Prediction of CO_2 absorption capacity of MEA absorption system in the presence of HSS

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***Abstract*—Heat Stable Salt (HSS) accumulation has a detrimental impact on amine system operations as it can reduce the effective capacity of the amine solution, contribute to corrosion and aggravate operational problems such as foaming, amine loss, and fouling. It was reported in a refinery experience, operational problems arise only when the HSS accumulate at high concentration especially at the absorber column. The main aim of this research is to study the effect on CO2 loading in the rich amine coming out from the absorber. This is done with the presence of sulfate, acetate, and formate at different temperatures, pressures and HSS concentrations. MEA is chosen as the lean amine because it is the most common amine used in the industry. It is observed that the presence of HSS lowers the CO_2 absorption performance. Temperature and HSS concentration have significant effect on the CO_2 loading in the rich amine stream while there is almost no changes when pressure changes. By forecasting the parameter that affect the HSS in the absorber, mitigation measures can be taken at early stage to prevent these unwanted problems and reduce downtime for the HSS removal treatment.**

Keywords—acid gas removal, amine, monoethanolamine, heat stable salts, CO_2 loading, sulfate, acetate, formate.

I. INTRODUCTION

Natural gas is one of the most important non-renewable resource that fuels a country daily activity. The demand for natural gas has increase radically due to its combustible characteristic for domestic and industrial purposes. Malaysia is blessed with large gas reserves which hold for the 14^{th} largest gas reserves in the world [1]. Natural gas need to be treated for contaminants before it can be used for various task. H_2S and CO_2 in natural gas are identified as contaminants that cause problems such as corrosion, erosion, health and environmental hazard. It is compulsory for all company to clean the natural gas.

To meet the high demand of clean natural gas, the acid gas removal units (AGRU) becomes compulsory to the oil and gas industry. There are many type of acid gas removal processes that are implemented in the industry. Generic amine is the most common method of them all. Although it is the most prominent way, it is known that an unwanted product produced over an extended period of operation. Ironically amine that is used to remove acidic components can form a product that lowers the performance of amine regeneration.

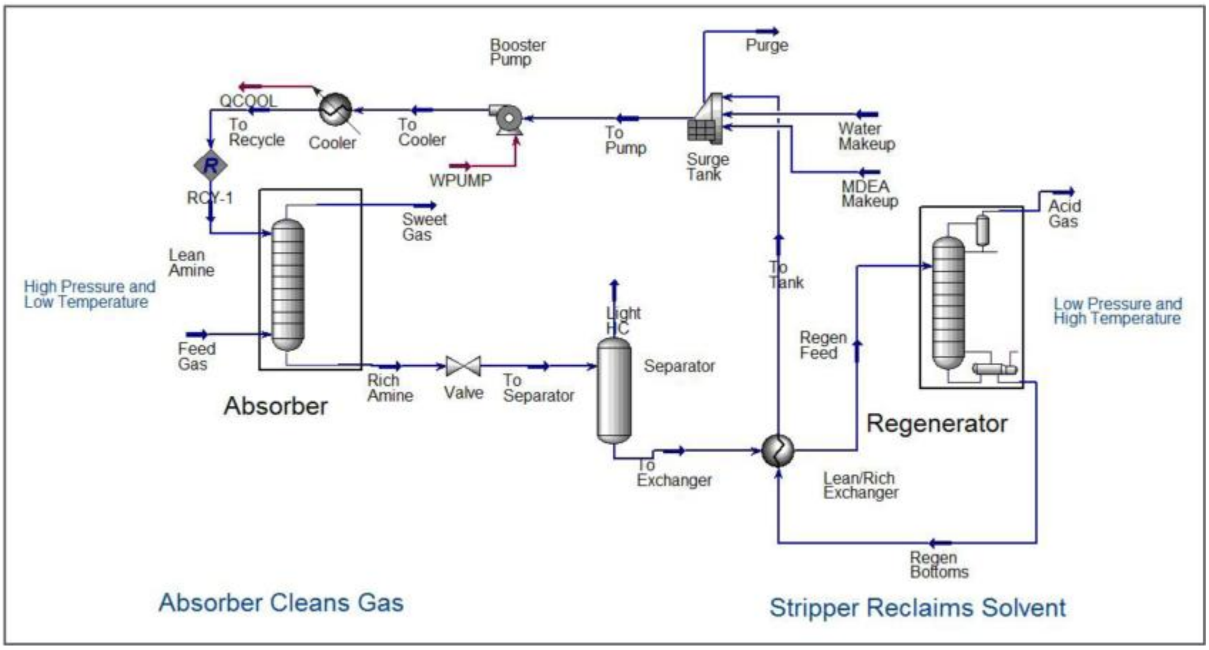
The performance or ability of amine chose as the solvent for the system highly depend on the acid gas composition, temperature, pressure, and type of amine. An undesirable product that are non-regenerable is called Heat-Stable Salt (HSS) that form when the strong acid anions from the acid gas bind with the amine molecule [2]. HSS accumulation has a detrimental impact on amine system operations as it can reduce the effective capacity of the amine solution, contribute to corrosion and aggravate operational problems such as foaming, amine loss, and fouling. However, refinery experience shows that operational problems arise only when the HSS accumulate at high concentration especially at the absorber column. This research aims to study the effect of sulfate, acetate, and formate on CO2 loading in the rich amine stream.and to study the effect on the CO2 absorption capacity with the presence of sulfate, acetate, and formate at different temperature, pressure and HSS concentrations.

There is numerous types of acid gas removal processes practiced in the industry such as solvent absorption, solid adsorption, direct conversion, and membrane. To select the optimum process for the acid gas removal is not an easy task due to the principal of the gas itself. With different properties and composition of the gas, a thorough cost and performance analysis is required to determine which process is the best for the condition of the gas. A guideline provided by Kohl & Nielsen, 1997 on the process selection shows all the process along with the factor that should be considered such as the plant size and composition of the gas.

Aspen Technology Inc. provided the standard flow diagram of gas treating units as shown in Figure 1. The feed flow or acid gas start to enter the separator to remove any entrained liquid or sand. From there it will enter at the bottom of the absorber column which can be a tray or packed tower. Packing tower is a better choice and highly favoured since it can handle high capacity and have better options for materials of construction. The stripping stage is the most important because should the contaminants exceeds the permitted safe levels, it can cause higher corrosion rate to the equipment, hazardous health impacts, and deterioration to environment.

Inside the absorber, the feed gas will flow upward, counter-current to solvent of choice which is introduced at the top of the absorber. The clean gas or sweet gas exits at the top of the column for other processes. Rich amines or the solvent with the absorbed acid gas is sent to a flash drum and a second stripper column, to be regenerated through heating should the solvent is chemical solvent. As for physical solvent, the regeneration is completed by reducing the pressure in stages, unless deep cleaning of H_2S or CO_2 is required by using stripper column. The specification of each equipment should be optimal to meet the objective of the treatment.

There are three main groups of amines with different molecular structure, which are primary, secondary, and tertiary. These amines



react with the impurities via an exothermic, reversible reaction in a gas/ liquid absorber. Selecting the best or proper amine can

Fig. 1: Typical acid gas treating unit: Absorber cleans gas, Regenerator (Stripper) reclaims solvent Chemical [17]

significantly reduce both the regeneration energy requirement and solution circulation rate. Besides that, those choice can have a dramatic influence on the overall cost associated with the process equipment. According to Polasek & Bullin, 1994, every type of amine have different operating conditions that is proven.

II. METHODOLOGY

The composition of Feed Gas used for this simulation as shown in table 1is taken from [5], that is collected from laboratory of Chemical Engineering Department in Bangladesh University of Engineering and Technology (BUET). This composition is chosen since it is comprising of all the necessary component that normally contain in a sour gas. [6] provides guideline for choosing the value of every equipment. The value chosen meets a typical absorber specification as shown in table 2. Figure 2 shows the flowchart of the running the simulation.

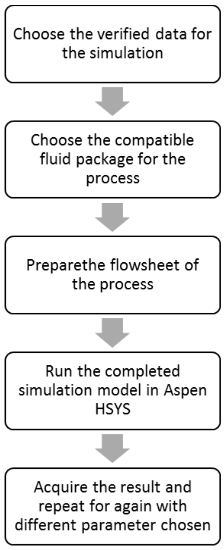


Figure 2: Flow Chart

Table 1: Composition of Feed Gas [5]

Name of the component	**Composition**
Methane	0.863413
Ethane	0.039246
Propane	0.008830
i-Butane	0.000748
n-Butane	0.000467
n-Pentane	0.000491
n-Hexane	0.000280
H_2O	0.046721
N_2	0.001766
CO_2	0.020377
H_2S	0.017661

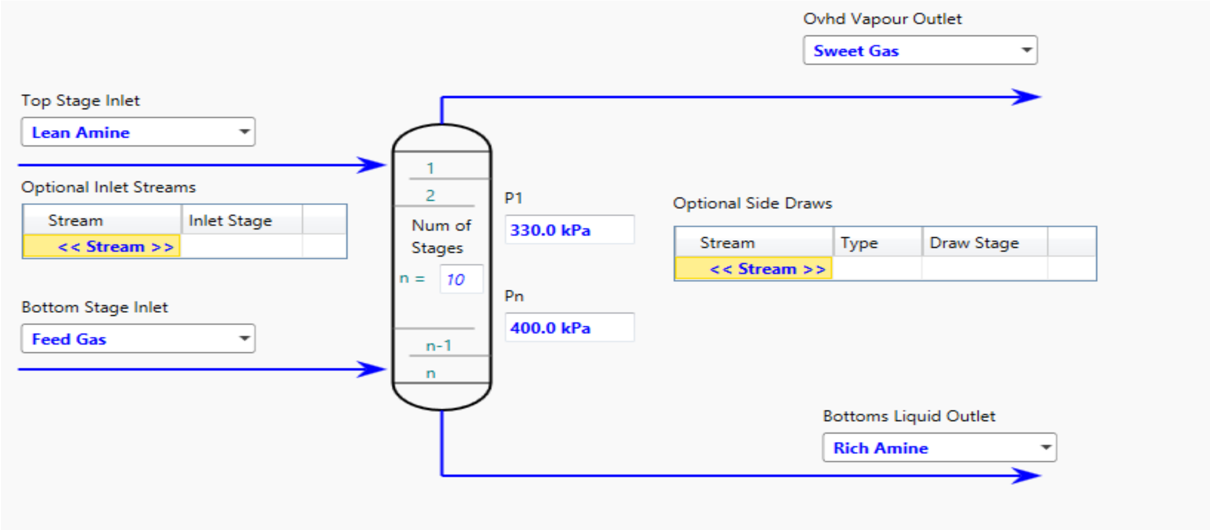


Fig 3: Absorber Configuration

Table 2: Equipment Specification

Equipment Specification	**Value**
Feed Gas Temperature	50°C
Lean Amine Temperature	40°C
Inlet Feed Gas Pressure	400kPa
Inlet Amine Pressure	330kPa
Feed Gas Molar Flow Rate	8500 kgmole/hr
Lean Amine Molar Flow Rate	12000 kgmole/hr
Number of Stages in Absorber	10 Tray

Aspen HYSYS V8.8 is used to stimulate the formation of HSS in the acid gas removal system. Aspen HYSYS capable to rigorously simulate gas processing from beginning to end, including the removal of acid contaminants. The main feature of Aspen HYSYS for this study is the amine treating for gas sweetening and make decision based on the impact of HSS. For this study, figure 4 is prepared in Aspen HYSYS to meet the objective of the simulation. The configuration of the absorber is shown in figure 3.

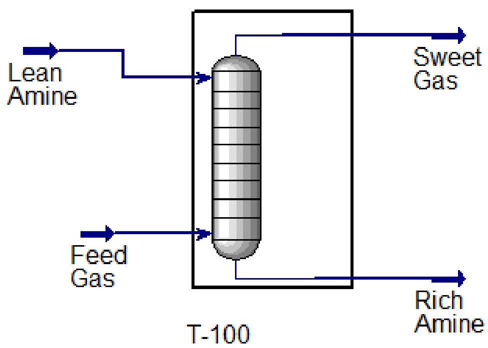


Fig. 4: Absorber flowsheet

The fluid package that has been chosen and offer from Aspen HYSYS V8.8 is Acid Gas. The required components to use this fluid package are amine, CO_2, H_2S, and H_2O. This fluid package can be used for various type of amine such as MEA, DEA, MDEA, piperazine (PZ), diglycolamine (DGA), triethylamine (TEA), and other mixtures of amine. For this study, the chosen amine is within the supported range of amine of this fluid package.

After choosing the component for the feed gas, the heat stable salts components are added by clicking the "Add Heat Stable Salts". This feature of Aspen HYSYS will then automatically add the remaining HSS that might form in the process. The table capture in Aspen HYSYS as shown in the figure 5 is the added heat stable salts.

NaOH	Pure Component
HCl	Pure Component
FormicAcid	Pure Component
AceticAcid	Pure Component
H2SO4	Pure Component
H2S2O3	Pure Component
HSCN	Pure Component
H3PO4	Pure Component

Fig. 5: Added Heat Stable Salt

The first simulation run is set for the base case at 40°C. For the others, the parameter such as concentration, temperature and pressure will be changed as shown in Table 3. All the parameter values are simulated for each HSS chosen for this simulation. However, the base case will only simulate for only 2 parameter which are lean amine temperature and pressure. There are 3 types of HSS simulated in this study, which are sulfate, formate, and acetate.

Table 3: Parameter Tested

Parameter	HSS Concentration	Lean Amine Temperature	Pressure
Values	0.05mol/kg	40°C	297kPa
	0.12mol/kg	45°C	330kPa
	0.24mol/kg	50°C	365kPa
	0.35mol/kg		
	0.45mol/kg		

III. RESULTS AND DISCUSSION

A. Effect of sulfate, acetate, and formate on CO_2 loading in the rich amine stream

The base case which means no heat-stable salt presence in the lean amine is tested at 40°C ,45°C and 50°C. According to [6], the normal range of lean amine temperature should be ranging from 90°F to 130°F. The CO_2 loading for the base case without any HSS is shown at table 4. The CO2 loading presented in this study is the CO2 loading at the rich amine. Based on figure 6, the base case shows the expected trend where the CO_2 loading at the rich amine output decreases as the temperature increase. It is common in most cases involving primary and secondary amine where increasing the temperature of absorber can decrease the performance [7].

Table 4: Base Case

Temperature (°C)	**40**	**45**	**50**
CO2 Loading (Rich Amine)	0.4908	0.4877	0.4825

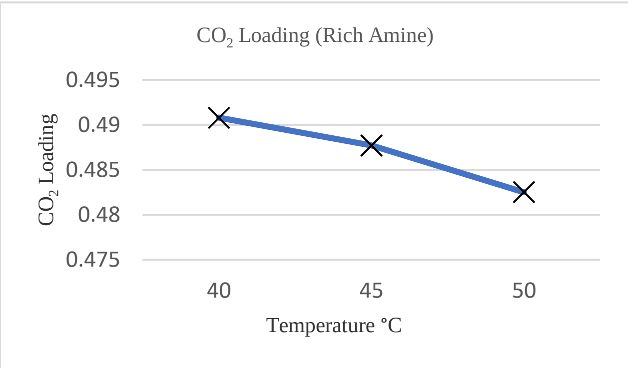


Fig 6: Base Case Trend

At higher temperature there would be a decrement in absorption capacity whilst lowering the temperature results in very slow rate of reaction for the system [8]. Therefore, the absorption would be unfeasible at temperature far from 40 °C. It is advisable to maintain a minimum temperature approach of 5°C between the feed gas and lean amine.

In this simulation, the sulfate ion mainly came from sulfuric acid that is present in the lean amine. Sulfuric acid is an inorganic acid which are classified as strong acid. The reaction of amines with acids would be amines donates electrons to form ammonium salts [9]. According to [10], acid gases are absorbed and held in amine solutions because the amine forms a salt with the acid gas.

Sulfate can be classified as non-amine HSS since it does not come from the degradation of amine. Table 5 shows the CO_2 loading for every concentration and temperature values tested. Figure 7 shows that the CO_2 loading decreases noticeably when the concentration sulfate increase. The same trend shows when the temperature of lean amine increases. However, there is not a significant difference when the temperature increases.

Table 5: Sulfate Case

Concentration (mol/kg)	**Temperature (°C)**	**CO_2 Loading (mol CO_2 / mol MEA)**
0.05	40	0.4869
	45	0.4828
	50	0.4784
0.12	40	0.4794
	45	0.4745
	50	0.4698
0.24	40	0.462
	45	0.4578
	50	0.4528
0.35	40	0.4389
	45	0.4322
	50	0.4266
0.45	40	0.4116
	45	0.4038
	50	0.3982

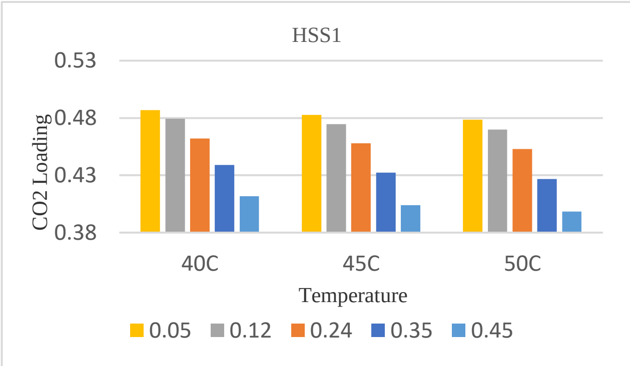


Fig 7:Sulfate CO_2 Loading

Acetate is commonly found from the acid in the feed gas, oxygen degradation, and thermal degradation [11]. Organic acids are known to be degradation products in MEA solutions [12]. Therefore, it was the best choice to test the acetate for this simulation. Acetate is a weak acid anion that will form HSS such as sodium acetate. In this study, the acetic acid forms because of MEA oxidation.

Monoethanolamine reacts with acetic acid (HAc) to form 2-(hydroxy)ethylammonium acetate (2-HEAA). Table 6 shows the CO_2 loading for every value of the parameter tested. Figure 8 summed up the behaviour of acetate towards the CO_2 loading in the rich amine. The CO_2 loading increase when the concentration of acetate increases. The same trend obtained when temperature.

Table 6: Acetate Case

Concentration (mol/ kg)	**Temperature (°C)**	**CO2 Loading (mol CO_2 / mol MEA)**
0.05	40	0.4886
	45	0.4857
	50	0.4816
0.12	40	0.4864
	45	0.4817
	50	0.477
0.24	40	0.4791
	45	0.4742
	50	0.4694
0.35	40	0.4726
	45	0.46778
	50	0.4627

0.45	40	0.4648
	45	0.4599
	50	0.4547

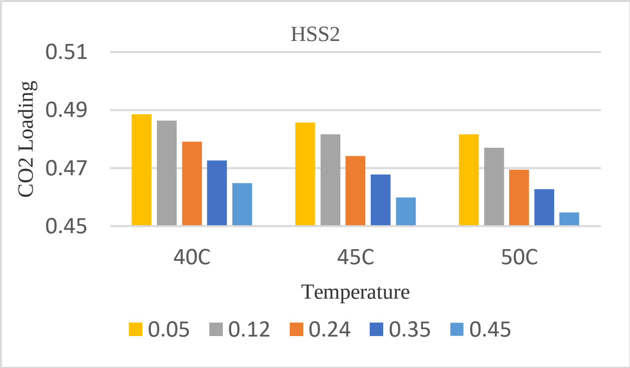


Fig 8: Acetate CO_2 Loading

Formate is another type of HSS that is common forms in acid gas cleaning system that uses MEA. Just like acetate, formate is also a weak acid anion. Formic acid Table 7 shows the CO_2 loading when formate is present in the lean amine. Based on the figure 9, the same trend which is decrement in CO_2 loading when concentration increases or when the temperature increases.

Table 7: Formate Case

Concentration (mol/kg)	**Temperature (°C)**	**CO2 Loading (mol CO_2 / mol MEA)**
0.05	40	0.4887
	45	0.4857
	50	0.4816
0.12	40	0.4861
	45	0.4809
	50	0.4769
0.24	40	0.4791
	45	0.4741
	50	0.4694
0.35	40	0.4727
	45	0.4677
	50	0.4626
0.45	40	0.465
	45	0.4591
	50	0.4546

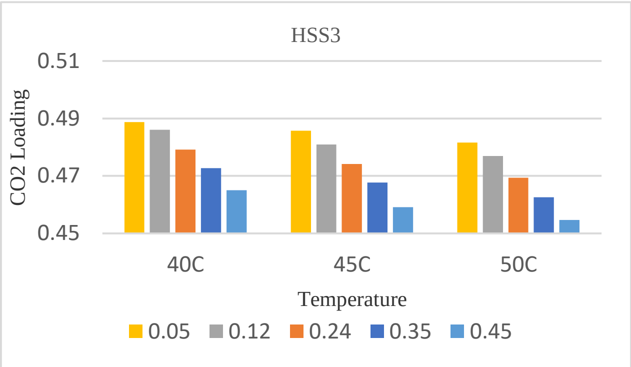


Fig 9: Formate CO_2 Loading

B. Effect on the CO2 absorption capacity at different temperature, pressure and initial HSS concentrations

Temperature, pressure and initial HSS concentration are a vital parameter that affect the CO_2 absorption. Each of these parameters has different amount of impact on the CO_2 absorption. According to [2], there might be an increment on the operation cost of amine unit due to the presence of HSS increase solution viscosity and decrease acid-gas carrying capacity.

1) Temperature

For temperature comparison, only the concentration of HSS of 0.12, 0.24, and 0.35 mol/kg is shown in graph. The reason for this is because there is not much difference in CO_2 loading for the concentration of 0.05 mol/kg for every HSS tested. As for 0.45 mol/kg of concentration is considered quite high in the industry. Therefore, it is not relevant to include both concentrations. Referring to figure 10, at 0.12mol/kg of concentration sulfate has the lowest CO_2 loading in the rich amine stream compared to other HSS. However, both acetate and formate have almost the same value of CO_2 loading.

As the concentration of HSS increases as shown in figure 11 and figure 12, it is shown that CO_2 loading decreases when the temperature increase for all HSS. There is less than 5% decrement of CO_2 loading when the temperature increases for all cases. Øi, 2007, found out that there is a reduction of absorption when there is an increment in gas and liquid inlet temperature. The expected results obtained for this study. This is due to with lesser kinetic involvement when the temperature of inlet increases.

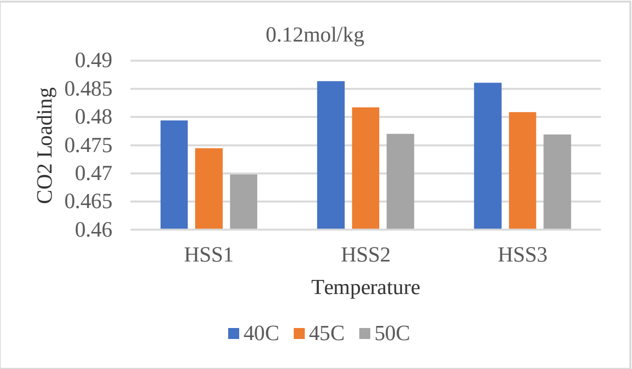


Fig 10: 0.12mol/kg Concentration

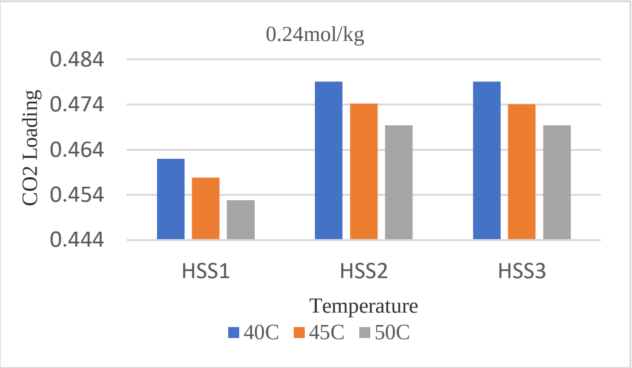


Fig 11: 0.24mol/kg Concentration

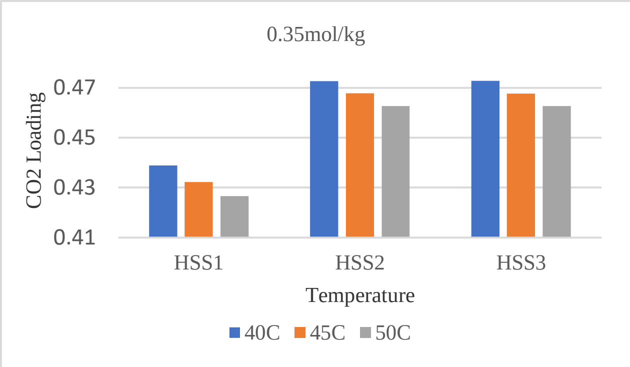


Fig 12: 0.35mol/kg Concentration

2) *Concentration*

HSS has a negative impact in CO_2 absorbing performance, and are also difficult to regenerate under normal regeneration conditions used in CO_2 absorption unit [14]. A neglected build-up HSS can cause various damages that would in turn cost money. HSS concentration has always been monitored in the industry because a high concentration of HSS is difficult to regenerate which in turn cause operational problems such as corrosion, foaming, and reduction in solvent capacity [12]

Referring to all the graph at 40°C, 45°C, and 50°C, the CO_2 loading is almost at the same point for 0.05mol/kg concentration. The value should be close to the base with no HSS which is 0.4908. There is less than 1% difference even with 0.05 mol/kg concentration. This shows how unaffected the system performance when there is little amount of HSS. As the concentration increases, there is a trend of decrease of CO_2 loading. This trend applies to all cases with HSS. However, based on all the figure, HSS1 or sulfate has the most impact on the CO_2 loading.

There is a great reduction in CO_2 loading for sulfate when the concentration increased. There is a huge difference of CO_2 loading reduction for sulfate compared to other HSS. The reason for this is because sulfate is a strong acid anion while acetate and formate are weak acid anion. Strong acid ionize completely in solution while weak acid dissociate partially [15]. Therefore, sulfate will have greater reaction and produce more HSS in the system compared to acetate and formate.

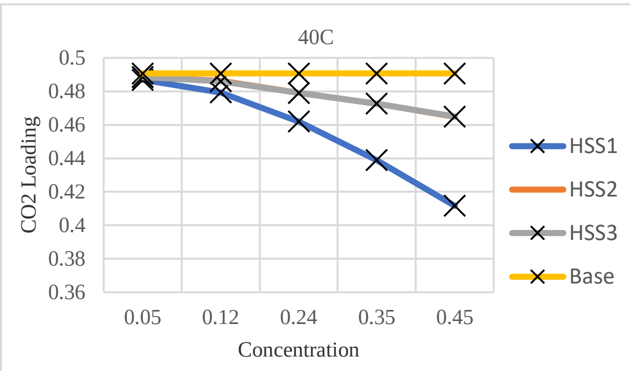


Fig 13: 40°C Temperature

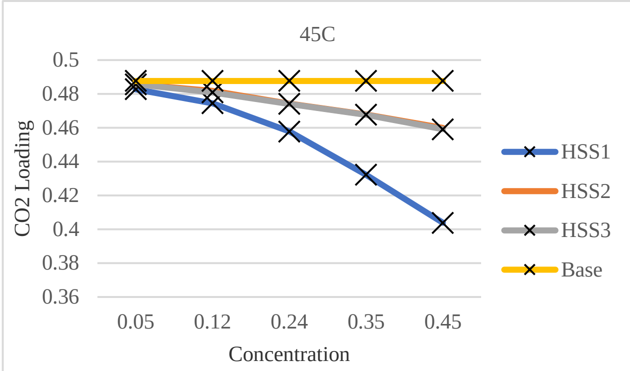


Fig 14: 45°C Temperature

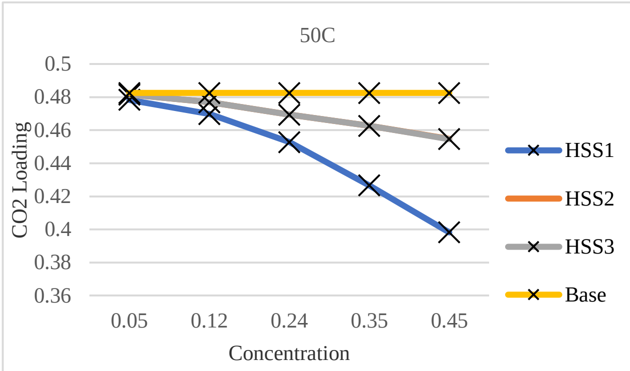


Fig 15: 50°C Temperature

3) *Pressure*

For a reaction to occur, the particles must collide or have collision between two different particles. Basically if the pressure is high, the chances of collision or rate of collision should be greater [16]. This study only alters the pressure for each case. The temperature is 40°C and the concentration of HSS for cases involve HSS is 0.24 mol/kg. The pressure differential is 10psi as stated in the methodology. Higher and lower pressure differential is then simulated. Table 4.5 shows the results obtain for pressure cases.

It is clearly showing in figure 16 that there is no significant difference in the CO_2 loading obtain by changing the pressure. There is less than 1% in difference of CO_2 loading for every case simulated. A study from [5], discovered that the change of pressure from 100 psia to 600 psia has very small effect on composition of sweet gas. This conclude that pressure would have very little or no effect on the CO_2 loading or composition of sweet gas.

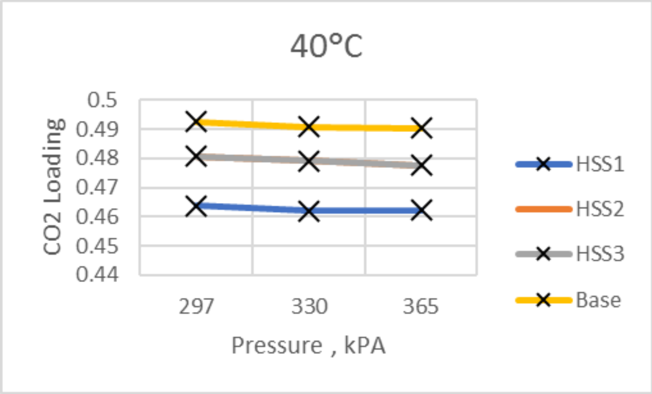


Fig 16: Pressure Case

IV. CONCLUSION

HSS accumulation has an unfavourable impact on amine system operations as it can reduce the effective capacity of the amine solution, contribute to corrosion and aggravate operational problems such as foaming, amine loss, and fouling. The presence of HSS studied which are sulfate, formate, and acetate are obviously having effect on the CO_2 loading in the rich amine stream. Even a low concentration of HSS is present would increase the CO_2 loading. Thus, leads to many operational problems. With the presence of HSS in the acid gas cleaning system, only 2 parameter that affect the CO_2 loading. Increasing the temperature of the lean amine that contains the HSS will significantly increase the CO_2 loading. Sulfate have the lowest CO_2 loading compared to other HSS when the temperature increases. Besides that, an increased concentration of HSS clearly shows that the system will have lower CO_2 absorption performance. The HSS that have the most effect when the concentration increase is sulfate also. Sulfate being the strong acid anion are expected to form more HSS compared to formate and acetate. However, there is almost no changes in CO_2 loading when the pressure of lean amine stream increases.

ACKNOWLEDGMENT

Thank you to my supervisor, Dr. Putri Nadzrul Faizura Megat Khamaruddin, my friends, my parents and Universiti Teknologi Mara. I am grateful the support and cooperation given by them for completing this study. Without them, this study might not meet the due date.

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