The 2nd International Conference on Inovations
in Social Sciences Education and Engineering (ICoISSEE)
August 07th, 2021

Simulation and Analysis of CO_2 Absorption Process for Natural Gas Treatment Using MDEA/Piperazine Absorbent

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Abstract. *The addition of Piperazine into MDEA in the CO2 absorption process sourced from producing gas wells is used to meet the specifications for the minimum CO2 content below 4% mol. The effect of absorbent composition, absorber pressure, natural gas temperature, were studied on CO2 separation, absorption rate and absorbent loss rate. This simulation is used for natural gas processing at a rate of 165 MMSCFD, with a fixed absorbent flow rate of 3000 USGPM. In the technical aspect, CO2 content above 35% requires the addition of Piperazine to reduce the CO2 content absorbed below 4%. This simulation is based on CO2 levels in the range of 30 - 60%. At 60% CO2 composition, increasing pressure is able to reduce the minimum addition of Piperazine to meet the specifications of the absorbed gas. Increasing the temperature will reduce the performance of the absorption process and reduce the need for regeneration energy. In the economic aspect, the addition of Piperazine for CO2 content above 35% can increase the % CAPEX and OPEX cost savings up to 38%.*

Keywords: *Absorption CO_2, MDEA, Temperature, Piperazine, Pressure*

1. INTRODUCTION

The energy sector in Indonesia is predicted to increase from year to year, one of which is the use of natural gas. In 2018 national natural gas production was 2,466 TCF, while gas consumption increased by 1.1% to 1,313 TCF from the previous year (BPSTATS, 2019). And it is predicted that it will continue to increase every year until 2027 with the assumption that gas demand is calculated based on the use of natural gas and does not extend long-term export contracts (Kementerian Energi dan Sumber Daya Mineral, 2018). Gas fuels, which have lower emissions than fossil-based fuels, are believed to replace these fossil-based fuels in the future. The International Energy Agency (IEA) report states that natural gas has a major impact on the world's energy supply. The advantage of using natural gas-based energy sources can be seen from the reduction of carbon dioxide (CO_2) emissions from combustion.

Reducing CO_2 emissions from oil to natural gas by 1.139 kg in the use of 1 m^3 of natural gas or 56 %. Reduction of CO_2 emissions from LPG to natural gas by 0.218 kg for the use of 1 m^3 of natural gas or 11 % (Kementerian ESDM, 2013). Natural gas that just comes out of production wells contains H_2S, CO_2, and a number of other impurities such as mercaptan, carbon sulfide compounds, carbon monoxide, and water, so it needs to go through a purification stage so that it can be used as a clean energy source or can be processed into gas derivative products other. Natural gas that still contains CO_2 is very corrosive, because CO_2 gas can bind with H_2O to form H_2CO_3, this can damage the equipment used such as piping systems (Kartohardjono et al., 2010). The CO_2 content is also very detrimental because it can decompose the heating value of the combustion (Kartohardjono et al., 2010). The most common gas sweetening is the use of amine alkanols in aqueous solutions as chemical solvents to absorb and remove acid gas components such as CO_2 and H_2S.

2. LITERATURE REVIEW

Methyl diethanolamine (MDEA) is a tertiary amine that selectively removes H_2S but still releases most of the CO_2 without being absorbed (Nexant Inc., 2009). MDEA has several advantages and disadvantages, including selective absorption, which can reduce the amount of acid lost, therefore, compared to other amine systems, the MDEA system is more economical in terms of solvent circulation rate and energy requirements are quite low. MDEA has a corrosion rate (the least corrosive amine) and a low vapor pressure, allowing use in high concentrations (up to 60 % by weight), resulting in lower circulation rates, and thus, smaller plant sizes and lower plant costs. MDEA has a high solution capacity, as well as excellent thermal and chemical stability, but MDEA has low reactivity so it is necessary to have an activator to improve MDEA performance [6]. The following chemical reaction shows the reaction of amines with H_2S and CO_2 during the sweetening process (Maddox , R.N. and Morgan, 2006).

$$RNCH_3 + H_2S \leftrightarrow RNHCH.HS \quad (1)$$
$$RNCH_3 + CO_2 + H_2O \leftrightarrow RNHCH.HCO_3 \quad (2)$$

MDEA has the advantage that it has a low heat of reaction, but has a low reactivity so that it requires an activator to improve MDEA performance. Activators are reactive molecules that react with other molecules to form chemicals that have better properties than if the reagents were separated (Ying et al., 2017). The addition of primary or secondary amines (alkanols) to MDEA solutions, has been used in the removal and absorption of CO_2. The principle of adding a 'driver' with a tertiary amine is based on a combination of a relatively high reaction rate of CO_2 with a primary or secondary amine alkanol and a low heat of reaction for the CO_2 of a tertiary amine (Derks et al., 2006). One of the activators currently used in the industry is piperazine:

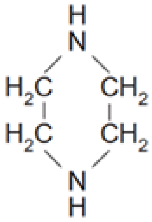

Figure 1 Structure Piperazine

Source : (Weiland & Sivasubramanian, 2004)

Compared to other amine compounds, Piperazine (PZ) has a very high reaction rate with CO_2 which is about 59.000 L $mol^{-1}s^{-1}$ and has a heat absorption of 76 KJ $gmol^{-1}$ (Weiland & Sivasubramanian, 2004)

Table 1. Comparison Of Reaction Rate Constants and Heat of Absorption of Various Amines (Based on Second-Order Kinetics At 25°C)

Amine	Reaction Rate Constant (L mol $^{-1}$ s $^{-1}$)	Heat of Absorption (kJ gmol^{-1})
MEA^P	6000	84
DGE^P	4500	83
DEA^S	1300	76
DIPA^S	100	73
Piperazine^S	59000	76
MMEA^S	7100	54
MDEA^T	4	58
AMP^P	600	85
NaGly^P	8000	85
KDiMGly^T	0	55
P = Primary	S= Secondary	T=Tertiary

Source : (Weiland & Sivasubramanian, 2004)

The reaction that occurs in an aqueous PZ solution is the formation of carbamate and bi carbamate. B can be a base or any compound available in solution such as PZ, PZC^- (carbamate), PZ H^+ (protonated PZ), H_2O, and OH^-

$$CO_2 + PZ + B \leftrightarrow PZCOO^- + BH^+ \quad (3)$$
$$CO_2 + PZH + B \leftrightarrow H^+ PZCOO^- + BH^+ \quad (4)$$
$$CO_2 + PZCOO^- + B \leftrightarrow PZ(COO^-) + BH^+ \quad (5)$$

3. RESEARCH METHODS/METHODOLOGY

This study used the HYSYS software, which was used to simulate CO_2. In this absorption study, natural gas is simulated to have a CO_2 content of 30% mol with a molar flow rate of 165 MMSCFD, a temperature of 120 F, and a pressure of 615 Psia.

3.1 Simulator

HYSYS v8.8 is used in this simulation. The amine package is used as a property package to estimate the thermodynamics and binary coefficients for the components in the gas sweetening process.

3.2 Process Flow Diagram

The process flow diagram is used to simulate the entire absorption process as illustrated in figure. 2. The gas is contacted with an amine solution with the composition Piperazine 0 – 14 % wt amine added to MDEA on a 50% wt amine basis in an aqueous solution in the absorber column. In this process, some of the amines will be lost due to evaporation. Furthermore, the amine rich in acid gas exits through the bottom of the absorber and enters the regeneration process. In the regeneration process, steam is the component used to separate the acid gas from the amine solution. The amine which has been cleaned of acid gas is drained from the bottom of the regenerator column and recirculated to the absorption column. In the regeneration process, it is possible for amines to be vaporized together with acid gas. The CO_2 absorption process uses process equipment consisting of a contactor, regenerator, pump, flash separator, mixer, and heat exchanger unit as shown in Figure 2

3.3 Process Parameters

The CO_2 absorption process in this study will be studied with several processes operating parameters such as:

1 Amine Composition
2 Pressure
3 Temperature

4. RESULTS AND DISCUSSION

In this section, the results obtained from studies and simulations with several process parameters will be discussed as follows:

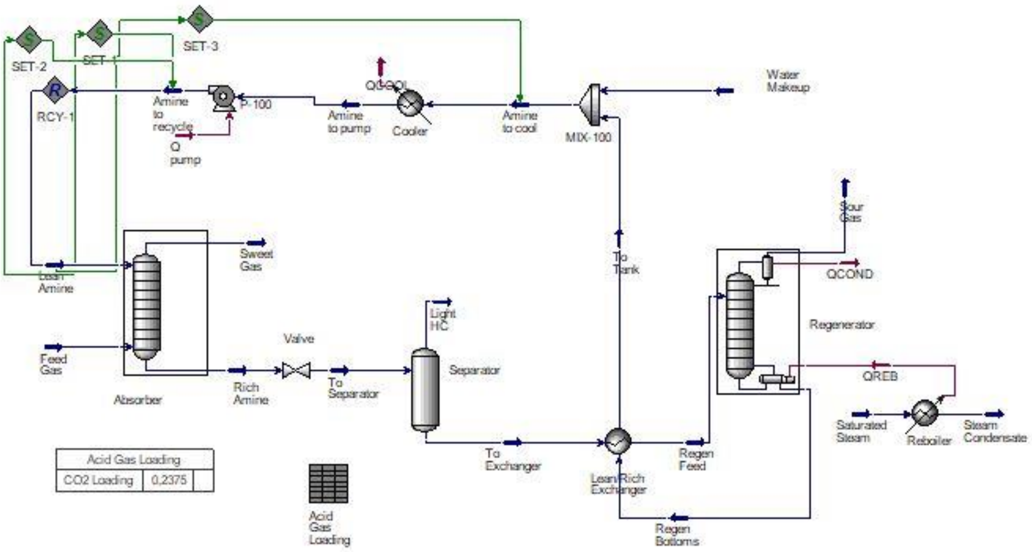

Figure 2 Flow Diagram Process Gas Process

4.1 *Effect of Addition of Piperazine into MDEA*

The results of this research and discussion are focused on analyzing the effect of the composition of MDEA/Piperazine for the purification of CO_2 from sour gas. Variations in addition of Piperazine from 0 – 14% by weight were mixed into MDEA based on 50% by weight of total amine in aqueous solvent. CO_2 gas from natural gas must be purified before use with considerations such as preventing CO_2 freezing, duct blockage, increasing the calorific value of natural gas, and corrosion. This natural gas processing is carried out to meet gas sales specifications with a CO_2 limit of 4% mol. The purpose of this study was to find the optimal variation of MDEA/Piperazine composition to absorb CO_2.

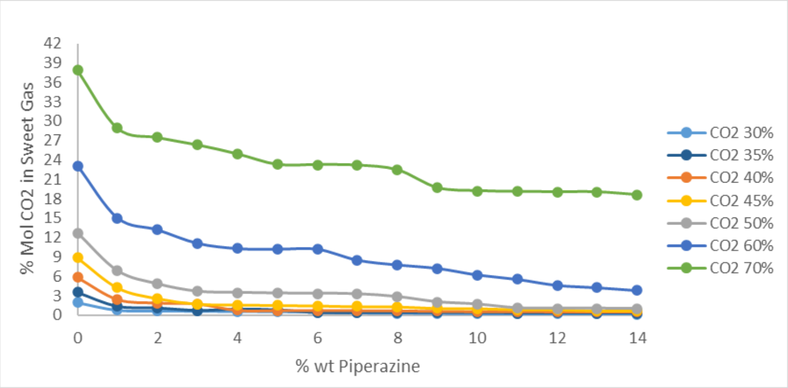

Figure 3 The Effect of Addition Piperazine on Absorption Process

The addition of Piperazine to a range of 0-14% by weight into MDEA with a flow rate of 3000 USGPM was able to reduce the CO_2 content of absorption in natural gas in the range of 30-70%. From the simulation results as shown above, for a very high

CO_2 content of 70%, the addition of 14% Piperazine was not able to reduce the CO_2 content below 4% mol to meet the specifications for the minimum CO_2 content in natural gas (sweet gas). The minimum requirement for Piperazine with an absorbent flow rate of 3000 USGPM to meet the specifications for CO_2 content below 4% mole can be seen in Figure 4 as follows.

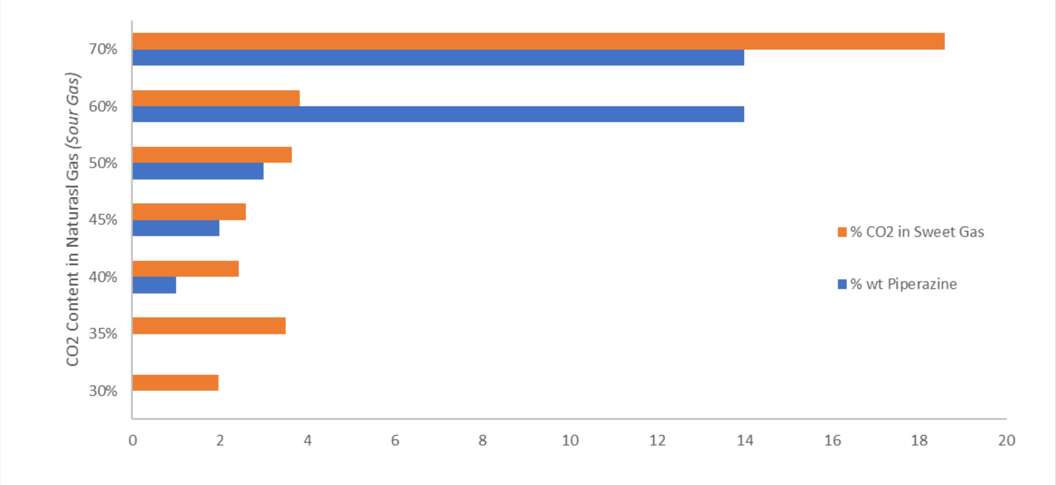

Figure 4 Minimal Addition of Piperazine to MDEA for Absorption Process

With an increase in the CO_2 content in natural gas (sour gas) will affect the minimum addition of Piperazine required in the absorption process to meet the minimum CO_2 specifications below 4% mol. At 30% and 35% CO_2 content, pure MDEA was able to reduce CO_2 content up to 1.98% and 3.51%, respectively. For 40% CO_2 content, the addition of 1% Piperazine was able to reduce CO_2 by 2.45%. At higher CO_2 content of 45%, 50%, and 60% will require the addition of higher Piperazine, which is 2%, 3%, and 4%, respectively. At a very high CO_2 content of 70%, the addition of 14% Piperazine with an absorbent flow rate of 3000 USGPM was not able to reduce the CO_2 content below 4% mol.

4.2 Effect of Addition of Piperazine into MDEA and Pressure on Absorption Rate

Absorber pressure will improve the performance of the absorption process. In this study, the effect of simulated pressure on the CO_2 content of 60%. The simulation results of pressure changes can be seen in Figure 5

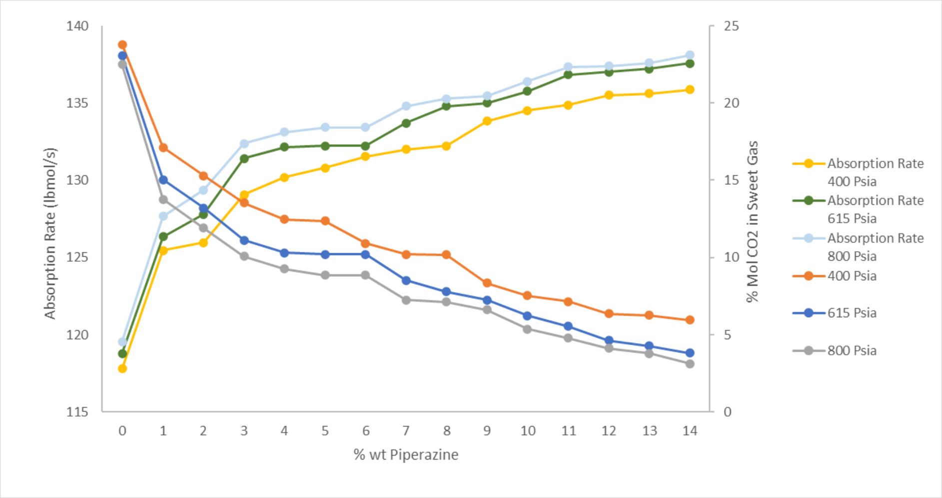

Figure 5 Effect of Absorber Pressure on CO_2 Absorption Process

The absorption process with 60% CO_2 content at low pressure with the addition of 14% wt Piperazine was not able to reduce the CO_2 content below 4% mol. As increased absorption pressure of 615 Psia, the addition of Piperazine 14% wt. able to reduce the CO_2 content up to 3.82%. At higher pressure elevations of 800 Psia, the CO_2 content below 4% mol, can be achieved by the addition of 13% by weight of Piperazine. The reaction rate will also increase with increasing pressure. The pressure in the absorption contributes to the partial pressure of CO_2 in natural gas and the rate of reaction with amine compounds. According to Henry's law, an increase in the partial pressure of a gas will affect the solubility of a gas (Ibrahim et al., 2014). Increasing the partial pressure of CO_2 will cause a higher concentration of CO_2 that is physically absorbed, so that more CO_2 reacts with amines in solution. Therefore, increasing the pressure can improve the performance of CO_2 absorption to meet the minimum specification of CO_2 content (Baltar et al., 2020).

4.3 Effect of Addition of Piperazine into MDEA and Temperature on Absorption Rate

The effect of variations in natural gas temperature on the purification of CO_2 gas for a composition of 60% CO_2 as shown in Figure 6.

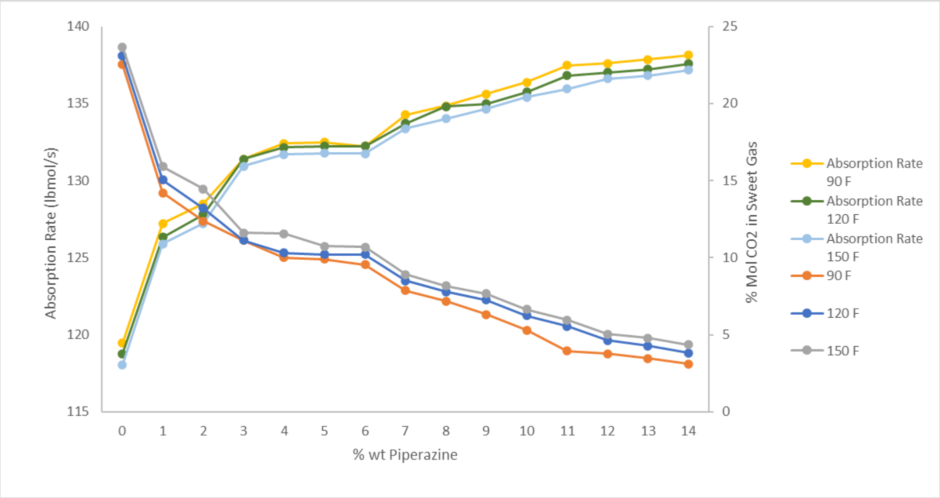

Figure 6 Effect of Natural Gas Temperature on CO2 Absorption Process

At low temperatures, natural gas will have the most optimal absorption performance, in this case, it is characterized by lower CO_2 absorption and higher reaction rates. At low natural gas temperatures, the addition of Piperazine to produce natural gas below 4% mole will experience a significant reduction. The addition of Piperazine as much as 11% by weight at 90ºF natural gas temperature can reduce CO_2 content up to 3.94% compared to 120ºF natural gas temperature which requires 14% Piperazine to reduce CO_2 content up to 3.81%. Piperazine has good performance at low temperatures, increasing temperature will increase the evaporation rate of Piperazine, decrease the solubility of Piperazine, and decrease pH (Ibrahim et al., 2014).

4.4 Effect of Addition of Piperazine to MDEA and Pressure on Regeneration Energy

Absorption is affected by pressure. The addition of pressure will increase the absorption rate as shown in the previous simulation. This study further studied the effect of absorber pressure on energy requirements for the composition of 60% CO_2.

Table 2. Comparison of Energy Requirements at various Absorber Pressures

% Addition Piperazine	Regeneration energy (kJ/jam)		
	400 Psia	615 Psia	800 Psia
14	2,90,E+08	2,89,E+08	2,88,E+08
12	2,77,E+08	2,76,E+08	2,75,E+08
10	2,63,E+08	2,62,E+08	2,61,E+08
8	2,47,E+08	2,46,E+08	2,45,E+08
6	2,30,E+08	2,30,E+08	2,29,E+08
4	2,13,E+08	2,13,E+08	2,11,E+08
2	1,95,E+08	1,94,E+08	1,93,E+08

The energy requirement in the CO_2 gas absorption process is dominated by the heat required for the regeneration process. CO_2 absorption reaction products using MDEA/Piperazine, namely carbamate ($PZCOO^-$), protonated carbamate (H^+PZCOO^-), dicarbamate ($PZ(COO^-)_2$), MDEA carbonate ($MDEACO_3^-$), and bicarbonate (HCO_3^-) / carbonate (CO_3^{2-}) (Inoue et al., 2013). With increasing temperature or pressure, mono carbamates ($PZCOO^-$) (including protonate) will dissociate into carbonate/bicarbonate (Inoue et al., 2013).

$$H_2O + PZCOO^- \leftrightarrow HCO_3^- + RNH_2 \tag{6}$$

Carbamate compounds have a negative effect on CO_2 regeneration (Nitta et al., 2014). Compared to carbamate compounds, bicarbonate is relatively easily decomposed by heating and is estimated to decompose at a significant rate at temperatures above 333K (Kim & Svendsen, 2007). Moreover, at the regeneration stage, breaking the less stable C-O bonds in bicarbonates and carbonates requires less energy than that required to break C-N bonds carbamate species(Kim & Svendsen, 2007). With the formation of more carbonate compounds, it can be an effective way to reduce energy requirements and also increase the effectiveness of CO_2 absorption.

4.5 Effect of Addition of Piperazine to MDEA and Pressure on Regeneration Energy

Changes in the temperature of natural gas (sour gas) will cause changes in the performance of the absorption process. In this study, the effect of natural gas temperature on energy requirements for the composition of 60% CO_2 natural gas is studied further

Table 3. Comparison of Energy Requirements at various Temperature of Natural Gas

% Addition Piperazine	Regeneration energy (kJ/jam)		
	90ºF	120ºF	150ºF
14	2,92,E+08	2,89,E+08	2,87,E+08
12	2,79,E+08	2,76,E+08	2,73,E+08
10	2,64,E+08	2,62,E+08	2,58,E+08
8	2,49,E+08	2,46,E+08	2,43,E+08
6	2,32,E+08	2,30,E+08	2,26,E+08
4	2,15,E+08	2,13,E+08	2,09,E+08
2	1,98,E+08	1,94,E+08	1,90,E+08

The energy requirement for regeneration will decrease with the increase in the temperature of natural gas (sour gas). This happens because the performance of the absorption process for natural gas at high temperatures will decrease, so that the CO_2 content in the absorbent will be smaller. Energy requirements in the regeneration process are used to release CO_2 gas contained in the absorbent in the form of carbonate and carbamate compounds.

4.6 Economic Evaluation of The Effect of Adding Piperazine into MDEA

An economic evaluation of the effect of mixing MDEA/Piperazine was only carried out to calculate capital and operating costs. Capital costs were determined based on the circulation rate of MDEA/Piperazine and operating costs were determined based on energy consumption of reboiler, pump, and solvent consumption.

Table 4. Calculation of Capital Costs and Operational Cost Comparative Effects of Addition of Piperazine and Pure MDEA

CO_2 in Natural Gas	MDEA Piperazine blend used	Absorbent Flow Rate (USGPM)	CAPEX (USD)		OPEX (USD/tahun)			% savings	
			Equipment	Absorbent Replacement	Steam	Electricity	Evaporated Absorbent Substitute	CAPEX	OPEX
30%	50 % wt MDEA	3000	1.263.500	1.395.700	11.320.676	552.062	1.385.480	-	-
35 %	50 % wt MDEA	3000	1.263.500	1.367.489	11.418.590	552.071	1.424.014	-	-
40%	49 % wt MDEA + 1 % wt Piperazine	3000	1.263.500	1.338.325	12.202.865	549.690	1.481.221	8	28
	50 % wt MDEA	4500	1.263.500	1.451.561	16.802.846	827.932	2.023.115		
45%	48 % wt MDEA + 2 % wt Piperazine	3000	1.263.500	1.308.891	12.921.737	547.233	1.535.078	28	38
	50 % wt MDEA	5600	1.263.500	1.806.371	20.739.292	1.030.313	2.465.655		
50%	47 % wt MDEA + 3 % wt Piperazine	3000	1.263.500	1.279.197	13.639.335	544.767	1.594.906	33	38
	50 % wt MDEA	5900	1.263.500	1.903.149	21.891.235	1.085.513	2.619.960		
60%	36 % wt MDEA + 14 % wt Piperazine	3000	1.263.500	1.396.344	19.665.047	516.884	2.293.842	32	20
	50 % wt MDEA	6400	1.263.500	2.064.422	23.854.868	1.177.533	2.905.019		

From the simulation results, CO_2 content below 35% does not require the addition of Piperazine to reduce the CO_2 content absorbed below 4%. The results of economic calculations, to produce CO_2 gas content below 4% mol, the use of pure MDEA will require greater capital costs for absorbent replacement, operational costs for steam and electricity, this is because the use of pure MDEA will require more absorbent flow to produce CO_2 below 4% mole. The addition of Piperazine can save capital costs and operating costs compared to using pure MDEA for CO_2 content above 35%

CONCLUSION

Simulation results, the addition of piperazine can improve the performance of the absorption process which will increase the absorption rate so that it will produce lower CO_2 in sweet gas. Increasing the pressure can improve the performance of the absorption process. As the temperature of natural gas increases, the performance of the absorption process will decrease, because piperazine will work better at lower temperatures. On the economic aspect, the addition of piperazine can save OPEX and CAPEX for CO_2 content of more than 35% in natural gas.

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