Investigation on the Performance of Amine-Based Absorption and Its Blend for the Removal of High CO_2 Concentration Using HYSYS

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***Abstract*— Removal of CO_2 from natural gas is currently a global issue. Apart from meeting the customer's product specifications; it is also a measure for reducing the damage to pipeline and equipment system. Those problems arised when the CO_2 removed is insufficient or still not enough to reduce the effect of CO_2 from becoming acidic and corrosive because it forms carbonic acid by reacting with water vapour. This research aims to determine the optimum ratio of diisopropanolamine (DIPA) and sulfolane for the removal of high CO_2 concentration and optimizing the performance of amine based absorption and its blend for the removal of high CO_2 concentration by using different values of operating conditions. A standard base case of typical CO_2 removal process was prepared first using Aspen HYSYS V8.8 process simulation tool. Then, the optimization of the conditions was done using Response Surface Methodology (RSM) analysis by controlling and modifying the parameters and conditions to improve process performance. The tool used was Minitab 18. To conclude the analysis, it can be said that the optimum ratio of DIPA and sulfolane is nearing 1:1, although the result shows that DIPA has a slightly bigger role in the removal of CO_2 as compared to sulfolane. For the effects of temperature and pressure, the analysis states that the temperature effect is greater than pressure. The mole fraction of CO_2 in sweet gas is lowest (less than 0.0005) at temperature approximately between 33°C and 49°C and pressure of 6780 kPa to 7300 kPa.**

Keywords*— *CO_2, sulfolane, DIPA, simulation, HYSYS

I. INTRODUCTION

Natural gas (NG) is basically shaped from the disintegration of living matters, for example, plants, creatures and microorganisms that lived more than a huge number of years prior and turned into a lifeless blend of gases, as other non-renewable petroleum derivatives. There are a number of types of formation that refer to different types of NG namely thermogenic, biogenic and abiogenic methane. All of the stated types of NG are unique in their own ways, which are different by means of how they are formed and at what depth they forms. Acid gases created in gasification forms primarily comprise of H_2S, CO_2 and carbonyl sulfide (COS). Therefore, acid gas removal unit, otherwise called gas sweetening unit are utilized to clean the NG from the acid gases (Shimekit and Mukhtar, 2012).

The function of acid gas removal unit is to purify NG from acid gases, including the removal of CO_2 from feedstock (natural gas) in order to increase energy content of the gas thus preventing the decline in quality of gas product. But, problems arise when the CO_2 removed is insufficient or still not enough to reduce the effect of CO_2 from becoming acidic and corrosive because it forms carbonic acid by reacting with water vapour. As a result, the product will not meet transport requirements and sale gas specifications in addition with the damaging of pipeline and equipment system by CO_2. So, this research will further verify the highest concentration of CO_2 that can be removed during an amine based absorption with its blend.

Two general classes of solvent are used – chemical and physical solvents. There are a few problems when using amine solvents such as impurity absorption limitation to chemical reactions' ratios, high-energy requirement for regeneration, and lower absorption of sulphur compound. These problems can be solved to some extent by using the alternative physical/chemical solvents like Sulfinol-M and Sulfinol-D. We can benefit from the features of mixed solvents as it is an attempt to combine the advantages of both physical and chemical solvents. Consequently, the efficiency of CO_2 removal will surely increase by using the mixed physical/chemical solvents.

The Sulfinol solvent comprises of sulfolane (tetrahydrothiophene dioxide) and an alkanolamine, normally DIPA and MDEA. DIPA is related with Sulfinol-D process, where it is utilized as a part of conjunction with a physical organic solvent. One of the benefits of DIPA is it has low recovery steam necessities and to be noncorrosive. At the point when the gas stream to be dealt with is at high pressure and the acidic parts exist in high concentrations, the nearness of the physical solvent upgrades the solution limit. Also, it can accomplish high proficiency removal of different contaminates, in particular COS, mercaptans and other organic sulphur composites. In general, Sulfinol-D is utilized when basically entire elimination of both H_2S and CO_2 and profound removal of COS is wanted (Kohl and Nielsen, 1997).

Traditional procedures for expelling acid gases commonly include their counter-current absorption from the syngas using a regenerative solvent in an absorber column. This procedure approach of gas-fluid contacting in order to expel acid gases is usually applied as a part of an extensive variety of process activities, including refining, chemicals, and NG manufacture. The physical solvent processes have a tendency to co-absorb more CO_2 than chemical/amine procedures, for example, methyldiethanolamine (MDEA). While the physical solvent processes have higher power usage than the chemical solvent processes, the chemical processes have higher steam utilization, which means diminished power yield from the power train. Accordingly, effect on general net power yield might be comparative between the two sorts of techniques. Likewise, it is critical to take note whether H_2S and CO_2 can be expelled either at the same time or specifically, depending upon the crude syngas composition and parameters, and the end syngas requirements (Mokhatab and Poe, 2012).

The research objectives will be to determine the optimum ratio of diisopropanolamine (DIPA) and sulfolane for the removal of high CO_2 concentration and to optimize the performance of amine based absorption and its blend for the removal of high CO_2 concentration by using different values of operating conditions. Lastly, the work scope of this research will be explained in this paragraph. Aspen HYSYS will be used to simulate and determine the optimum ratio of amine and its blend at which the CO_2 removal will occur and optimizing its performance by using different sets of values for the operating conditions. This research will be done based on the industrial problem and the established Acid Gas Removal Unit (AGRU) process flow sheets. Firstly, the ratio of DIPA and sulfolane will be manipulated in order to achieve the optimum ratio. Usually, Sulfinol solution with the concentration of 40% sulfolane, 40% DIPA and 20% water is the normal standard for acidic gas removal. Next, the operating conditions at the inlet of absorber and desorber will be kept in a certain range. For temperature, the range shall be in between 25-45°C. For pressure, the range will be in between 6800-7000kPa. Meanwhile, in this case the flowrate will be kept constant. Results obtained will be investigated and compared with data from previous research for validation purpose. At the end of the research, the highest concentration of CO_2 that can be removed during an amine based absorption with its blend will be acquired.

II. METHODOLOGY

A. *Aspen HYSYS Software*

Aspen HYSYS is a market-driving process simulation instrument and it has been made concerning the program design, interface configuration, building capacities and intuitive operation. At the same time, in the oil and gas business this application is basically utilized as a part of research, improvement, demonstrating and planning (Hamid, 2007). Aspen HYSYS offers an expansive thermodynamics establishment for exact estimation of physical and transport properties, including the phase behaviour of the oil and gas in refining businesses. Simulation can be utilized to demonstrate the inevitable genuine impacts of optional conditions and approaches (Mondal *et al.*, 2015).

In HYSYS, the correct decision of a fluid package and thermodynamic models are critical on the grounds that it contains all important data about pure components flash and physical properties computations. Any process can be considered not substantial if the simulation depends on a wrong fluid package and thermodynamics models. Simulation of the constructed process stream outline is accomplished by providing some imperative physical, thermodynamics and transport information of the stream and equipment to be used, this is done until the point when each one of the units and the streams are solved and converged (Ebenezer, 2005).

In order to study about the performance of amine-based absorption and its blend for the removal of high CO_2 concentration, a computer simulation was conducted using Aspen HYSYS Version 8.8. The related data obtained after the simulation were used to study the performance of carbon dioxide removal when the operating parameters are manipulated.

B. *Response Surface Methodology (RSM)*

Minitab is a software package for carrying out statistical, numerical and graphical calculations or analysis. It often relies on a good background knowledge of the phenomenon to be analysed, requires a series of steps and the main are:

- Data analysis with graphs
- Perform statistical analysis and procedures
- Evaluation of the quality of a measure

Referring to the third step as stated earlier, Minitab offers a variety of method to assess the quality of a measure qualitatively and quantitatively, definitely its uncertainty – control charts, statistical tools, quality planning, process capability and reliability (Zanobini, 2015).

The application of Response Surface Methodology (RSM) in the software Minitab is due to its ability to collect statistical and mathematical techniques useful for developing, improving and optimizing processes. In RSM, the performance measure or output variable is called the response, while the input variables are called independent variables. After a series of tests, in which changes in the input variables are made, we can identify the reason for variations in the output response (Carley, Kamneva and Reminga, 2004). For this research that is applying RSM, the most suitable approximation model is very important, hence the use of second-order design – The Central Composite Design (CCD). This design is developed to work out with the sequential nature of a response surface method that starts with a first-order design, followed by the addition of design points to fit the larger second-degree model. The first-order model is used to get information and to assess the importance of the factors in an experiment. The additional experimental runs are chosen for the purpose of getting more information that can lead to the determination of optimum operating conditions on the control variables using the second-degree model (Khuri and Mukhopadhyay, 2010).

C. *Process Description*

Every so often, the problems of CO_2 removal unit can be caused by the impurities carried in along with the pipeline gases. Corrosion inhibitors, liquid slugs or even the compressor lubricating oils are the common types of pipeline impurities that can exist. Slug catcher is used to prevent those contaminants from getting into the components. The next few paragraphs is the explanation of the key equipment that is needed for the modelling of a CO_2 removal unit in order to solve any problems, mainly to meet the pipeline gas specifications.

The first equipment essential for a gas sweetening plant is the HP inlet vessel. The role of the inlet vessel is to evacuate the entrained fluid amine brought along with the gas from the pipeline before getting to the contactor. The vapour and fluid in the vessel are made to achieve equilibrium, before they are isolated. Next, the absorber column or the contactor permits counter-current stream of lean amine from the top and sour gas from the bottom. Here the amine solvent assimilated the CO_2 and rich amine moves downward while the sweet gas moves upward for next step in processing. The conditions and composition of the inlet feed and additionally the working pressure characterize the following convergence in the simulation. The throttling valve is also an important in gas sweetening as the pressure of the gas can be decreased before it arrives at the flash tank by the use of this valve that can expand the rich amine from the contactor.

The rich/lean heat exchanger is where hot lean solvent preheats the cooler rich solvent. In HYSYS, the Heat Exchanger can be the answer for temperature, pressure, heat flows (counting heat loss and leaking), material streams and so forth. The last main equipment needed to design a gas sweetening process system is the distillation column or regenerator. It comprises of a few parts, for example, reboiler, condenser and reflux drum that is utilized either to exchange heat energy or improve material exchange. The reboiler gives fundamental vaporization to the refining procedure while the condenser is to cool and condense the vapour leaving the highest point of the column. The reflux drum will hold the condensed vapour with the aim that reflux fluid can be reused back to the section. Figure 1 below shows the completed simulation of an acid gas removal unit.

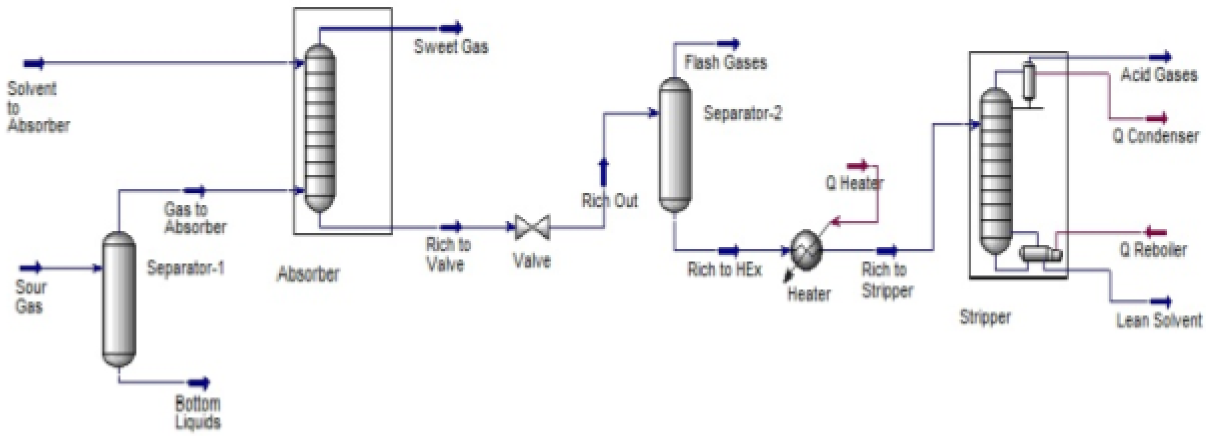

Figure 1: Complete simulation of acid gas removal unit.

D. Simulation

A standard base case was prepared first for the simulation using Aspen HYSYS V8.8. The next step is to choose the component to be used. The components were selected by opening the component list window in the software. After that, for a Sulfinol process which uses Sulfolane and DIPA for the amine blends, only Acid Gas is eligible for the simulation to proceed. Hence, it is chosen as the fluid package. The simulation can now start to take place after the component list is completed and the fluid package is chosen. It starts by specifying the conditions of the sour gas (feed) material stream such as the temperature, pressure and molar flow rate while the other parameters will be calculated by HYSYS itself. Table 1, 2 and 3 shows the list of composition and parameters to simulate the process plant.

Table 1: Composition for sour gas feed and solvent.

Parameters	Component	Composition
Feed	CO_2	0.0204
	H_2S	0.0177
	H_2O	0.0467
	N_2	0.0018
	C1	0.8634
	C2	0.0392
	C3	0.0088
	i-C4	0.0007
	n-C4	0.0005
	n-C5	0.0005
	n-C6	0.0003
Solvent	Sulfolane	0.4
	Diisopropanolamine (DIPA)	0.4
	Water, H_2O	0.2

Table 2: Operating conditions for sour gas and solvent.

Parameters	Temperature, °C	Pressure, kPa	Molar Flow
Feed	30	6895	1245 kgmol/h
Solvent	35	6895	43.15 m3/h

The other operating parameters need to be specified are the material compositions, solvent to absorber temperature, pressure and flow rate, heat exchanger temperature and rich solvent to stripper temperature, which is before it is send to regenerator. HYSYS will automatically calculate the other parameters needed after all the required data is specified in order to completely simulate the process. The most challenging part is where we need to converge the absorber and the regenerator by identifying the correct parameters such as temperature and pressure, so that the simulation can run smoothly. After the convergence of the absorber and regenerator columns, a finished simulation for an acid gas removal unit has completed. The optimization of the procedure was done by controlling and altering the parameters and conditions in order to meet the research objectives.

Table 3: Operating conditions at absorber and stripper.

Absorber	Number of stages	10
	Top/Bottom Pressure (kPa)	6860/6895
	Top/Bottom Temperature (°C)	37.78/71.11
Stripper	Number of stages	18
	Top/Bottom Pressure (kPa)	189.6/217.2
	Top/Bottom Temperature (°C)	88.73/125.4

III. RESULTS AND DISCUSSION

A. Effects of mass fraction of diisopropanolamine (DIPA) and sulfolane on CO_2 in sweet gas

A total of thirteen experiments were executed using the computer software Minitab and the experimental results are shown in Table 4. Firstly, the use of response surface methodology (RSM) need to be validated by interpreting the matrix plot. Figure 2, which is the matrix plot illustrate that the relationship between the mole fraction of CO_2 in sweet gas and the mass fractions of sulfolane and diisopropanolamine (DIPA) are not in linear form. Thus, the RSM analysis should be suitable to be used for this research.

Table 4: Effect of mass fraction of sulfolane and DIPA on CO_2 composition in sweet gas.

No. of experiment	Mass Fraction of Sulfolane	Mass Fraction of DIPA	CO_2 in Sweet Gas (mol)
1	0.2000	0.2000	0.0023
2	0.4500	0.2000	0.0011
3	0.2000	0.3500	0.001
4	0.4500	0.3500	0.0003
5	0.1482	0.2750	0.0016
6	0.5018	0.2750	0.0005
7	0.3250	0.1689	0.0023
8	0.3250	0.3811	0.0009
9	0.3250	0.2750	0.0009
10	0.3250	0.2750	0.0009
11	0.3250	0.2750	0.0009
12	0.3250	0.2750	0.0009
13	0.3250	0.2750	0.0009

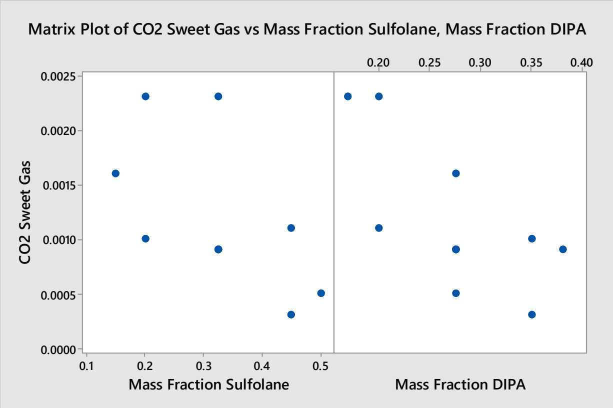

Figure 2: Matrix plot of CO_2 in sweet gas against mass fraction of sulfolane and DIPA.

The variation in a set of data from the experiment can also be observed by using the residual analysis plot as displayed in Figure 3. The normal probability plot shows that the line is in a straight, diagonal form meaning that the data comes from a normal distribution. Next, the histogram lays out a bell curve shape along the graph. It means that the data used for the experiment is normally distributed. As for the other two graphs on the right-hand side, it emphasized the randomness of the data indicating that the process is in control. All of those residual plots stated above is used to check the validity of the data and to know whether it is acceptable or not to use in statistical study. In fact, it was proven in the plots that the data from the experiment is suitable to be applied for further analysis.

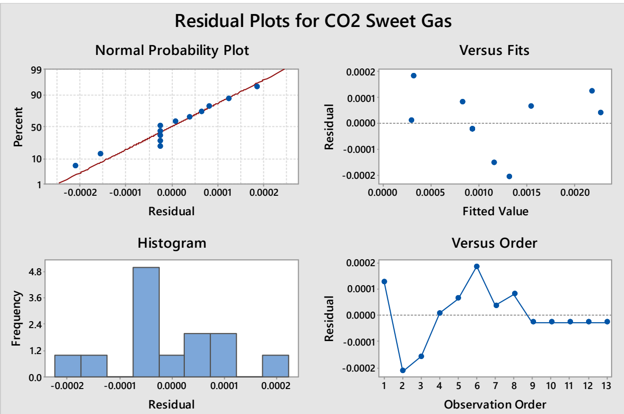

Figure 3: Residual plots for CO_2 sweet gas.

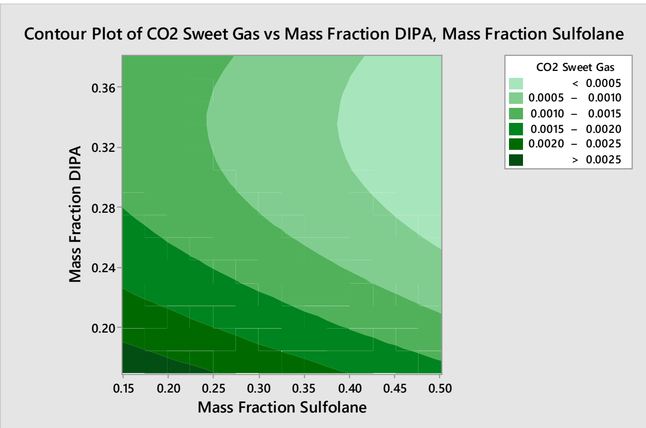

Figure 4: Contour plot of CO_2 sweet gas versus the mass fraction of sulfolane and DIPA.

The contour plot in Figure 4 shows that the mole fraction of CO_2 in sweet gas is the lowest at mass fraction of sulfolane between 0.38 and 0.50 and mass fraction of DIPA of 0.26 to 0.36 and above. The mole fraction of CO_2 in sweet gas in those range is equal to less than 0.0005. Arnold and Stewart (1999) states that typically a Sulfinol solution of 40% sulfolane, 40% DIPA and 20% water can remove 1.5 moles of acid gas per mole of Sulfinol solution. Thus, it is proven that the normal mass fraction for Sulfinol-D process stated earlier can indeed have a good performance during gas sweetening. Moreover, at the bottom-left side of Figure 4, it illustrates the increment of the mass fraction of sulfolane and high mole fraction of CO_2 under the circumstances of low mass fraction of DIPA. Nevertheless, moving upwards across the contour plot at the same mass fraction of sulfolane but with the increase of DIPA, the mole fraction of CO_2 in sweet gas decrease gradually. This is due to the greater role of mass fraction of DIPA in the removal of CO_2 compared to sulfolane's mass fraction.

The optimization plot in Figure 5 that is generated by the computer software Minitab depicts that the optimum mole fraction of CO_2 can be obtained in sweet gas is 0.0029. The mass fraction of sulfolane and DIPA required to obtain the optimum condition are 0.1482 and 0.1689 respectively. From the optimum mass fractions of both sulfolane and DIPA, it can be said that the optimum ratio is nearing 1:1, although the result shows that DIPA has a slightly bigger role in the removal of CO_2 as compared to sulfolane. This can be proved in the right hand side of Figure 5 where a curve is formed meaning that the mass fraction of DIPA has an effect towards the amount of CO_2 in sweet gas. On the contrary, the graph for sulfolane is a straight line, which means that it has no or less effect towards CO_2 removal.

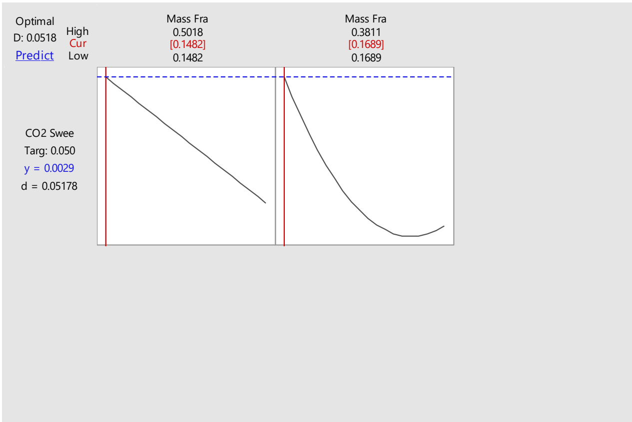

Figure 5: Optimization plot of CO_2 sweet gas against mass fraction of sulfolane, DIPA.

B. Effects of temperature and pressure on CO_2 in sweet gas

First, the use of response surface methodology (RSM) need to be confirmed by interpreting the matrix plot as shown in Figure 6.

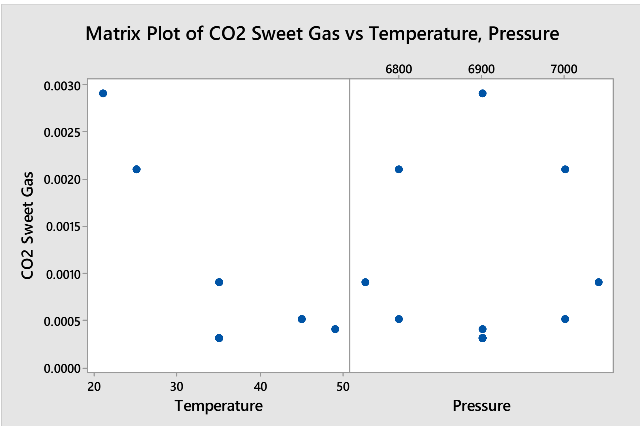

Figure 6: Matrix plot of CO_2 in sweet gas against temperature and pressure.

By using a similar method with the earlier analysis, thirteen experiments were executed using the computer software Minitab and the experimental results are shown in Table 5. Figure 6, which is the matrix plot illustrate that the relationship between the mole fraction of CO_2 in sweet gas and the temperature and pressure are not in linear form. Thus, the RSM analysis should be suitable to be used for this research.

Table 5: Effect of temperature and pressure on CO_2 composition in sweet gas.

No. of experiment	Temperature (°C)	Pressure (kPa)	CO_2 in Sweet Gas (mol%)
1	35	6900	0.0003
2	45	6800	0.0005
3	35	6900	0.0003
4	25	7000	0.0021
5	35	6900	0.0003
6	45	7000	0.0005
7	35	7041	0.0009
8	35	6900	0.0003
9	25	6800	0.0021
10	49	6900	0.0004
11	35	6759	0.0009
12	35	6900	0.0003
13	21	6900	0.0029

The variation in a set of data from the experiment can also be observed by using the residual analysis plot as displayed in Figure 7. The normal probability plot shows that the line is in a straight, diagonal form meaning that the data comes from a normal distribution. Next, the histogram lays out a bell curve shape along the graph. It means that the data used for the experiment is normally distributed. As for the other two graphs on the right-hand side, it emphasized the randomness of the data indicating that the process is in control. All of those residual plots stated above is used to check the validity of the data and to know whether it is acceptable or not to use in statistical study. As a matter of fact, it was proven in the plots that the data from the experiment is suitable to be applied for further analysis.

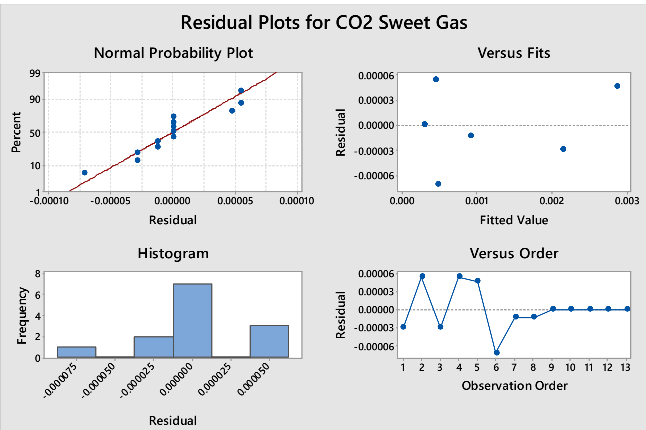

Figure 7: Residual plots for CO_2 sweet gas.

The contour plot in Figure 8 shows that the lowest mole fraction of CO_2 in sweet gas is at temperature approximately between 33°C and 49°C and pressure of 6780 kPa to 7300 kPa. The mole fraction of CO_2 in sweet gas in that range is less than 0.0005. Furthermore, at the left-hand side of Figure 8, it illustrates the increment of pressure and high value of mole fraction of CO_2 under the circumstances of low temperature. However, moving across the contour plot to the right at the same pressure but with the increase of temperature, the mole fraction of CO_2 in sweet gas decrease steadily. This is because the temperature has a bigger role in the removal of CO_2 compared to pressure.

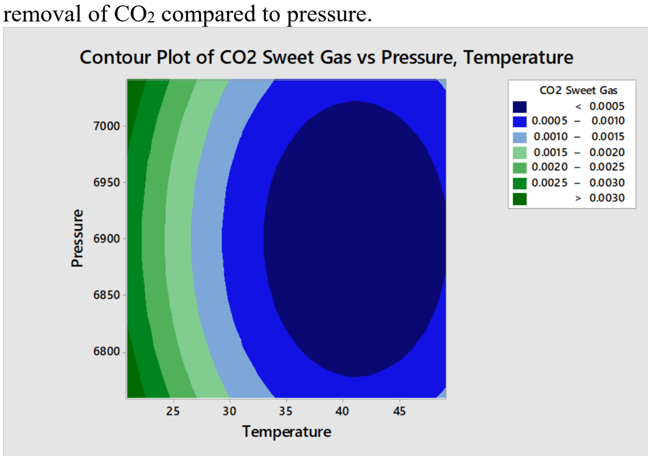

Figure 8: Contour plot of CO_2 sweet gas versus temperature and pressure.

The optimization plot in Figure 9 obtained from the computer software Minitab shows that the optimum mole fraction of CO_2 that can be achieved in sweet gas is 0.0035. The temperature and pressure required to obtain the optimum condition are 20.86 °C and 7041 kPa respectively. The graph of temperature optimization at the left hand side of Figure 9 illustrates a more significant curve in comparison with the pressure's one. In other words, different range of temperature affects the process under the settings of unchanged pressure. Hence, it can be said that the process depends more on temperature to achieve a lower amount of CO_2 sweet gas.

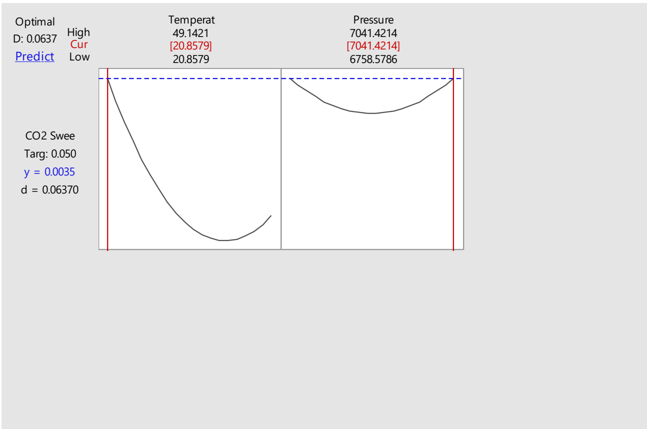

Figure 9: Optimization plot of CO_2 sweet gas against temperature, pressure.

IV. CONCLUSION

The removal of high CO_2 concentration using mixed solvent of sulfolane and DIPA will differ with variety of changes within the parameter. In the first analysis that is to determine the optimum ratio of diisopropanolamine (DIPA) and sulfolane for the removal of high CO_2 concentration involving the effect of mass fraction of sulfolane and DIPA, the analysis states that the ratio for both of the solvent is almost equivalent (1:1). Still, by conducting further analysis using the response optimizer, it has been proven that the mass fraction of DIPA has a greater role in the removal of CO_2 compared to the sulfolane's mass fraction. In another analysis regarding the second objective, which is to optimize the performance of amine-based absorption and its blend for the removal of high CO2 concentration by using different parameters, it is confirmed that the temperature plays a bigger part in the removal of CO_2 as compared to pressure. For future research, the investigation on the performance of amine-based absorption shall be conducted by using different types of solvent, with different parameters in order to verify which type of solvent is more effective in term of performance and cost.

ACKNOWLEDGEMENT

Thank you to my supervisor, Dr. Putri Nadzrul Faizura Megat Khamaruddin and Universiti Teknologi MARA.

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