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OPTIMIZATION OF PROCESS PARAMETERS FOR NATURAL GAS SWEETENING USING ASPEN HYSYS AND RESPONSE SURFACE METHODOLOGY

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Abstract

Amines process remains the most economic and efficient technology available today for the removal of acid gases. However, the costs associated with pumping higher flow rates and cost of increased energy needs for the regeneration of solution can undermine the economic feasibility of the project portfolio.Theabsorber pressure, the composition and temperature at which the sour gas is availabledictates sour gas and amine flow rates needed to meet the sweet gas specifications. To improve absorber capacity for a given sweet gas specification, optimization are commonly carried out using spread sheet with an adjust function to manipulate sour gas flow rate for fixed amine flow rate. Thisstudy performed optimization using response surface methodology on a simulated and calibrated amine plant. The result shows that the optimum operating conditions for 96% CO_2 removal were temperature of 30 ^oC, mass flow rate of 868.75 kg/hr and 20 numbers of plates. In conclusion, using experimental design and response surface methodology the parameter manipulation for attainment of optimal conditions is overcome.

1. Introduction

Hydrogen sulfide, carbon dioxide, water vapor and other sulfur containing compounds constitute major impurities in natural gas and pose serious operational challenges. The unique size of H_2S and CO_2 permits a perfect fitting into cavities formed by water molecules that result in gas hydrate formation under high pressures and relatively low temperatures (Paez et al. 2001). Natural gas that contains more than 5.7 milligrams of H_2S per one cubic meter of natural gas is “sour”. That containing only CO_2 and no sulfur compounds is termed “sweet” gas. However, it is a good practice to remove both impurities to prevent corrosion problems and increase the heating value of the gas by removing the CO_2. In this regard, sweetening of natural gas is an important step to minimize the risks of health hazards, meeting the sales contract, minimizing the corrosion and preventing the gas hydrate formation.

The utilization of natural gas as domestic fuel necessitates H_2S removal due to associated health hazards. The prolonged exposure to H_2S beyond the threshold limit of 10 ppm portends serious health danger. At 0.13 ppm, H_2S can be sensed by smell. At 4.6 ppm, the smell is quite noticeable. As the concentration increases beyond 200 ppm, the sense of smell fatigues, and the gas can no longer be detected by odor. At 500 ppm, breathing problems have observed and death can be expected in minutes. At 1000 ppm, death occurs immediately (Arnold and Stewart, 1999).

Produced gases from reservoirs usually contain H_2S and CO_2 in varying concentrations ranging from barely detectable quantities to more than 3000 to 4000 ppm for H_2S and CO_2 respectively. From economic side, most contracts for the sale of natural gas require less than 4 ppm of these gases and heating value ranging from 920 to 980 Btu/scf (Mokhatab, 1999). Therefore, these impurities are treated so that the gas can be transported without restrictions. There exists several gas sweetening processes for the removal of CO_2 from natural gas. These include Chemisorption, Physical absorption, Adsorption, Hybrid solvents and Membrane separation (Kohl and Riesenfeld, 1997).

Notwithstanding, the design of the sweetening plant and the amount of solvent requirement are determined by the absorption behavior of the least soluble compound to be removed (Douglas et al., 1987). Process selection depends upon the pressure and composition of the raw natural gas, the trace components and their composition, and the desired quality of marketable natural gas (pipeline specification of LNG). The chemisorption and physical absorption or combination of these two has been used extensively in existing LNG facilities (Jaswar Koto, 2014).

A typical LNG plant's overall flow diagram, and the main process units, is shown in Fig. 1. In this scheme, the feed gas is delivered at high pressure (up to 1,300 psi and 90 bar) from upstream gas fields via trunk lines and any associated condensate is removed. The gas is metered and pressure-controlled to the plant's design operating pressure.

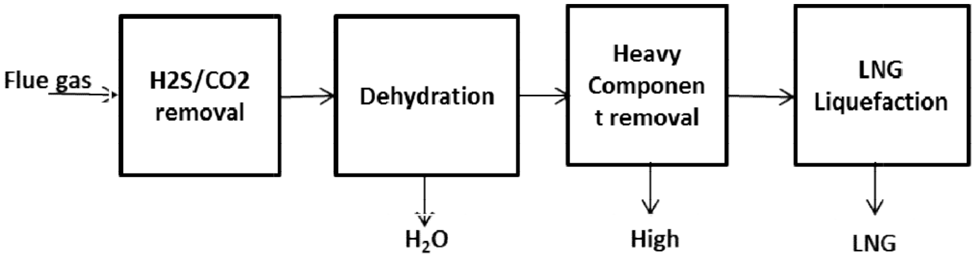


Figure 1: Typical LNG plant's block diagram

For optimum efficiency and effective impurity removal, the operating parameters of the sweetening unit must be maintained at optimum. Technically, when the gas reservoir pressure declines, the contracted gas flow rate decreases.Newwells are usually drilled to maintain production rate and front end compression may become necessary in the later stages of field life. But after a while when front end compression is also unable to supply gas with enough pressure, the pressure of the sweetening unit starts declining. Consequently, the efficiency of the unit keeps reducing with time.

In this paper the effect of declining pressure, number of plates and flow rate on the chemisorption processes are simulated using HYSYS. Usually, optimization are carried out using spread sheet with an adjust function to manipulate sour gas flow rate for fixed amine flow rate.Experimentaldesign and response surface methodology were integrated with the numerical simulation for process optimization.

2 Theory

2.1 Chemisorption

Many solvent systems have been proposed and studied for removing $CO_2$by chemical absorption. Mono Ethanol Amine (MEA) has been the most widely studied system (Alie et al., 2005, Abu-Zahra et al., 2007). The use of aqueousMEA for the removal of CO_2 from flue gases is a popular technology which has been described in detailed in a number of sources (Reddy et al., 2003, 2008). Other amines include tertiary amines such as Methyl Di Ethanol Amine (MDEA)(Lu et al., 2005). Sterically hindered amines have also been investigated (Yih and Shen, 2002, Xu et al., 2002). The performance of hindered amines was found to be better suited to absorption in higher CO_2 partial pressure atmospheres (8-15% CO_2).

Mixed amine blends are designed to take advantage of the desirable properties in primary and tertiary amines. It is desired that these have the high capacity and low heat of absorption characteristic of tertiary amines and the fast rate of reaction characteristic of primary amines. This will lead to reduced circulation rates of the solvent and yield a lower heat duty in the stripper (Idem et al., 2006).

Irrespective of amine type, process selection depends upon the pressure and composition of the raw natural gas, the trace components and their composition, and the desired quality of marketable natural gas (pipeline specification of LNG specification). The design of the absorber and the amount of solvent required are determined by the absorption behavior of the least soluble compound to be removed (Wiley & Sons, 2007).In general, two reagents are available for chemisorption: the hot potassium carbonate solution and amines.

The hot potassium carbonate process is used to remove both CO_2 and H_2S in the gas stream. It works best on a gas with CO_2 partial pressures in the range of 30-90 psi (Kumar et al., 2003). Amines are well suited for applications where the acid gas partial pressures are low and low levels of acid gas are desired in the residue gas. MEA,DEA and MDEA are extensively used in industry for CO_2 removal.

The flow scheme for all amine sweetening units is generally similar. MEA reacts with CO_2 and H_2S as follow (Kumar et al., 2003):

$$2(RNH_2) + CO_2 \underset{\text{high temp.}}{\overset{\text{low temp.}}{\rightleftharpoons}} RNHCOONH_3R$$

$$2(RNH_2) + H_2S \underset{\text{high temp.}}{\overset{\text{low temp.}}{\rightleftharpoons}} (RNH_3)_2S$$

The fundamental underlying principle is the exothermic, reversible reaction between a weak acid (e.g., CO_2) and a weak base (e.g., amine) to form a soluble salt. The choice of amine-concentration is often arbitrary and made on basis of experience. In general, corrosion inhibitors are effective in sweetening processes which allows the use of high concentration of amine. DEA concentration range is 30-40 wt. % but HYSYS can be applicable up to 50 %.

3 Methodology

3.1 Model specification and description

The flowsheet model from Abu-Zahra et al., (2007), was adopted for simulation and optimization of CO_2 removal (Figure 2).

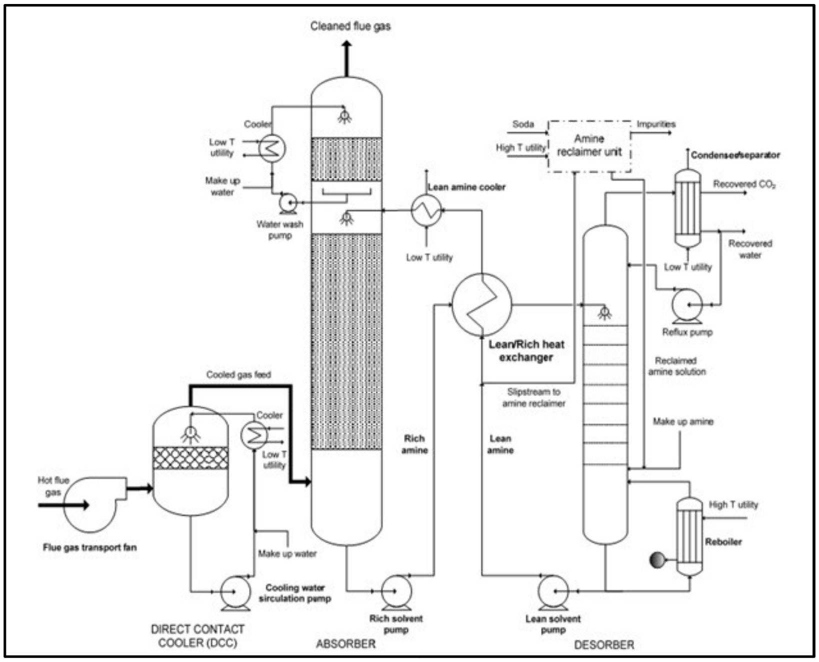


Figure 2: General flow diagram of a CO_2 removal process plant (Abu-Zahra et al., 2007)

The natural gas enters the plant through a knock-out vesselthat removes any free liquid or entrainment solids. The gas leaves the top of the scrubber and enters the bottom of the absorber in countercurrent contact with aqueous lean amine solution. Sweet gas leaves the top of the absorber and flow to a dehydration unit before liquefaction. Lean amine flows downward to the sour gas and absorbs the CO_2 constituent and becomes rich solution. The rich solvent from the bottom of the absorber is flashed in a separator to recover some absorbed hydrocarbon in the rich solvent and then passed through amine-amine heat exchanger to the stripper where the acid gas absorbed is stripped off at a very high temperature and low pressure. The acid gas then leaves the top of the stripper column. The lean amine from the bottom of the reboiler attached to the stripper flows through amine-amine heat exchanger and through a water air cooler before being introduced back to the top of the absorber.

These processes were modelled in the HYSYS simulation environment. Simulation was done using the in-built amine package with Kent Eisenberg’s thermodynamic model for aqueous amine solutions and non-ideal vapor phase model. The components and the fluid package are added. The un-simulated process flow diagram (PFD) developed is shown in Figure 3.

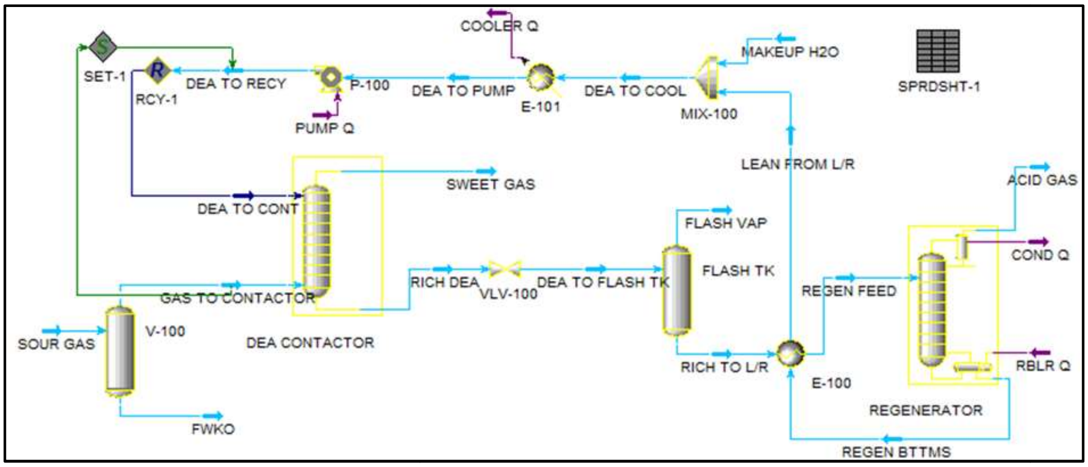


Figure 3: Un-simulated process flow diagram

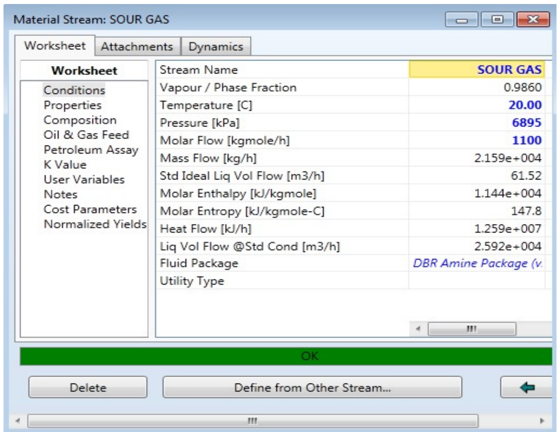
3.2Process Simulation

Table 1 shows the stream composition for HYSYS simulation. The simulation of the process begins with the simulation of the feed sour gas stream by specifying the gas temperature, pressure and flow rate.The natural gas enters the gas sweetening plant at temperature of 20℃, pressure of 6895 kPa and with mass flow rate of 1100 kg mole/h.The remaining process parameters were estimatedusing EOS and the result is shown in Figure 4.Other streams specifications made are, the regenerated feed out of the amine-amine heat exchanger temperature to control the exchanger factor, DEA to Contactor temperature pressure and flow rate, make up water temperature and DEA to recycle temperature. The material and energy balance is shown in Figures5and6. Specification of sweet gas is around 50 ppm CO_2.

In order to ensure convergence on the absorber, the absorber top and bottom temperature and pressure was specified and simulated. Similarly, the regenerator convergence was attained by specifying the condenser and re-boiler pressure, the reflux ratio and the vent rate, the column was then simulated.

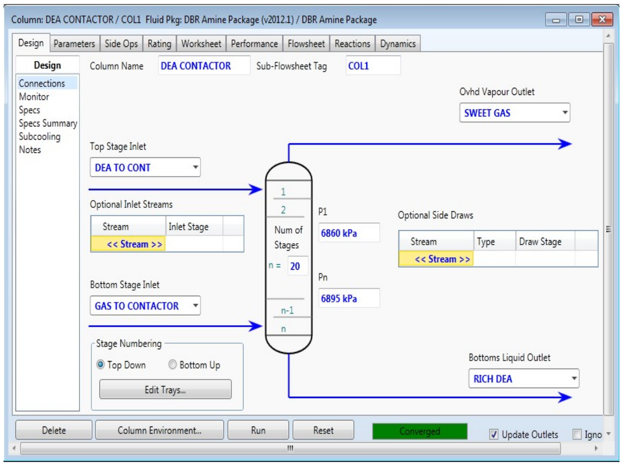
Table 1 Sour gas composition

Component	**Molar Composition**
Nitrogen	0.0016
Carbon Dioxide	0.0480
Hydrogen Sulphide	0.0171
Methane	0.8631
Ethane	0.0390
Propane	0.0092
i-Butane	0.0026
n-Butane	0.0029
i-Pentane	0.0014
n-Pentane	0.0012
n-Hexane	0.0018
n-Heptane	0.0071
Water	0.0050



Stream Name	SOUR GAS
Vapour / Phase Fraction	0.9860
Temperature [C]	20.00
Pressure [kPa]	6895
Molar Flow [kgmole/h]	1100
Mass Flow [kg/h]	2.159e+004
Std Ideal Liq Vol Flow [m3/h]	61.52
Molar Enthalpy [kJ/kgmole]	1.144e+004
Molar Entropy [kJ/kgmole-C]	147.8
Heat Flow [kJ/h]	1.259e+007
Liq Vol Flow @Std Cond [m3/h]	2.592e+004
Fluid Package	DBR Amine Package (v
Utility Type	

Figure 4: Natural gas property estimated at inlet conditions



Column Name: DEA CONTACTOR
Sub-Flowsheet Tag: COL1
Top Stage Inlet: DEA TO CONT
Ovhd Vapour Outlet: SWEET GAS
Optional Inlet Streams:

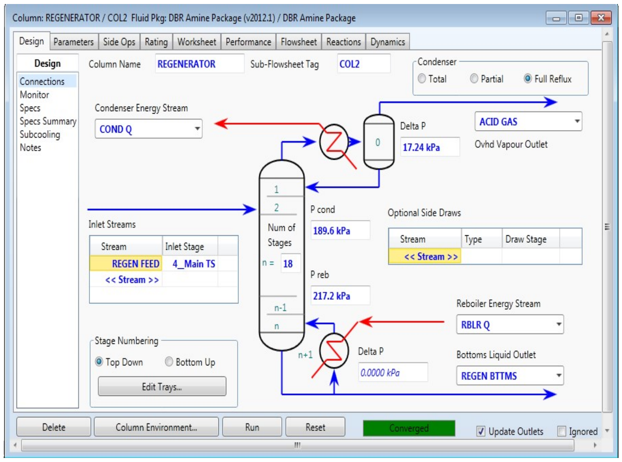
Stream	Inlet Stage
<< Stream >>	

Num of Stages: n = 20
P1: 6860 kPa
Pn: 6895 kPa
Optional Side Draws:

Stream	Type	Draw Stage
<< Stream >>		

Bottom Stage Inlet: GAS TO CONTACTOR
Bottoms Liquid Outlet: RICH DEA
Stage Numbering: ● Top Down ○ Bottom Up

Figure 5: Converged absorber



Column Name: REGENERATOR
Sub-Flowsheet Tag: COL2
Condenser: ○ Total ○ Partial ● Full Reflux
Condenser Energy Stream: COND Q
Delta P: 17.24 kPa
Ovhd Vapour Outlet: ACID GAS
Inlet Streams:

Stream	Inlet Stage
REGEN FEED	4__Main TS
<< Stream >>	

Num of Stages: n = 18
P cond: 189.6 kPa
P reb: 217.2 kPa
Optional Side Draws:

Stream	Type	Draw Stage
<< Stream >>		

Reboiler Energy Stream: RBLR Q
Delta P: 0.0000 kPa
Bottoms Liquid Outlet: REGEN BTTMS
Stage Numbering: ● Top Down ○ Bottom Up

Figure 6: Converged regenerator

Figure 7 shows acomplete amine simulation for the base case parameters. The validity of the model was established by matching its performance with the historical data. An average absolute relative error less than 1.3% suggested that the model is representative and useful for optimization.

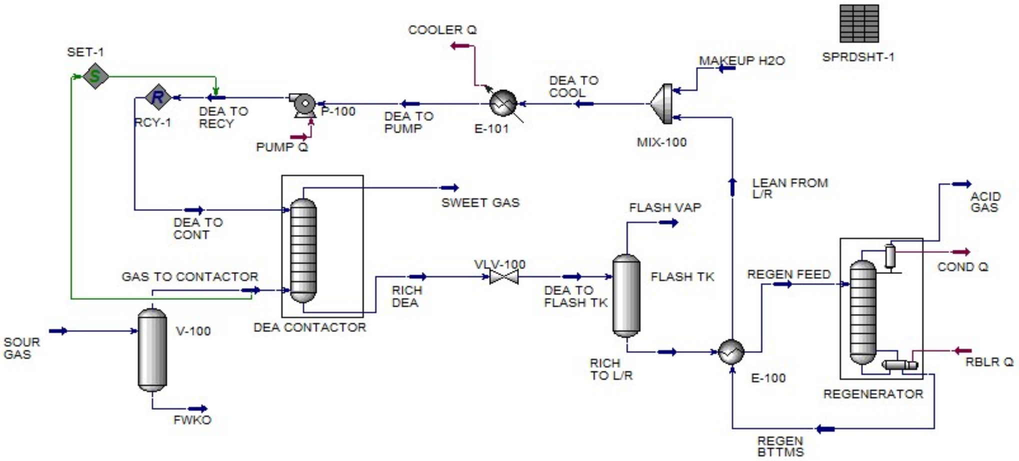


Figure 7: The complete simulation for base case Model

3.3Sensitivity Analysis

Sensitivity analysis shows that the molar flow rate, temperature and number of plates are key process parameters. As shown in Figure 8 and 9, the temperature, number of plates and molar flow rate has a tremendous effect on amount of CO_2 removal. From Figure 8, it is observed that at constant molar flow rate the removal efficiency increases with decreasing number of plates. For example, at 850 kg/h, maximum CO_2 remaining was recorded with minimum numbers of plates. The CO_2 removal decreases as the number of plate decreases until 15 plates. Similar observation was made for different temperature.

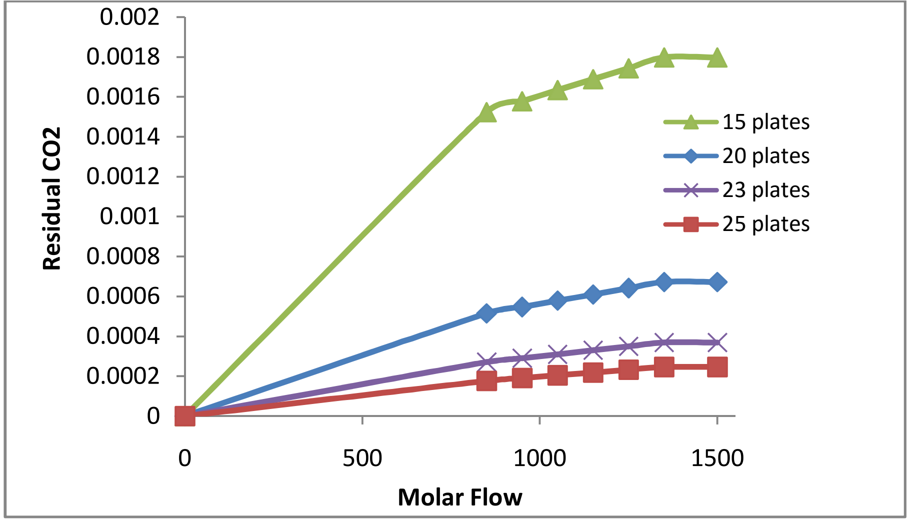


Figure 8 Sensitivity of CO_2 removals to molar flow rate for different number of plates at 20°C and 6898 kpa

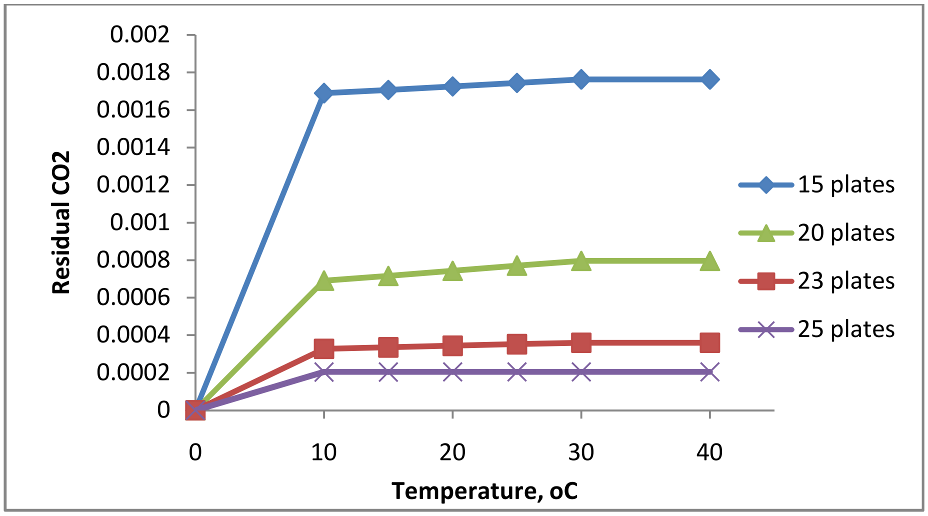


Figure 9 Sensitivity of CO_2 removals to molar flow rate for different number of plates at Molar flow rate of 1150 kg/h at different temperatures

3.4 Process Optimization

For optimization study, the parameters were sampled using Box-Behnken Design (BBD) algorithm. BBD belongs to the family of 3 level experimental design algorithms in which each numeric factor can be varied over 3 levels. Table 2 shows the factors setting for experimentation. An overall of 17 experiments were performed as shown in Table 3. The result was analyzed by analysisof variance using response surface methodology (RSM).

Table 2 Parameter settings for optimization case

Name	Units	Low Actual	High Actual	Low Coded	High Coded
Temperature	oC	10	30	-1	1
Flow rate	kg/hr	850	1350	-1	1
Number of plate		15	25	-1	1

Table 3 Design Matrix for Box-Behnken Design

Std	Run	A:Temperature	B:q	C:NP	CO2 removal
5	1	-1	0	-1	0.046415
10	2	0	1	-1	0.046075
1	3	-1	-1	0	0.047474
8	4	1	0	1	0.047812
2	5	1	-1	0	0.047503
11	6	0	-1	1	0.047825
12	7	0	1	1	0.04769
14	8	0	0	0	0.04747
13	9	0	0	0	0.04747
3	10	-1	1	0	0.047326
17	11	0	0	0	0.04747
9	12	0	-1	-1	0.046492
4	13	1	1	0	0.047219
7	14	-1	0	1	0.047813
15	15	0	0	0	0.04747
16	16	0	0	0	0.04747
6	17	1	0	-1	0.038734

3.5 Response Surface Modelling

The development of valid response surface was based on careful analysis of variance for selection of model regressor and parameter interactions using value of "Prob > F" statistics. The F-statistics can be viewed as the ratio of signal (desirable) to noise (undesirable). The result obtained from the ANOVA is presented in Table 4. TheModel F-value of 1208.55 implies the model is significant with high desirebility. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. It was observed that the probability coefficients (p-value) for T, Q, Np, Q2, Np2, T*Q, and Q*Np were less than 0.05, given a certainty level of 95%. This validate the choice of quadratic model consisted of main, quadratic terms for Q and Np as well as the interaction terms (T*Q and Q*Np).

Table 4 Analysis of variance

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	4.11E-06	7	5.87E-07	1208.55	< 0.0001	significant
T	9.63E-08	1	9.63E-08	198.37	< 0.0001	
Q	1.21E-07	1	1.21E-07	249.24	< 0.0001	
Np	3.29E-06	1	3.29E-06	6776.87	< 0.0001	
Q2	7.72E-08	1	7.72E-08	159.12	< 0.0001	
Np2	4.98E-07	1	4.98E-07	1025.61	< 0.0001	
T*Q	4.67E-09	1	4.67E-09	9.61	0.0147	
Q*Np	1.99E-08	1	1.99E-08	41.05	0.0002	
Residual	3.88E-09	8	4.85E-10			
Lack of Fit	3.88E-09	4	9.71E-10			
Pure Error	0	4	0			
Cor Total	4.11E-06	15				

3.6 Factors interaction

The ANOVA table shows clearly that all the selected main factors have significant effects on the CO2 removal. The interaction of some of these factors exhibits significant effect on the model developed. Figure 9 and 10 are the 3-dimensional diagrams showing the main effects of flow rate, temperature, number of plates and their interaction on the CO_2 removal. A close observation of the base contour in these diagrams shows that main factors Q, T and Np independently have influence on the response setting a variable in its base value. For instance, as can be observed in

Figure 10, as the temperature increases from minimum to its maximum value, the amount of CO_2 removed was observed to increased. This observation is expected because transport of masses is enhanced at higher temperatures. Thus, temperature controls the transmissibility of mass and as such as temperature increases, gas mobility increases so also the CO_2 removed. Keeping temperature constant at maximum value and increasing molar flow rate from minimum value to maximum, the amount of CO_2 removed increass untill around 1100 kg/hr when a further increase in flow rate resulted in a decrease in amount of CO_2 removed. There is therefore an optimality conditions for efficient absorption of CO_2 in the absorber.

Figure 11 shows the interaction of number of stages (Np) and amine flow rate (Q). The absorber number of stages have a dominat effect on the efficiency of the plant. For example, at low amine flow rate say 850 kg/hr, the amount of CO_2 removed increases with number of plates. Similarly, by setting the amine flow rate at its maximum value, the same observation was observed but with a corresponding lower efficiency. Thus it is desired to establish the optimum conditions for maximum removal of impurity from the natural gas.

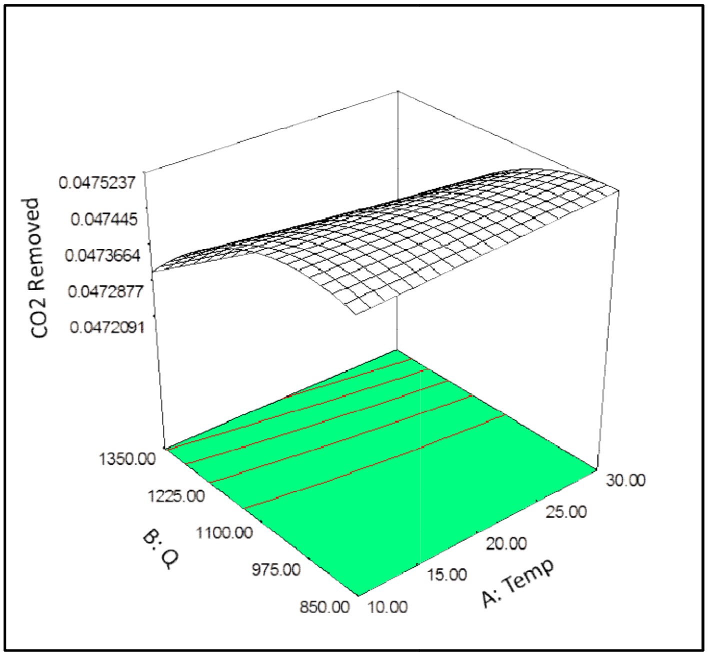


Figure 10 3-Dimensional diagram for the effect of mass flow rate (Q), temperature (T) and and their interaction on CO_2 removal.

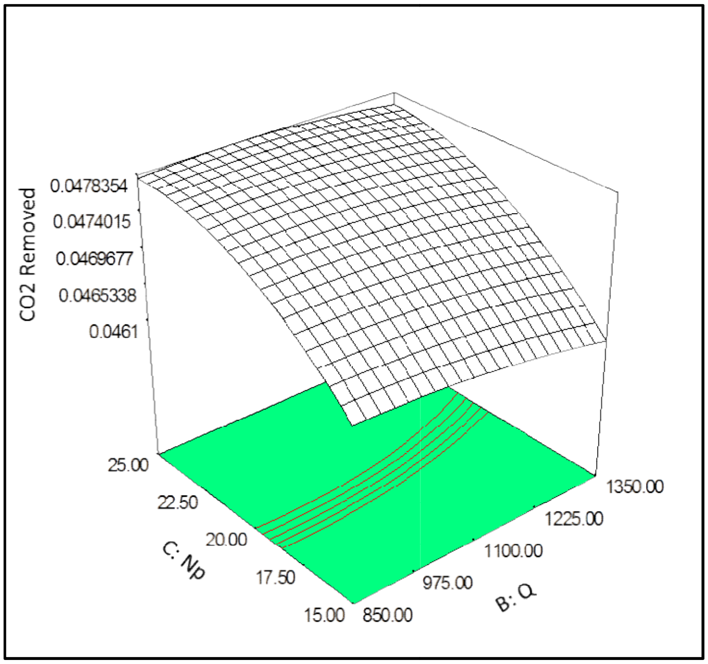


Figure 11 3-Dimensional diagram for the effect of mass flow rate (Q), number of plate (Np) and and their interaction on CO_2 removal.

To find the optimum process parameters that favor removal of CO_2 from the gas stream, an optimization problem was set up thus:

Maximize the objective function:

$$\begin{aligned} CO_2\ removed = {} & 0.038604 + 1.33647E - 05 * T \\ & + 1.64146E - 06 * Q \\ & + 6.66542E - 04 * N_p \\ & - 1.35878E - 09 * Q^2 - 1.4594E \\ & - 05 * N_p^2 - 1.366E - 08 * T * Q \\ & + 5.646E - 08 * Q * N_p \end{aligned}$$

Subject to

$10 \leq T \leq 30,$

$850 \leq Q \leq 1350$

$15 \leq N_p \leq 25$

The standard deviation, multiple regression correlation coefficient, and predicted R-square values for the response surface model representing the objective function are 0.00002203, 0.9982 and 0.9911 respectively.The problem was solved numerically with the target criteria (CO_2 removed) set at maximum leaving the constraints at their ranges.

Figure 12 shows the ramp of numerical optimization in response surface methodology for temperature, mass flow rate and number of plate with CO_2 removedof 0.0475238 moles. Thus, the optimum operating conditions for column CO_2removal weretemperature of 30 °C, mass flow rate of 868.75 kg/hr and 20 numbers of plates.

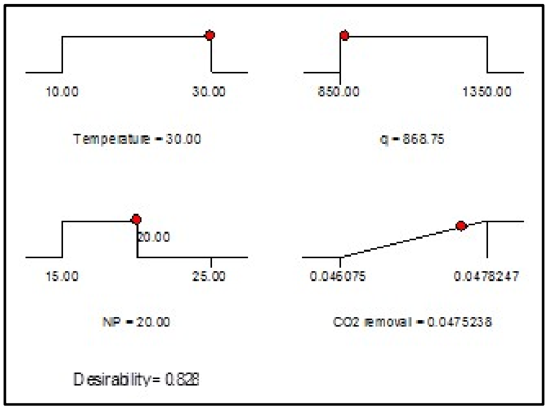


Figure 12 Ramp of numerical optimization in response surface methodology for Temperature, mass flow rate and numbers of plates for CO_2 removal from a natural gas.

4 Conclusions and Recommendations

4.1 Conclusions

An optimization approach for CO_2 removal by integrating process simulator with the response surface methodologies is presented. Theimpacts of the amine flow rate, sour gas inlet temperature and absorber number of plates were analyzed. The results show that the number of absorber plates has a significant impact on the CO_2 removal. The efficiency was optimum as the number of plates reduces from 25 to around 20 for the selected solvent. The increase in amine circulation rate led to corresponding increase in amount of CO_2 removed. This could however increase the cost of the operation. The inlet temperature of the sour gas slightly affects the CO_2 removal. Thus, as the temperature decreases it is expected that the amount of energy requirement will tend to decrease.

4.2 Recommendations

Based on the experiment conducted, analyses and conclusions of this work, the following are recommended:

(i). Detailed optimization framework for integrated equipment and process design parameters is recommended.

(ii). The definition of the objective function in terms of cost is desirable. The use of Net Present Value (NPV) for example could give a more realistic analysis taking into account all the CAPEX and OPEX.

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