainly of methane along with heavier alkanes and alkenes in varying amount. The NG may also contain significant amount of acid gases mainly CO₂ and hydrogen sulphide (H₂S) and Sulphur compounds (carbon disulphide (CS₂), carbonyl sulphide (COS), elemental sulphur and mercaptants (RSH)) [4, 5]. Among these, CO₂ and H₂S are identified as the most common impurities and cause several technical problems. These gas-phase impurities are corrosive and toxic in nature with very low heating value. The composition and performance of NG processing criteria are mainly based on Wobbe number and heating value (which relates to combustion characteristics), oxygen, total inerts, water, and sulphur content (which relates to pipeline plugging and corrosion) [6].

More importantly, the gas-phase impurities shall be removed to meet pipeline specifications. The pipeline specifications are usually negotiated in contract and standards exits for all the products. However, the pipeline specification for quality NG can range for the major components (Methane >75 mol%, ethane ≤10 mol%, propane ≤5 mol%, butanes ≤2 mol%, pentane and heavier ≤0.5 mol%, Nitrogen and other inerts ≤3 mol%, CO₂ ≤2-3 mol% and total diluents gases ≤4-5 mol%), trace components (H₂S 6-7 mg/m³, water vapour 60-110 mg/m³, oxygen 1%, and total sulphur 115-460 mg/m³), gross and saturated heating value (35400-42800 kJ/m³) [4, 6].

NG treatment process involves reducing the acid gases (CO₂ and H₂S) and other sulphur compounds to low concentration to meet pipeline specifications. H₂S is highly toxic. The lower threshold limit value of H₂S for prolonged exposure is 10 ppmv and concentration greater than 1000 ppmv can cause death within few minutes of exposure. Above 1000 ppmv, the raw NG can hold other sulphur compounds, such as CS₂, mercaptants (RSH), and sulphides (RSR) and elemental sulphur [7]. In addition, the presence of CO₂ in raw NG may also contain trace amounts of COS. CO₂ is non-flammable and large quantity is undesirable in fuel gas, whereas H₂S can form weak acids with water. NG treatment processes are classified as chemical absorption, physical absorption, membrane separation, solid adsorption,

hybrid solvent, direct conversion and cryogenic fractionation [6].

The selection criterion for the chemical absorption process is mainly based on acid gases partial pressure in the feed gas and product gas. Chemical absorption of acid gases with amine solvent has gained increasingly attention in industrial applications due to the fact that H₂S and CO₂ can be reduced to ppmv levels. A regular amine NG treating uses the Girbotol process. This involves the chemical reaction of acid-gas components in NG with alkanolamine via exothermic reaction. The reaction is carried out in gas-liquid contactor called amine absorber, where amine solution becomes rich in acid gases. The rich amine is then treated in a regenerator which removes the acid-gases from the solvent operated at low pressure and high temperature and is recycled back to the amine absorber as lean amine [8]. Alkanolamines such as monoethanol amine (MEA), methyl diethanol amine (MDEA), diethanol amine (DEA), triethanol amine (TEA), diisopropanol amine (DIPA) and diglycol amine (DGA) have been used in industrial absorption of acid-gases from raw NG [9-12].

NG reserves of Pakistan are located in all of its provinces. The Uch gas field operated by Oil and Development Corporation Limited (OGDCL) is situated in Dera-Bugti of Balochistan province and is producing 220-225 MMSCFD of treated NG which is supplied to Uch Power Limited (UPL) for power generation. The pipeline specification demands H₂S less than 20 ppm and CO₂ and N₂ not less than 54 mol%. Recently, OGDCL has planned to increase the Uch gas field treatment facility to 380 MMSCFD. This increase in plant capacity suggests exploring several possible alternatives to improve system performance. Amine absorber unit can be considered an important unit in gas field processing since it controls the degree of purification levels and determine downstream process requirements. For this reason, this study primarily focuses on improving the system performance of amine absorber with amine solutions and to observe changes in sweet gas and rich amine composition. The finding of this study can be helpful for the plant operator to plan system modifications and improve sale gas specifications. The primary objective of this study is to treat 380 MMSCFD raw NG plant data obtained from Uch gas field and analyse acid-gas loading with various amine solutions using Aspen HYSYS V9.0. Furthermore, different analysis runs were carried out to study the effects of amine and their blend on amine absorber performance. The parameter considered for performance analysis was lean amine recirculation rate, number of trays, amine

concentration (MDEA and amine blends). The absorber performance was reported as CO₂, H₂S, water in sweet gas and hydrocarbons (HCs) and rich amine temperature.

2. Methods

2.1 Process Analysis

The analysis was carried out using raw NG composition and molar flow rates data obtained from plant facility as shown in Table 1. NG treatment facility is shown in Fig. 1. The process analysis was performed on amine absorber flow sheet scheme as shown in Fig. 2. The fluid package used for the process analysis was Acid Gas-Chemical Solvents. The feed gas design operating pressure and temperature were set to 5548 kPa and 40.56°C, respectively. The operating conditions and composition were held constant. Lean amine recirculation rate of 500-2500 m³/hr in isolation and blends were tested on absorber performance i.e. CO₂ and H₂S in sweet gas (mol%), rich amine temperature (°C), HCs in rich amine (mol%) and water content in sweet gas (mol%). Initially, the effects of lean amine recirculation rate and amine concentration in isolation on number of stages and absorber performance were tested and analysed.

Table 1

Operating conditions and composition of feed gas

| Plant Location Uch Gas Field, Dera-Bugti, Balochistan, Pakistan | | | | | |
|-----------------------------------------------------------------|-----------------------------|-------|------------------|------------------|-------|
| Feed gas | Raw NG | | | | |
| Gas density | 73.90 kg/m ³ | | | | |
| Pressure | 790 psig (5548 kPa) | | | | |
| Temperature | 105°F (40.56°C) | | | | |
| Molar flow | 20010 kg.mol/h (380 MMSCFD) | | | | |
| Components | Molecular weight | mol% | Components | Molecular weight | mol% |
| Methane | 16.04 | 37.20 | n-Pentane | 72.15 | 0.080 |
| Ethane | 30.07 | 1.000 | n-Hexane | 86.17 | 0.100 |
| Propane | 44.09 | 0.380 | H ₂ O | 18.02 | 0.105 |
| i-Butane | 58.12 | 0.110 | H ₂ S | 34.08 | 0.055 |
| n-Butane | 58.12 | 0.120 | CO ₂ | 44.01 | 40.56 |
| i-Pentane | 72.15 | 0.090 | N ₂ | 28.01 | 20.20 |

2.2 Simulation Runs

Chemical absorption with amine solvent has gained widespread industrial applications due to higher H₂S and CO₂ selectivity. The summary of widely used NG chemical treatment processes with degree of purification levels, H₂S selectivity, COS, CS and mercaptants removal and solvent degradation information are presented in Table 2. In this study, MDEA is selected as

the primary amine and is based on the fact that it is capable of meeting H₂S specification [13]. In addition, MDEA has the potential of removing bulk CO₂ with no solution degradation. The selection of secondary amines MEA, DEA and Sulfolane are related to fact of meeting H₂S specifications and can be capable of removing CO₂ to 50-100 ppmv. The selection of secondary amine is also related to fluid package limitation provided in Aspen HYSYS V9.0. Among various acid gas treating fluid packages, acid gas-chemical solvent was selected since it supports large number of amines and amines blends. The acid gas-chemical solvent is supported with primary amines (DEA, DGA, DIPA, MDEA, MEA and TEA) and amine blends (MDEA + Sulfolane, MDEA + MEA, MDEA + DEA and DIPA + Sulfolane). MDEA as a primary amine was selected since found much effective in bulk CO₂ removal with no solution degradation, where secondary amines are based on CO₂ removal to low levels as indicated in Table 2. The selected primary and secondary amines are shown in the table. The simulation performed under various conditions are reported in Table 3.

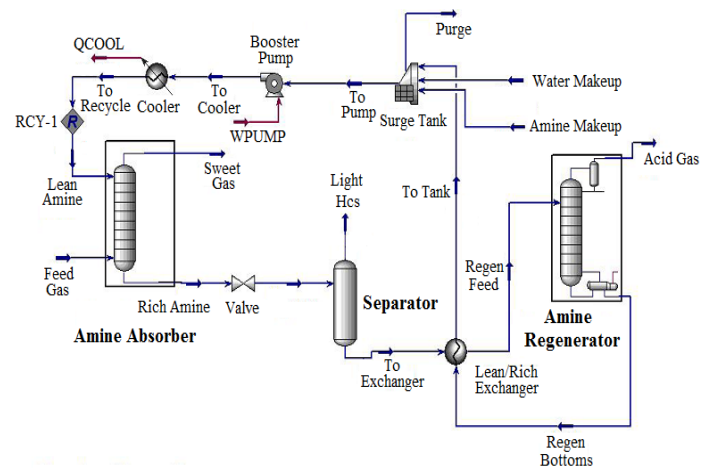


Fig. 1. NG treatment facility

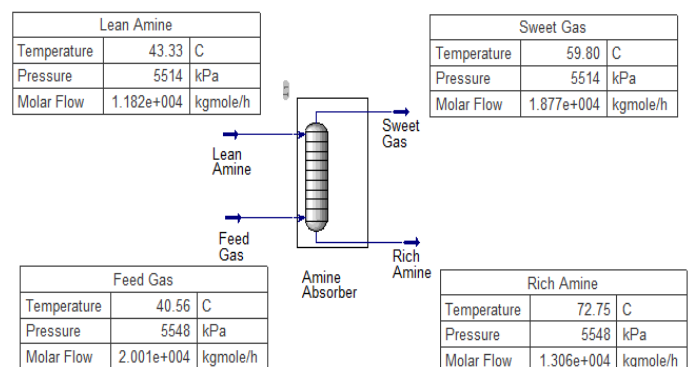


Fig. 2. Amine Absorber flow sheet case with 25 mol% MDEA in aqueous solution, lean amine recirculation rate of 500 m³/h, 24 valve trays and pressure drop of 34 kPa

Table 2

Summary of NG chemical treatment processes and selection criteria [6]

| Solvent/Process | Capable of meeting H ₂ S specifications of 6 mg/m ³ | Selective H ₂ S removal | Capable of removing CO ₂ | Removes COS, CS ₂ and mercaptants | Solution subject to degradation (degrading species) | Selected amines for this study |
|------------------------------|---------------------------------------------------------------------------|------------------------------------|-------------------------------------------------------------------|----------------------------------------------|--------------------------------------------------------------------------------------------------|--------------------------------|
| Monoethanol amine (MEA) | Yes | No | 100 ppmv at low to moderate pressure | Partial | Yes (COS, CO ₂ , CS ₂ , SO ₂ , SO ₃ and mercaptants) | Secondary |
| Diethanol amine (DEA) | Yes | No | 50 ppmv in SNEA-DEA process | Partial | Some (COS, CO ₂ , CS ₂ , HCN and mercaptants) | Secondary |
| Triethanol amine (TEA) | No | No | Minimum partial pressure of 0.5 psia (3 kPa) | Slight | Slight (COS, CS ₂ and mercaptants) | - |
| Methyldiethanol amine (MDEA) | Yes | Some | Bulk removal only | Slight | No | Primary |
| Diglycol amine (DGA) | Yes | No | 100 ppmv at moderate to high pressure | Partial | Yes (COS, CO ₂ and CS ₂) | - |
| Diisopropanol amine (DIPA) | Yes | Yes | Not applicable | COS only | Resistant to degradation by COS | - |
| Sulfolane | Yes | Yes | 50 ppmv, 50% slippage while meeting H ₂ S product spec | Partial | Some (CO ₂ and CS ₂) | Secondary |
| Hot potassium carbonate | Yes, with special design features | No | Not reported | Partial | Not reported | - |
| Stretford | Yes | Yes | No significant amounts of CO ₂ are removed | No | Yes (CO ₂ at high concentration) | - |
| Slexol® | Yes | Some | Can be slipped or absorbed | Slight | No | - |
| Rectisol | Yes | No | 1 ppmv | Yes | Not reported | - |
| Molecular sieves | Yes | Some | Can meet cryogenic spec when CO ₂ feed content <2% | Yes (excluding CS ₂) | Not applicable | - |
| Membranes | No | No | Feed gas concentration dependent | Slight | Not applicable | - |

3. Results and Discussion

3.1 Effects of MDEA in Isolation on Absorber Performance

Initially, MDEA in isolation with 25 mol% in aqueous solution was analysed with varying lean amine recirculation rate and number of trays on absorber

performance and the simulation results are presented in Fig. 3. The results indicated that the increase in lean amine recirculation rate decreases CO₂ and H₂S in sweet gas (Fig. 3 (a) and (b)). H₂S in sweet gas was observed to reach almost zero with increase in recirculation rate and number of trays (Fig. 3(b)). This suggests that MDEA at

low concentration of 25 mol% can achieve essentially complete removal of H₂S. This complete removal is mainly due to the reason that raw NG contains much less H₂S of 0.055 mol% (550 ppm) and concentration of MDEA at 20-50 mol% is highly selective for H₂S at low concentrations under most operating conditions [13].

Table 3

Simulation runs under various conditions

| Amine category | Amine abbreviation | mol% in aqueous solution | | |
|----------------|--------------------|--------------------------|-------|-------|
| | | 25 | 50 | 75 |
| Primary Amine | MDEA | 25 | 50 | 75 |
| Blends | MDEA/MEA | 25/5 | 25/10 | 25/15 |
| | MDEA/DEA | 40/5 | 40/10 | 40/15 |
| | MDEA/Sulfolane | 40/5 | 40/10 | 40/15 |

Fig. 3(a) indicates that CO₂ in sweet gas was observed 36.55 mol% at 500 m³/h which then decreases to 31.65 mol% at 2500 m³/h with 6-Trays. The CO₂ was detected lowest at 22.63 mol%, 17.07 mol%, 14.13 mol% and 12.78 mol% in sweet gas with 12, 18, 24 and 30-Trays respectively with 2500 m³/h of lean amine recirculation rate. The highest CO₂ removal observed was 68.48%, calculated by $((40.56-14.13)/40.56) \times 100$, and 65.16%, calculated by $((40.56-12.78)/40.56) \times 100$ with 24 and 30-Trays respectively, where it was observed 44.21% and 57.91% with 12 and 18-Trays respectively at 2500 m³/h. Fig. 3(c) indicates that rich amine temperature reaches at 70°C at 500 m³/h, which then decreases to 60°C at 2500 m³/h with 6-Trays. This decrease in rich amine temperature can be correlated to less residence time of amine in absorber column thereby decreasing absorber performance. Similar behaviour was observed with 12-Trays, where small increase in rich amine temperature was observed. The maximum rich amine temperature was observed at 78.5°C, 81.11°C and 82.13°C with 18, 24 and 30-Trays, respectively at 2500 m³/h. This increase in rich amine temperature at higher recirculation rate suggests sufficient contact between the amine and CO₂ improved CO₂ removal, which was indicated by lowest detected CO₂ in sweet gas of 17.07 mol%, 14.13 mol% and 12.78 mol% with 18, 24 and 30-Trays, respectively (Fig. 3(a)). Based on the above discussion, it can be concluded that increase in recirculation rate and number of trays improved absorber performance.

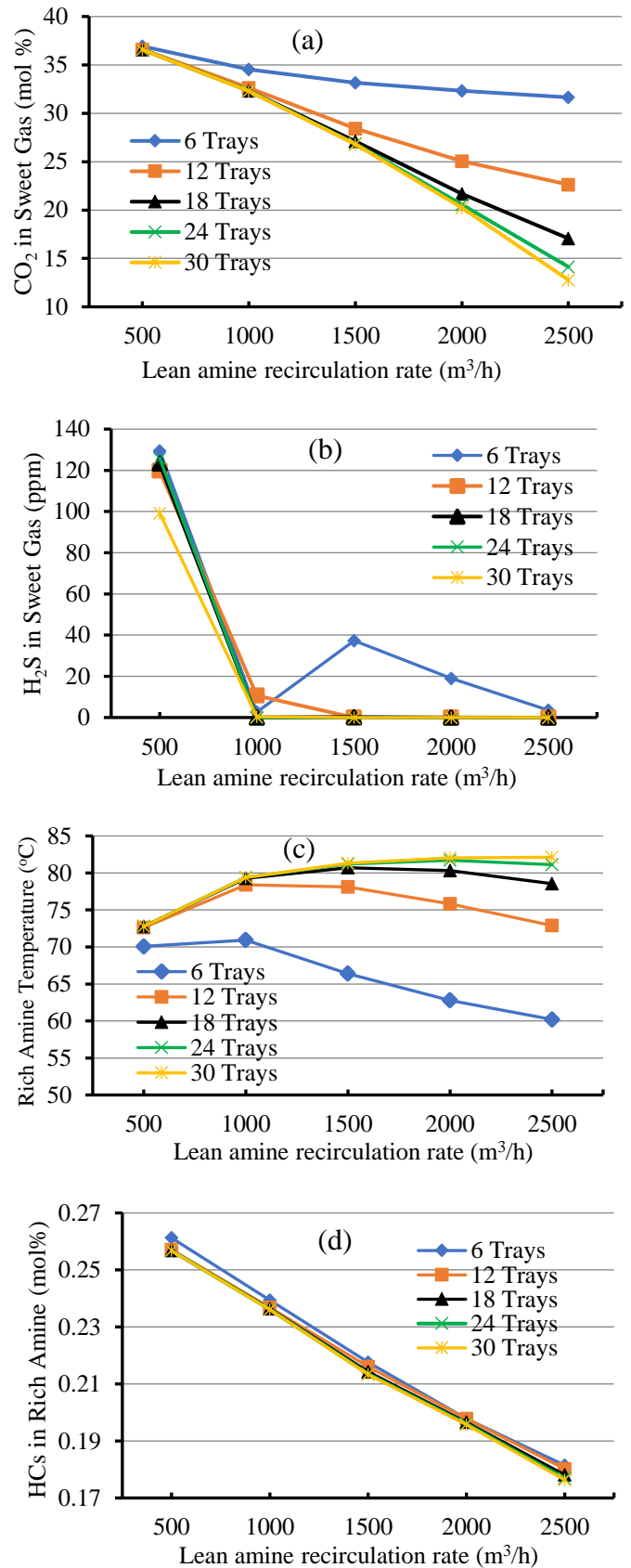


Fig. 3. Amine absorber performance with increasing recirculation rate and trays and 25 mol% MDEA in aqueous solution at pressure drop of 34 kPa

However, 24 and 30-Trays achieved lower CO₂ in sweet gas and higher rich amine temperature compared to

6, 12 and 18 Trays. In addition, 24 and 30-Trays achieved <15 mol% CO₂ in sweet gas at 2500 m³/h. This suggests that 24-Trays can be selected as a basis for further studies to improve system performance. Fig. 3(d) shows that the HCs absorbed in rich amine remained constant for all trays. The HCs carried in rich amine were detected 0.26 mol% at low recirculation rate and 0.18 mol% at high recirculation rate. The loss of HCs suggests production losses which can result in higher amine regeneration energy.

3.2 Effects of MDEA Concentration in Isolation on Absorber Performance

The effects of increasing MDEA of 25-50-75 mol% in aqueous solution on CO₂, H₂S and water content in sweet gas, rich amine temperature and HCs in rich amine are reported in Fig. 4 (a)-(e). Fig. 4(a) indicates that increase recirculation rate decreases CO₂ in sweet gas. However, no significant difference in CO₂ was observed with increase in MDEA concentration. The CO₂ was found lowest 15.16-16.48 mol% in sweet gas at 2500 m³/h. H₂S in sweet gas was observed to reach zero with increase in recirculation rate with 25 and 50 mol% MDEA compared to limited H₂S removal with 75 mol% MDEA (Fig. 4(b)). Fig. 4 (c) and (d) demonstrated that 25 mol% MDEA improved system performance by maintaining higher rich amine temperature (72.84-81.71°C) and lower HCs in rich amine (0.18-0.26 mol%). However, the water content in sweet gas was observed higher (0.20-0.40 mol%) indicating load on glycol dehydration unit (Fig. 4(d)).

3.3 Effects of MDEA and MEA Blends on Absorber Performance

MDEA with increasing MEA loading of 5-10-15 mol% indicated no significant improvement in terms of CO₂ in sweet gas (Fig. 5(a)) when compared to isolated MDEA (Fig. 4(a)) under same conditions. However, H₂S in sweet gas under all MEA loading condition quickly attained zero levels at lower recirculation rate (Fig. 5(b)) compared to isolated MDEA (Fig. 3(b)). The increasing MEA loading showed small decrease in rich amine temperature (Fig. 5(c)). The HCs in rich amine (Fig. 5(d)) and water content in sweet gas (Fig. 5(d)) also indicated small difference. These small differences observed in rich amine temperature and water content in sweet gas indicated that the system can be controlled with MEA loading if downstream restrictions pertain.

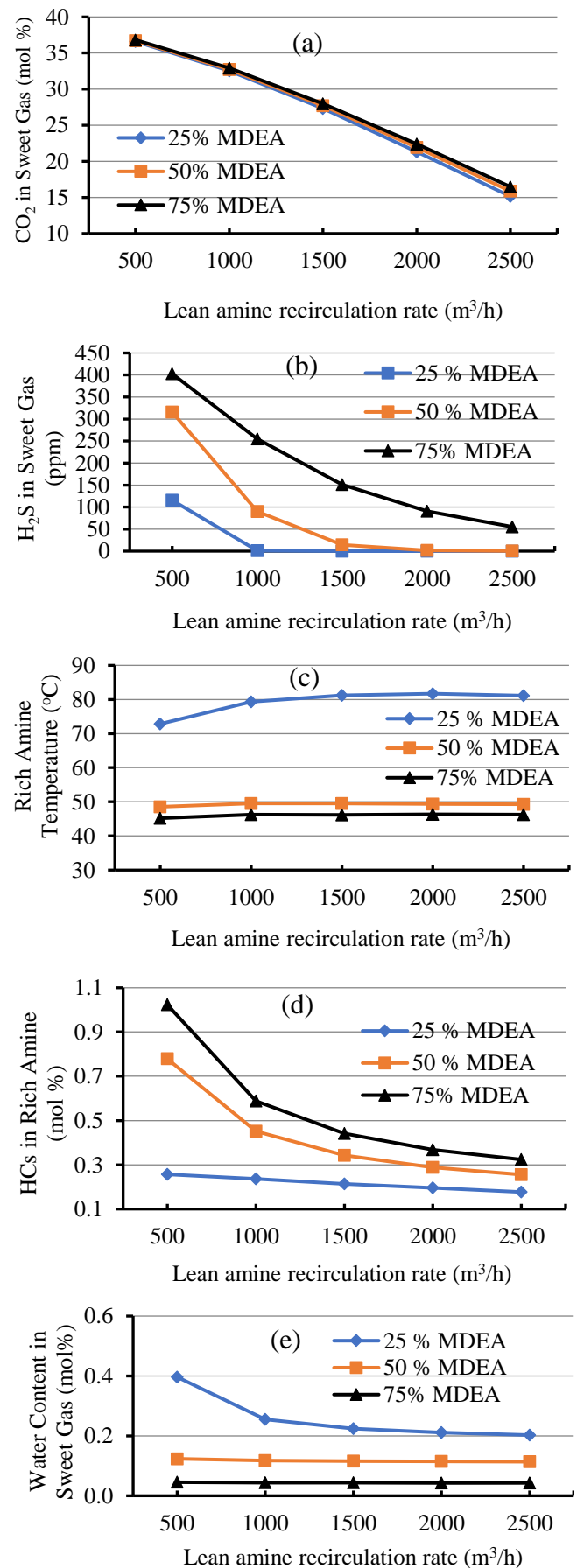


Fig. 4. Amine absorber performance with increasing recirculation rate and 25-50-75 mol% MDEA in aqueous solution at pressure drop of 34 kPa and 24 Trays

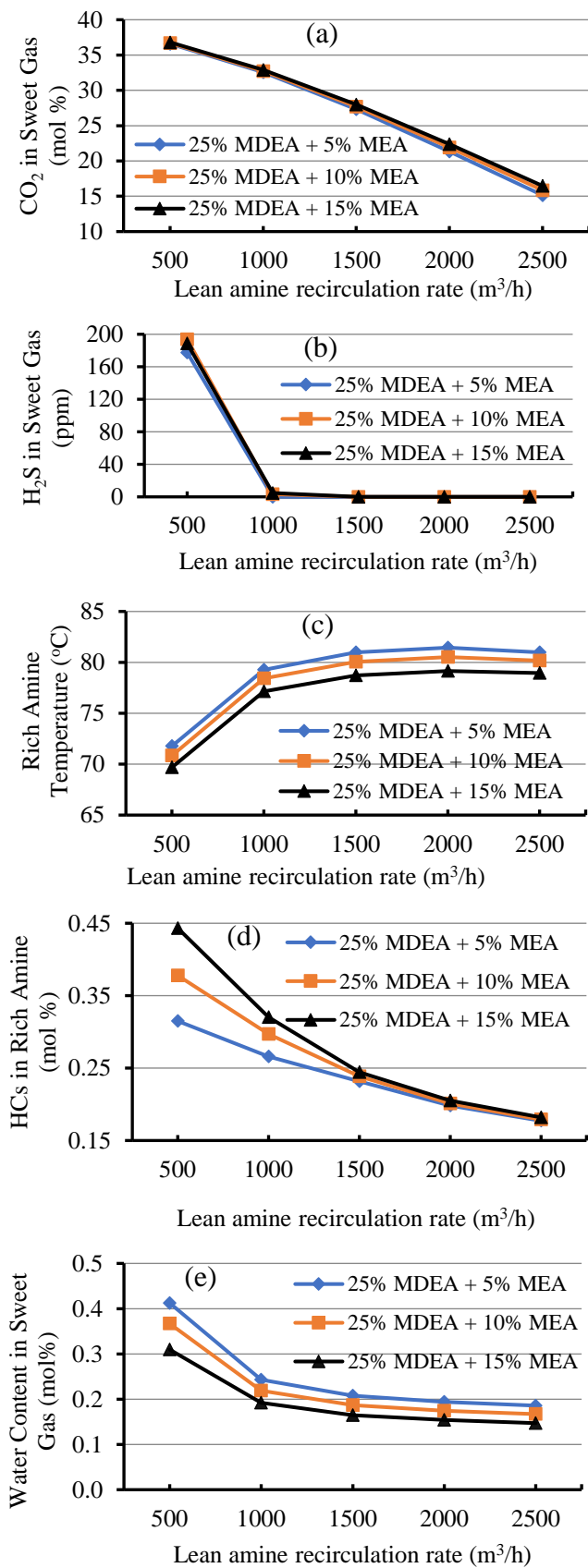


Fig. 5. Amine absorber performance with increasing recirculation rate with 25 mol% MDEA and 5-10-15 mol% MEA in aqueous solution at pressure drop of 34 kPa and 24 Trays

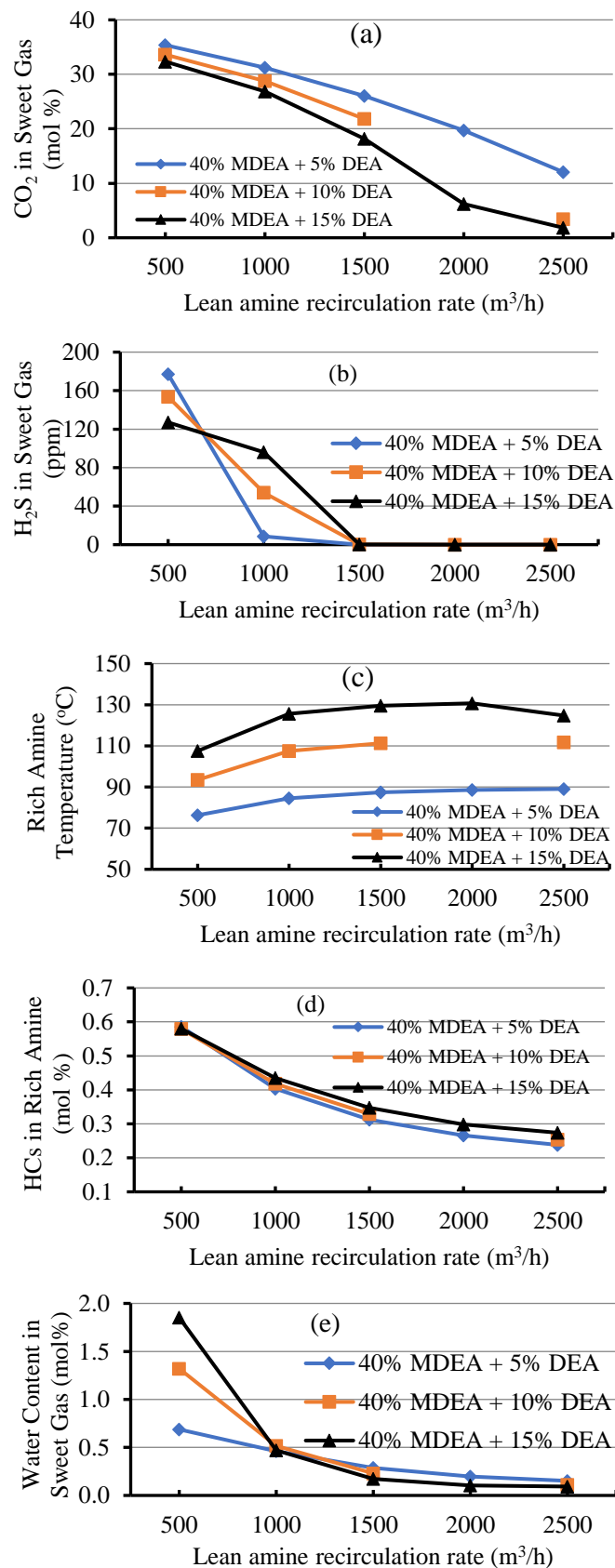


Fig. 6. Amine absorber performance with increasing recirculation rate with 40 mol% MDEA and 5-10-15 mol% DEA in aqueous solution at pressure drop of 34 kPa and 24 Trays

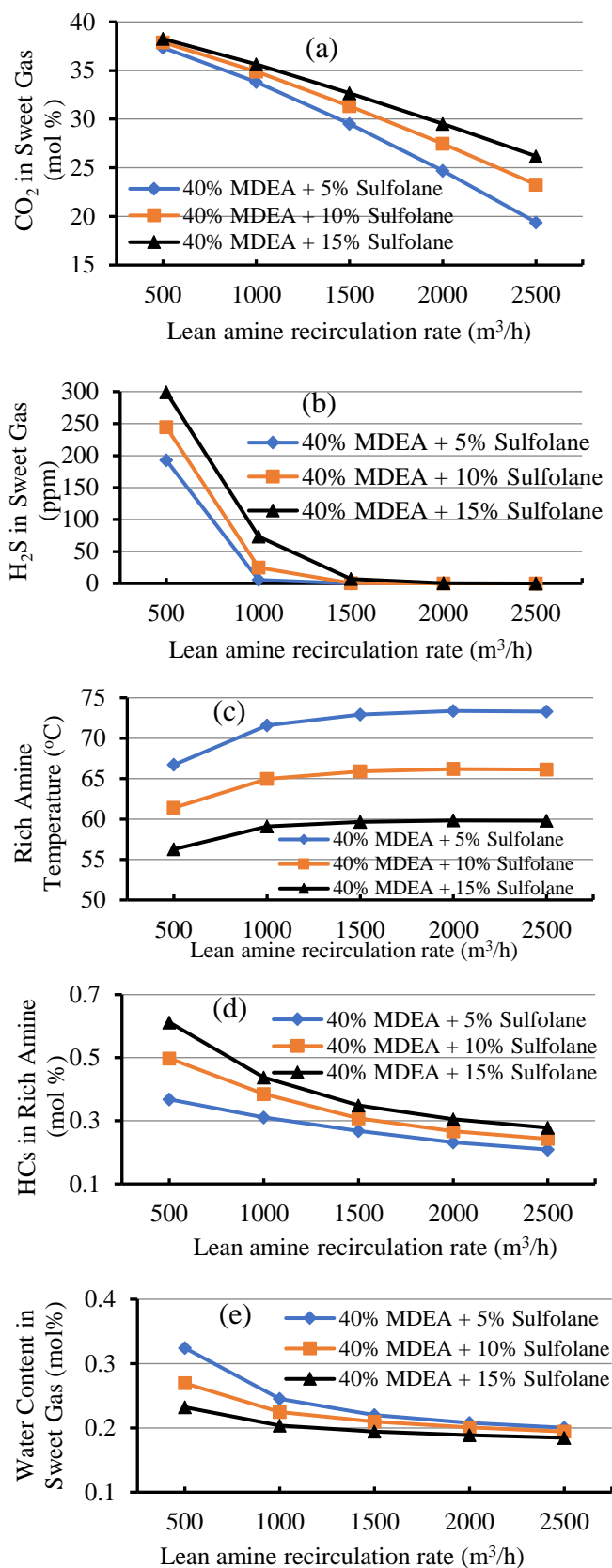


Fig. 7. Amine Absorber performance with increasing recirculation rate with 40 mol% MDEA and 5-10-15 mol% Sulfolane in aqueous solution at pressure drop of 34 kPa and 24 Trays

3.5 Effects of MDEA and Sulfolane Blends on Absorber Performance

The addition of Sulfolane in MDEA did not significantly improved the CO₂ in sweet gas (Fig. 7(a)) compared to MDEA and DEA (Fig. 6(a)). However, a reversal effect of decreasing CO₂ loading and decreasing rich amine temperature with increasing Sulfolane loading was observed.

3.6 Comparison of Isolated and Blended Amines on Amine Absorber Performance

The summary of the simulated results are compiled in Table 4. The results indicated the among the tested amine blends, MDEA with DEA was found of highly effective which resulted in lowest CO₂ in sweet gas.

4. Conclusion

Aspen HYSYS V9.0 was utilized to simulate amine absorber to observe levels of CO₂ in sweet gas. The results indicated that MDEA in isolation can achieve <17 mol% CO₂ in sweet gas with high amine recirculation rate. Among the tested blends, MDEA/MEA and MDEA/Sulfolane showed no significant CO₂ reduction with higher amine flow rate. However, MDEA/DEA blend demonstrated improved absorber performance in terms of CO₂ removal. The use of 40/5-15 mol% MDEA/DEA loading achieved lowest CO₂ in sweet gas of 1.85-12.07 mol% at 2500 m³/h recirculation rate with rich amine temperature of 89.05-124.80°C. The results of this study suggests that MDEA/DEA blend can be considered as a potential and alternate to MDEA to improve NG quality and maximize heat content in sales gas. The higher rich amine temperature observed with the use of MDEA/DEA blend can be serious concern in plant operation. However, the use of heat stabilized salts with blend to observe and control rich amine temperature is potential candidate for further studies. In addition, the future study can be focused on exploring blends to observe and analyse the effects of CO₂ residual of regenerated amine on amine absorber performance.

Table 4

Summary of the simulated results

| Amine category | Amine name | mol% in aqueous solution | Sweet gas | | | | | | Rich amine | | | |
|----------------|--------------------|--------------------------|--------------------------|---------------------------|--------------------------|---------------------------|--------------------------|---------------------------|--------------------------|---------------------------|--------------------------|---------------------------|
| | | | CO ₂ (mol%) | | H ₂ S (ppm) | | Water (mol%) | | HCs (mol%) | | Rich Amine Temp. (°C) | |
| | | | 500 m ³ /h | 2500 m ³ /h | 500 m ³ /h | 2500 m ³ /h | 500 m ³ /h | 2500 m ³ /h | 500 m ³ /h | 2500 m ³ /h | 500 m ³ /h | 2500 m ³ /h |
| Primary Amine | MDEA | 25 | 36.60 | 15.16 | 116 | 0 | 0.40 | 0.20 | 0.26 | 0.18 | 72.84 | 81.11 |
| | | 50 | 36.70 | 15.87 | 316 | 0 | 0.12 | 0.11 | 0.78 | 0.26 | 48.54 | 49.24 |
| | | 75 | 36.81 | 16.48 | 403 | 55 | 0.05 | 0.04 | 1.02 | 0.32 | 45.18 | 46.21 |
| Blends | MDEA/ MEA | 25/5 | 36.60 | 15.16 | 178 | 0 | 0.41 | 0.19 | 0.31 | 0.18 | 71.77 | 80.98 |
| | | 25/10 | 36.70 | 15.87 | 194 | 0 | 0.37 | 0.17 | 0.38 | 0.18 | 70.84 | 80.17 |
| | MDEA/ DEA | 25/15 | 36.81 | 16.48 | 189 | 0 | 0.31 | 0.15 | 0.44 | 0.18 | 69.68 | 78.95 |
| | | 40/5 | 35.37 | 12.07 | 177 | 0 | 0.69 | 0.15 | 0.59 | 0.24 | 76.31 | 89.05 |
| | MDEA/ Sulfolane | 40/10 | 33.62 | 3.41 | 154 | 0 | 1.32 | 0.11 | 0.58 | 0.25 | 93.46 | 111.72 |
| | | 40/15 | 32.34 | 1.84 | 127 | 0 | 1.85 | 0.09 | 0.58 | 0.27 | 107.52 | 124.80 |
| | MDEA/ Sulfolane | 40/5 | 37.35 | 19.39 | 193 | 0 | 0.32 | 0.20 | 0.37 | 0.21 | 66.69 | 73.31 |
| | | 40/10 | 37.90 | 23.28 | 244 | 0 | 0.27 | 0.19 | 0.50 | 0.24 | 61.39 | 66.13 |
| | | 40/15 | 38.25 | 26.19 | 299 | 0 | 0.23 | 0.18 | 0.61 | 0.28 | 56.26 | 59.81 |

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