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Absorption of acid gases (CO_2, H_2S) from natural gas using a ternary blend of N-methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and Sulfolane

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Abstract. Natural gas (NG) must be treated to remove sulphur compounds and acid gases i.e., carbon dioxide (CO_2) and hydrogen sulfide (H_2S) to ensure that it complies with requirements for sale and transportation. More than 95% of the NG processing plants are operated through the acid gas removal unit (AGRU) using aqueous amine solvent in removing sour gas components from the hydrocarbon gas due to the availability of amine solvent at a low cost. However, the main limitation of this process is the high operating cost of providing sufficient thermal energy at the reboiler for solvent regeneration. Meanwhile, the reboiler duty requirement generally increases with the requirement of CO_2 removal efficiency as higher energy consumption is required to strip off a more significant amount of CO_2 from the rich solvent. This current study addresses the absorption performance of acid gases using ternary hybrid solvents of MDEA, AMP, and Sulfolane. A study on the effects of solubility on H_2S and CO_2 absorption was performed at varying pressure (1000-6000 kPa) and temperatures (25°C-50°C) using Aspen HYSYS®V12.1. The results revealed that the concentration of CO_2 and H_2S in sweet gas increased with the decrease in pressure, while increasing temperature increased the concentration of H_2S and CO_2 in sweet gas. The future study will look at the reboiler duty required for solvent regeneration using this ternary blend of MDEA, AMP, and Sulfolane.

Introduction

For the past few decades, fossil fuels have become the primary source of electricity generation worldwide due to their high heating value. In 2021, nearly 80% of the electricity production in Malaysia will be produced from the combustion of fossil fuels of which 43.6% is contributed by natural gas (NG), followed by 31.1% from coal [1]. NG is one of the cleanest fossil fuels compared to other hydrocarbon deposits such as coal and oil [2]. NG consists primarily of Methane (CH_4), the primary component, but it also contains heavier hydrocarbons, acid gases (CO_2, H_2S), water, mercury, and inert gases in different proportions. These impurities must be removed to obtain rich amine NG and comply with emissions regulations and sales gas specifications [3]. Among the non-hydrocarbon components in NG, CO_2 and H_2S may severely damage the environment and

industrial equipment. For example, in water (H_2O), CO_2 and H_2S can form an acidic solution, contributing to pipeline corrosion problems [4].

Table 1 shows the typical NG composition in the Malaysian gas field. In Malaysia, most of the NG reserves are found to be sour gas fields whereas sour gas refers to NG that consists of a high amount of CO_2 and H_2S. Typically, the NG reserves in Malaysia are high in CO_2 content which ranges between 28% and 87%, and relatively low H_2S content of less than 1% [5]. Therefore, this shows that removing high CO_2 content from raw NG has always been a significant challenge for Malaysian oil and gas operators to meet the sales of gas specifications.

Table 1:Typical composition of NG in Malaysia.

Components	Composition (%)
Methane	40-50
Ethane	5-10
Propane	1-5
Carbon dioxide	20-30
Hydrogen Sulphide	0-1

Many technologies have been used to separate acid gases from NG, including distillation, absorption, adsorption and membrane separation. Out of the mentioned technologies, absorption using alkanolamines is the most effective and widely used on an industrial scale to remove CO_2 and H_2S. However, due to this process maturity and economic feasibility, more than 95% of the gas processing plants are operated through chemical absorption using an aqueous amine solvent [6]. The common alkanolamines used in the current industry are monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), and diisopropanolamine (DIPA) and methyldiethanolamine (MDEA). Usually, the reaction between H_2S and amines is instantaneous. However, for CO_2 different amines have different reactivity and selectivity. MEA and DEA amines react with CO_2 to form carbamate while MDEA is hindered from reacting with CO_2 due to nitrogen atoms in the structure. MDEA is thus said to react selectively with H_2S in the presence of CO_2. MDEA is more favorable in industries because of its loading capacity of 1 mole of CO_2 per mole of the amine as compared to 0.5 moles of CO_2 per mole of amine for MEA and DEA, but the main disadvantage of MDEA is that its rate of reaction and reaction kinetics are very slow as compared to primary and secondary amine [7].

To overcome this problem, an activator typically primary, secondary, and hindered amines like MEA, DEA, 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), and DIPA is introduced to improve the rate of carbamate hydrolysis and dissolved CO_2 absorption kinetics of tertiary amines. Hindered amines such as AMP have high CO_2 and H_2S absorption rates and high absorption capacity. Therefore, activator AMP is added to increase the reaction rate and the loading capacity of MDEA [8]. Despite the maturity of the technology in AGRU using aqueous amine absorption since the 1960s, one of the major challenges in this process is the high reboiler duty necessary to regenerate the solvent for continuous operation. In most cases, up to 70% of the operating costs excluding the labor force result from the regeneration [9]. Contrary, physical solvents are also one of the alternatives used to reduce reboiler duty for solvent regeneration since the acid gases in AGRU can be stripped off by reducing the pressure without giving extra heat. Removal of acid gases using physical solvents is usually beneficial at a high partial pressure of acid gases while a lower pressure system favors absorption by chemical solvents. Typical physical solvents are Sulfolane, N-methyl 2- pyrrolidone (NMP), and methanol [10].

To eliminate contaminants, a hybrid solvent, a combination of physical and chemical solvents was used as an alternative solvent in this case. In physical solvents, the solubility of acid gas and

Sulphur compounds is nearly linear. Therefore, mixing chemical and physical solvents gives advantages at the same time. Sulfinol, a combination of DIPA, tetramethylene sulfone, and H_2O was the first mixed solvent employed. MDEA eventually substituted DIPA, and the solvent was renamed Sulfinol-M [11].

In the past, numerous researchers depicted MDEA-based solutions in different gas-sweetening industries. Nejat et al. [12] performed the exergy and energy analysis on the khangrian sweetening plant using MDEA as a solvent. He proposed that replacing MDEA with a hybrid solution of MDEA-sulfolane required less energy than aqueous MDEA. Ghanbarabadi et al. [13] evaluated and contrasted the practicability of sulfolane-MDEA-water, DGA, MDEA-AMP, and MDEA for CO_2, H_2S, and other components. Their findings demonstrate that a sulfolane-MDEA-water solution with a lower flow rate absorbs more than 25-35% of mercaptans and acid gases, and regeneration requires 15-20% more energy. Sarker et al. [14] discovered that employing a blend of amines for natural gas sweetening produces better results than using a single amine.

The primary objective of this investigation is to capture both CO_2 and H_2S from NG using a hybrid amine blend of MDEA, AMP, and sulfolane. Simulation software Aspen HYSYS V12.1 was used to build a gas-sweetening plant. The novelty of this work is that no study has been done so far on the high content of CO_2 (40%) and H_2S (1%) at high pressure using a hybrid solvent. Different operating parameters affecting the absorption process i.e., the effect of temperature (25-50°C), pressure (1000-6000 kPa) and solvent flow rate at different concentrations were then observed on the composition of sweet gas using an aqueous alkanolamine solvent.

Methodology

Process Description

The inlet separator was used to eliminate soluble, heavy hydrocarbons as liquid, suspended liquid, and entrained hydrocarbons from the incoming feed gas. The CO_2 was then brought into contact with the amine solvent by the evacuated gas from the top of the inlet separator entering the bottom of the absorption tower. Sour gas enters the absorber from the bottom while solvent enters from the top. The sour gas enters an absorber at 35°C with a flow rate of 25965 kgmole/h. Specification of the simulation of AGRU is given in Table 2. The lean amine solvent enters at a temperature 42°C higher than the input feed gas and departs at the bottom of the absorption tower after passing the counter-current through the packed column. The solvent temperature is at least 5°C higher than the temperature of feed gas to avoid condensate forming.

Table 2: Input specification for Aspen Hysys simulation.

Absorber Specifications	
Solvent temperature (°C)	42
Inlet gas temperature (°C)	35
Solvent pressure (kPa)	5220
inlet gas pressure (kPa)	5210
inlet gas flow rate (kgmol/h)	25965
Number of stages	23
CO_2 in inlet gas (mol.%)	45
H_2S in inlet gas (mol.%)	1
Solvent feed tray	1

After the absorption of acid gases in the absorber, the output gas becomes hotter because of the exothermic reactions inside the absorber. It exits the tower from the top as sweet gas, while rich amine containing CO_2 and H_2S goes from the bottom of the absorption column at 57.3°C. Figure 1 shows the complete flow diagram of AGRU built on Aspen Hysys Simulation software. Before

entering the stripping or regenerator column, to remove soluble hydrocarbons from rich amine, in the flash tank the pressure was reduced to 656 kPa and then heated again to 95°C. The heat from a steam reboiler generates vapor in the stripping column, which removes CO_2 and H_2S from the rich amine as it passes up the column. The stream that carries the lean amine leaves the column from the bottom and exchanges heat with the exchanger. Then this lean amine is sent to a cooler where it is cooled to 40°C before returning to the absorber. The acid gas can be expelled from the top of the stripping column.

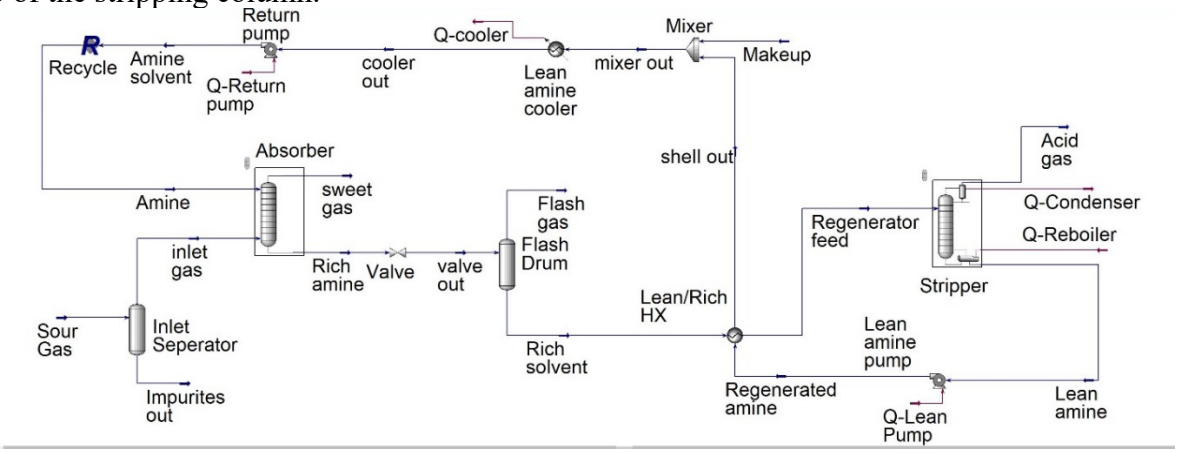

Figure 1: Aspen HYSYS flow sheet of AGRU using amine solvents.

Simulation basis

For the modeling of the column, the two most prominent methods are the rate-based model and the equilibrium model. The equilibrium model assumes that the liquid and vapors leaving at each column level are in equilibrium. Contrary, the rate bases model uses transport characteristics and concentration gradient to study heat and mass transfer happening between the contracting phase. That's why the output of the rate-based model is closer to actual plant data, allowing for estimating different parameters under different conditions. The removal of acid gases using chemical absorption is based on an acid-base reaction. CO_2 and H_2S are acid gases as they dissociate to form a weak acidic solution in an aqueous solution [15]. The reaction paths undergone by the acid gases with alkanolamines strongly depend on the structural characteristics of the alkanolamines. The reactions for CO_2 and H_2S are both exothermic where the aqueous alkanolamine solution absorbs the acid gases at a relatively low temperature with the release of heat energy.

Formation of amine hydrosulphide from the reaction between H_2S and amine solution:

$$RR'R''N + H_2S \leftrightarrow RR'R''N\,H^+ + HS^- \quad (1)$$

Formation of amine carbamate via zwitterion mechanism for the primary and secondary amines:

$$RR'R''N + CO_2 \leftrightarrow RR'R''N\,H^+COO^- \quad (2)$$

Hydrolysis and dissociation of CO_2 for tertiary amine:

$$RR'R''N + CO_2 + H_2O \leftrightarrow RR'R''N\,H^+ + HCO_3^- \quad (3)$$

For the removal of H_2S, it reacts instantaneously with all types of amines regardless of the structural characteristics via a direct proton transfer reaction as given in Eq. 1. Meanwhile, CO_2 can react with the amine solution in two different reaction mechanisms depending on the amine structure. Primary and secondary amines are very reactive where they react with CO_2 to form carbamates via direct reaction as shown in Eq. 2. However, since tertiary amine has no N-H bond.

Therefore, it can only form a protonated amine and bicarbonate ion through hydrolysis and dissociation of CO_2 given by Eq. 3. Hence, compared to primary and secondary amines, tertiary amine has a lower CO_2 absorption rate due to the relatively slow reaction of carbonic acid dissociation to the bicarbonate [16]. Since the reaction of H_2S with amine occurs almost instantaneously, it can be said that the H_2S absorption process takes place in the gas phase, and a relatively slow reaction of CO_2 with amine occurs in the liquid phase [17].

Result & Discussion

Validation of actual plant data

AGRU model was developed using Aspen HYSYS® V12.1 simulation software and validated against the actual plant data from a gas processing plant in Malaysia to ensure the reliability and applicability of the results on the specific plant setup. Figure 1 shows the developed ARGU model in the Aspen HYSYS simulation software based on the actual plant data and equipment specification (Table 2). In contrast, Table 3 presents the percentage deviation between the simulation model and the real plant data for the sweet gas stream is less than 5% [18].

Table 3: Validation of actual plant data with simulation data.

Parameters	Actual plant data	Simulation model	Deviation (%)
Temperature (˚C)	44.40	45.18	1.73
Pressure (kPa)	5140	5210	1.34
Flowrate (kgmol/h)	25965	25302	2.51

Effect of temperature on the absorption of CO_2 & H_2S

The sensitivity analysis was performed at six different temperatures ranging from 25°C-50°C to study the effect of absorption of acid gases. Figure 2 depicts the influence of temperature on CO_2 and H_2S concentrations in sweet gas. The amine solvent loading capacity drops considerably as the system temperature rises, implying that CO_2 and H_2S concentrations also rise. The same trends were seen in previous studies: lower temperatures always enhance absorption, and higher temperatures inhibit absorption. This is because the diffusion of gas molecules in chemical solvents is reduced at higher temperatures. Another factor could be increased temperature reduced absorption for both acid gases, namely H_2S and CO_2, and vice versa. This is due to the gas molecules being activated, which raises their average kinetic energy and causes the molecules of the absorbate to move through the absorbent more quickly, lowering the contact time. For both physical and chemical absorption, the better the absorption the longer the contact time between the absorbent and the absorbate.

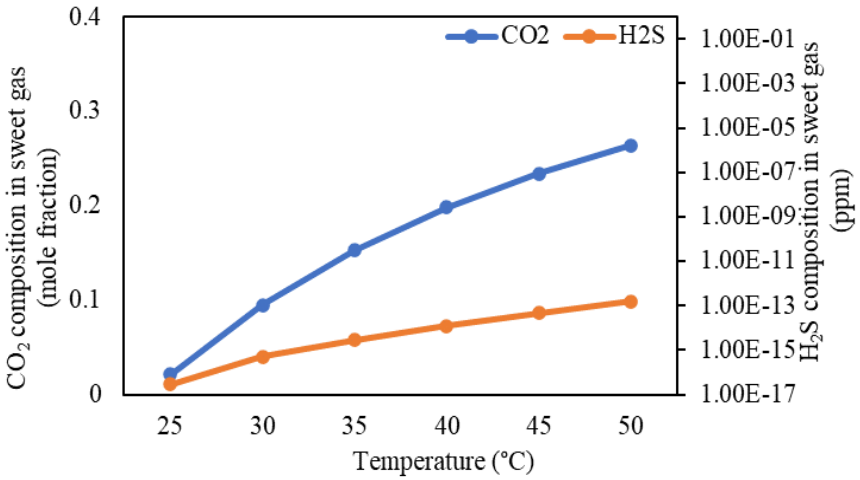

Figure 2: Effect of temperature on CO_2 & H_2S Concentration in the sweet gas.

Effect of pressure on the absorption of CO_2 & H_2S

Over a wide pressure range, the effect of operational pressure on the aqueous amine solvent absorption ability was examined (1000-6000 kPa). To establish the chemical solvent ability to absorb CO_2 gas efficiently, the absorption performance of the hybrid solvents was assessed in terms of loading capacity, which is an essential attribute in the absorption process. According to the simulation investigation, the higher pressure of the system promoted the absorption process. Figure 3 shows how pressure substantially impacts CO_2 and H_2S concentrations in sweet gas. As the pressure increases the solubility of CO_2 and H_2S increases in amine solvent. The better loading capacity could be attributable to two factors. First, increased pressure promotes absorption. Secondly, physical diffusion occurs at higher pressure. The increased pressure aids the diffusion of CO_2 gas in the amine solvent aqueous solution. Higher pressure causes more CO_2 gas molecules to diffuse into the aqueous solution, increasing the solvent loading capacity. According to a literature review, higher pressure encourages the absorption process, and chemical solvent uptake capability improves when the partial pressure of CO_2 gas increases.

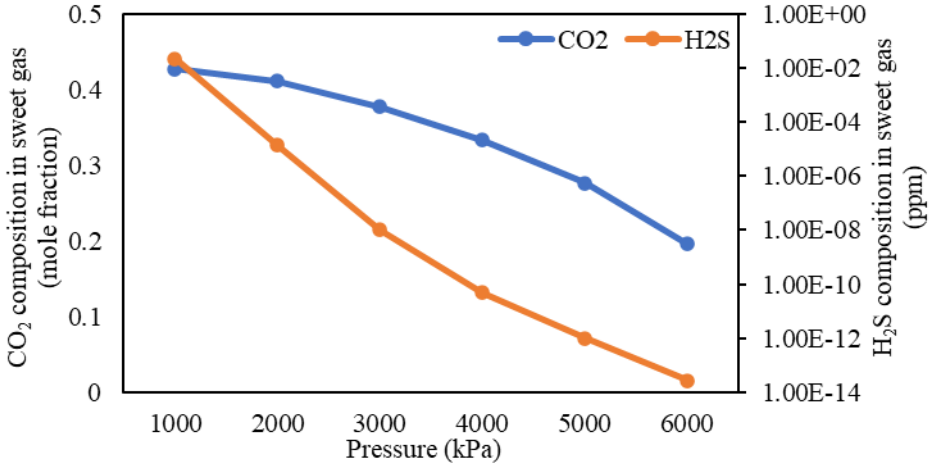

Figure 3: Effect of pressure on CO_2 & H_2S Concentration in the sweet gas.

Effect of solvent flow rate on the absorption of CO_2 and H_2S

One of the most critical factors which affect the operating cost of AGRU is the solvent flow rate. The effect of solvent flow rate was observed by keeping the chemical solvents (MDEA and AMP) composition constant while changing the concentration of sulfolane. The results reveal that by increasing the concentration of sulfolane less flow rate was required to achieve the allowable specifications of acid gases in the sweet gas stream. This is because the physical solvents are not constrained by any absorption limits, as the partial pressure of the gases is directly affected the absorption capacity of the system. The concentration of chemical amines MDEA and AMP are kept constant at 20% and 5% respectively. As shown in Figure 4, as the sulfolane concentration was increased less flow rate was required for the absorption of acid gases below 3% CO_2 and 4 ppm H_2S. The results depicted that the solvent containing 40% sulfolane requires a 35% less flow rate than the solvent containing 20% sulfolane to achieve the allowable limit for CO_2.

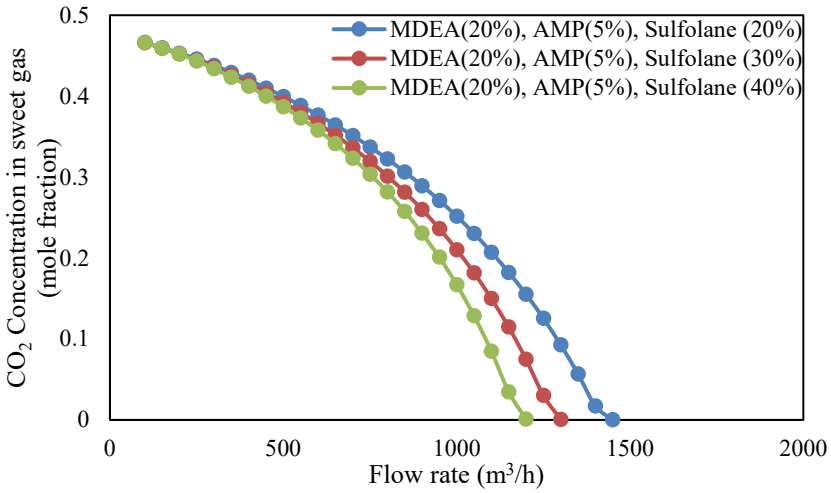

Figure 4: Effect of flow rate on the absorption of CO_2 in sweet gas.

Conclusion

The overall CO_2 and H_2S absorption in a ternary hybrid mixture of MDEA+AMP+Sulfolane was investigated using Aspen HYSYS®V12.1 simulation software. Operating parameters i.e., Pressure and temperature, and their effect on the concentration of CO_2 and H_2S in sweet gas were studied. It was investigated that the pressure positively impacts the CO_2 and H_2S concentration in the sweet gas. At the same time, temperature shows a negative effect as the temperature increases the concentration of CO_2 and H_2S increases in the sweet gas. In addition, increasing the percentage of sulfolane (40%) in a solvent requires a 35% less flow rate than Sulfolane (20%). This solubility data will be further used to study the effect of solvent circulation rate and concentration of amines for solvent regeneration in the stripper column to lessen the reboiler duty.

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