## REDUCING AND CONTROLLING THE HYDROCARBON EMISSIONS FROM RICH AMINE REGENERATOR UNITS IN THE NATURAL GAS SWEETENING PROCESS: A CASE STUDY AND SIMULATION

## R. K. Abdulrahman<sup>1</sup> and I. M. Sebastine<sup>2</sup> and <sup>3</sup>R. A. Suramairy

 <sup>1</sup>Faculty of Engineering,
 Koya University, Kurdistan Region, F.R. Iraq.
 <sup>2</sup> School of Science and Engineering, Teesside University, UK.
 <sup>3</sup>Faculty of Engineering,
 Koya University, Kurdistan Region, F.R. Iraq.

**ABSTRACT**: Natural gas has been the most popular fossil fuel in recent years, and the demand for it has been dramatic. In fact, natural gas possesses several useful features: it has a high heating value, it can be utilised as a raw material in several petrochemical industries and it is a cheap fuel source. However, raw natural gas usually contains a variety of nonhydrocarbon components, e.g., acid gases, helium, nitrogen and mercury. Raw natural gas sources with large amounts of acid gases are known as sour gas. Sour gases should be treated and sweetened to meet natural gas pipeline specifications and sale contracts. The amine gas sweetening process is widely utilised in the gas industry, either to reduce or to remove acid gases from sour natural gas streams. Indeed, amine gas sweetening has several advantages over other sweetening processes; it is more economical than other processes, and it operates continuously. Indeed, the global hydrocarbon emissions from the oil and gas industries have been dramatic. Moreover, methane, ethane and propane may be the most obvious gases that are emitted by the natural gas industry. In many cases, these emissions occur from gas processing units, e.g., gas sweetening and gas dehydration processes. In fact, these hydrocarbon gas emissions contribute to global warming and environmental pollution. Moreover, hydrocarbon emissions lead to huge losses of precious hydrocarbons every hour. Therefore, this study aims to study the effects of the solvent circulation rate on the hydrocarbon carryover from the amine gas sweetening using Aspen HYSYS software. The study also used a Murban gas stream in the simulation process because it is loaded with a high concentration of acid gases. The study determined that the amine circulation rate may have significant effects on the hydrocarbon losses during the sweetening process. Moreover, the study also recommended several methods to reduce this effect and the emission, e.g., balancing the amine circulation rate with both the sweetening efficiency and the hydrocarbon emissions.

**KEYWORDS**: Natural gas sweetening, Murban field, Amine solution, Process simulation, Aspen HYSYS, Process optimisation, Global warming, Hydrocarbon emission, Amine circulation

#### NOMENCLATURE

- $RMM \quad Relative \ Molecular \ Weight \quad H_2S \quad Hydrogen \ sulphide$
- CO<sub>2</sub> Carbon dioxide DEA Dimethylamine
- BTEX Benzene, toluene, ethylbenzene, and xylenes

## **INTRODUCTION**

In recent years the demand for and consumption of natural gas have been notable. Indeed, natural gas possesses several advantages, e.g., a high heating value, environmental friendliness and low cost. However, raw natural gas may contain several impurities, e.g., water vapour and acid gases [1]. Therefore, it should be processed in a natural gas processing plant to either remove or reduce these impurities (i.e., natural gas sweetening and dehydration). Indeed, during the operation of these processes large quantities of hydrocarbons (for example, methane and ethane) may be emitted into the environment, and these hydrocarbons could be contributing to the global warming phenomena. In fact, global methane emissions from the natural gas industry have been inadequately recognised and quantified in many countries [2]. As a result, in many cases, the emissions are not well known even at the country level [3]. Indeed, in many cases, the emissions from the wellhead and gas processing sector are included but emissions from the equipment associated with the fractionation of propane, butane, and natural gas liquids were excluded [1]. Due to growing environmental concerns, limiting the hydrocarbons emissions (e.g., BTEX and methane) from gas processing plants is of primary importance. Indeed, glycol units have been under scrutiny for some time [2]. However, the amine process has recently been targeted as well. Indeed, switching from coal and oil to natural gas fuels could serve as an interim measure to reduce the effects of global climate change caused by greenhouse gas emissions. Methane is the main greenhouse gases and its content in the atmosphere has increased dramatically over the past 300 years [3]. Amine solutions can absorb a considerable amount of light hydrocarbons, e.g., methane, ethane, propane and BTEX. Furthermore, these dissolved hydrocarbons in rich amine solution are obtained via contact with feed gas during the sweetening process. The rich amine solution with dissolved hydrocarbons is processed in the amine regenerator unit to recover the lean amine and reuse it in the sweetening process [3]. In fact, the dissolved hydrocarbons in the rich amine solution are released in the regenerator's overhead. This overhead either vents to the atmosphere or feeds a sulphur recovery unit. The HC content discharged from the regenerator vent to the atmosphere must comply with the recently established stringent regulations. For acid gas feeds to a Claus unit, a high HC content may result in catalyst fouling, a low quality sulphur product, or the need for a more sophisticated burner design. However, many oil and gas companies may release these hydrocarbons into the environment. Amine gas treatment is considered one of the most common processes in petrochemical plants, onshore refineries and offshore natural gas processing plants, as well as other industries [2].

## **Basic Amine Process Descriptions**

The amine process could be considered the most economical and common process in the gas industry sector. This process is uses an alkanamine solution as a chemical solvent to remove acid gases from natural gas streams [7]. Alkanamines possess high affinity toward acid gases, and there are several types of amines that are used in the amine process, e.g., monoethanolamine (MEA) and dimethylamine (DEA). The amine process consists of several operation units: the contactor tower, regenerator tower and heat exchanger [6]. Figure (1) shows a typical amine process.

The chemical reaction of amines with H<sub>2</sub>S and CO<sub>2</sub> are given below:

 $2RNH_2 + H_2S = (RNH_3)_2S$ 

 $2RNH_2+CO_2 = RNHCOONH_3R *R = mono, di, tri-ethanol.$ 

## Figure 1: General flow diagram for an amine plant [6].



#### Murban Gas Composition and Water Content Calculations

The Murban gas stream composition and operating conditions are show in table (1). Based on the gas composition, it appears that these values were determined on a dry basis. Thus, estimating the water content before the process design or simulation is recommended.

			Component	Mole %
Murban Field data			Methane	76.4
			Ethane	8.1
Location	United	Arab	Propane	4.7
	Emirates			
Gas density	0.65 Kg/m <sup>3</sup>		Butane	2.6
Gas S.G (Air=1)	0.67		pentane	1.9
Pressure	7000 K.pa		Carbon dioxide	4.5
Temperature	38 °C		Nitrogen	0.1
Flow rate	120,000 stdr	n <sup>3</sup> /hr	Hydrogen	1.7
(Assumed)			sulphide	

Table 1: Murban associated natural gas [4].

The natural gas water content can be estimated using the McKetta-Wehe Chart [6]. Therefore, the raw natural gas water content is approximately 1000 kg/MMstd.m<sup>3</sup> = 128.265 kg/hr. The new natural gas composition could be calculated and summarised as shown in table (2).

Component	Mol%	Mwt	Kmol / hr	kg/hr	Mol%
H <sub>2</sub> S	1.7	34.076	91.0145	3101.41	1.69774
CO <sub>2</sub>	4.5	44.01	240.921	10602.9	4.49402
N2	0.1	28.02	5.3538	150.013	0.09987
CH4	76.4	16.02	4090.3	65526.6	76.2984
C2H6	8.1	30.07	433.658	13040.1	8.08923
СзНа	4.7	44.09	251.628	11094.3	4.69375
C4H10	2.6	58.123	139.199	8090.65	2.59654
C5H12	1.9	72.15	101.722	7339.25	1.89747
H <sub>2</sub> O		18	7.12585	128.265	0.13292
TOTAL	100		5360.92	119074	100

Table 2: Murban natural gas compositions and quantities (wet basis).

## Murban Sour Gas Sweetening Simulation

The amine gas sweetening plant for Murban sour gas is simulated using Aspen HYSY. DEA is utilised as an aqueous absorbent to absorb acid gases from the sour gas stream. An amine fluid was adopted for the simulation work, and figure (2) shows the Murban sour gas sweetening process. It is important to use an inlet gas separator to remove any undesirable impurities, e.g., solid particulates and liquids. The amine contactor is also an important part of the sweetening plant, and it has certain requirements, for example, stream temperature and pressure. Moreover, the rich amine needs to be regenerate, which could be achieved by installing the amine regenerator after the amine heat exchanger. The installation of a flash tank for the rich amine solution is important to avoid any technical problems that might be caused by rich amine impurities. The water content of the stream should also be considered in the process to maintain the amine concentration during the process. See appendix (A) for more details of the HYSYS work.





# **RESULTS AND DISCUSSION**

First, the study used a 35 % (w/w) DEA amine solution to perform the sweetening process, which achieved an acceptable sweetening result. Figure (3) shows the relationship between the amine circulation rate and the hydrogen sulphide mole percent in the sweet gas stream. Furthermore, figure (4) shows the relationship between the amine circulation rate and carbon dioxide mole percent in the sweet gas stream.

# Figure 3: Effects of the 35 % DEA circulation rate on the hydrogen sulphide mole fraction in the sweet gas stream.



Figure 4: Effects of the 35 % DEA circulation rate on the carbon dioxide mole fraction in the sweet gas stream.



Based on figure 3 and 4, increasing the 35 % DEA circulation rate will lead to an increase the acid gas removal. Moreover, at an amine rate of 400 m<sup>3</sup>/hr the amount of H<sub>2</sub>S in the sweet gas was approximately 5 ppm. However, the optimum amine rate is about 300 m<sup>3</sup>/hr, which

results in 4 ppm  $H_2S$  in the sweet gas stream, resulting in the optimum liquid residence time on the tray. However, the cost of the amine process should be considered because any increase in the amine rate leads to an increase in the operation cost.

Figure (5) shows the relationship between the amine circulation rate in cubic meters per hour and the hydrocarbons emission from the amine regenerator unit.

# Figure 5: The relationship between the 35 % DEA rate and the HCs emitted from the amine regenerator unit in kg/hr.



Based on figure (5), increasing the DEA circulation rate will lead to an increase in the amount of hydrocarbons emitted from the rich amine regenerator unit. The total hydrocarbon emission at an amine circulation rate of approximately 530 m<sup>3</sup>/hr is quite high, approximately 25 kg/hr. The emissions at 200 m<sup>3</sup>/hr are lower, approximately 5 kg/hr. Thus, a 300-m<sup>3</sup>/hr amine circulation rate is recommended because it achieves an acceptable sweetening result and produces a moderate hydrocarbon emission of approximately 14 kg/hr.

## CONCLUSIONS

This study successfully simulated a Murban gas sweetening process using Aspen HYSYS. Moreover, it attempted to investigate and describe the effects of the lean amine circulation rate on the hydrocarbon emissions or losses from the sweetening process. The Murban gas contained a high concentration of acid gases. Moreover, the simulation work showed high removal of the acids, which met the gas pipeline specifications. A 35 % DEA solution with a 300 m<sup>3</sup>/hr circulation rate achieved optimum gas removal, and the outlet natural gas stream met the gas pipeline specifications. Furthermore, using 35 % DEA is recommended for the process. The amine circulation rate has a significant effect on the hydrocarbon losses from the amine regenerator tower. In other words, increasing the amine circulation rate will increase the hydrocarbon emissions into the environment. Therefore, maintaining a moderate amine circulation rate could reduce the hydrocarbons emissions from amine regenerator unite.

#### REFERENCES

- [1].Junhong, T., Zhengyu, B. and Wu, X. 2008. Geological emission of methane from the Yakela condensed oil/gas field in Talimu Basin, Xinjiang, China. Journal of environmental sciences 20(1), pp. 1055 -1062.
- [2].Kirchgessner, D. and Lotf, R. 1997. Estimate of methane emission from the US natural gas industry. Chemosphere 35(6), pp. 1356-1390.
- [3].Barroso, J., Solis, J., Ballester, J and Pina, A. 2009 Evaluation of methane emissions from polyethylene gas distribution systems at medium pressures. Journal of Natural Gas Science and Engineering 1 (4), pp. 144 -153.
- [4]. Roussak, O. and Gesser, H. (2012) *Applied Chemistry: A Textbook for Engineers and Technologists*. New York: Springer.
- [5]. William, B. and Ghalambor, A. (2007) *Petroleum production engineering: a Computer-assisted approach*. Oxford: Gulf Professional Publishing.
- [6].Manning, F. and Thompson, R. (1991) *Oilfield Processing of Petroleum: Natural gas.* Oklahoma: PennWell Books.
- [7]. Abdel-Aal, K. and Aggour, M. (2003) *Petroleum and Gas Field Processing*. New York: CRC Press.

## Appendix (A)

## Figure: Shows the simulation basis manger.

Simulation Basis Manager	
Component Lists Databank Selection HYSYS Databanks Component List - 1 [HYSYS Databanks] Delete Copy Import View Export Refresh Reimpgt Convert	
Components Fluid Pkgs Hypotheticals Oil Manager RefSYS Assay Manager Reactions Component Maps User Prop	erties_
Enter EVT Environment	nt

Figure: Shows the simulation fluid package manger.

🖕 Fluid Package: Basis-1			
<ul> <li>HYSYS</li> <li>Aspen Properties</li> <li>COMThermo</li> <li>Property Package Selection</li> <li>Amine Pkg</li> <li>Antoine</li> <li>Astrone</li> <li>Astrone&lt;</li></ul>	Thermodynamic Models for Aqueous Amine Solutions <ul> <li>Kent-Eisenberg</li> <li>Li-Mather</li> </ul> Vapor Phase Model <ul> <li>Ideal</li> <li>Non-Ideal</li> </ul>		
Component List Selection Basis-1 Component List (HYSYS Databar View			
Set Up         Parameters         Binary Coeffs         StabTest         Phase Order         Rxns         Tabular         Notes           Delete         Name         Basis-1         Property Pkg         Amine Pkg - KE         Edit Properties			

<sup>a</sup> Component List View: Basis-1 Component Lis	t [HYSYS Databanks]	
Add Components Components Traditional Hypothetical Selected Components Nitrogen H2C CO2 Methane Ethane Propane n-Pertane H2O DEAmine	Components Available in the Component Li Match C Sim Name C Full Name / Sync iButane iC4 iC5 nHexane C6 nHexane C6 nHexane C6 nHexane C7 nHexane C8 nNonane C9 nDecane C10 nC11 C11 nC12 C12 nC13 C13 C13 C14 C14 nC15 C15 View Component View Component View Component View Component View Synonyms Clus	View Filters           onym         C           CSH12         C           CSH14         C           CSH18         C           CSH19         C           CH10         C           CH14         C           C1H2         C           C1H22         C1H24           C12H26         C13H28           C13H28         C14H30           C15H32         C16H34           C17H36         C           C18H38         ✓
Selected Component by Type		
Delete	Name Basis-1 Component List	

Figure: Shows the simulation component manger.

Figure: Shows the simulation contactor tower manger.

" Column: Conta	ctor-01 / COL3 Fluid Pkg: Basis-1 / Amine Pkg - KE
Design	Column Name Contactor-01 Sub-Flowsheet Tag COL3
Connections Monitor	O <u>v</u> hd Vapour Outlet Sweet gas ▼
Specs Specs Summary Subcooling Notes	Top Stage Inlet       Dx       Dptional Inlet Streams       Stream       Inlet Stage   P1 Optional Side Drgws
	I         Stream >>         Stream
	Stage Numbering © Top Down © Bottom Up Edit Trays
Design Parame	sters Side Ops Rating Worksheet Performance Flowsheet Reactions Dynamics
Delete	Column Environment Run Reset Converged 🔽 Update Outlets 🗆 Ignored

Vol.3, No.2, pp.17-26, June 2015

Published by European Centre for Research Training and Development UK (www.eajournals.org)

* Column: T-100	) / COL4 Fluid Pkg: Basis-1 / Ami	ine Pkg - KE
Design Connections Monitor Specs Specs Summary Subcooling Notes	Column Name T-100 Condenser Energy Stream Q2 Injet Streams Stream Inlet Stage Y1 5_Mair << Stream >> Stage Numbering © Top Down © Bottom Up Edit Trays	Sub-Flowsheet Tag COL4 Congenser C Total  Partial Full Reflux Delta P Delta P Delta P Delta P Delta P Delta P Delta P Dyenhead Outlets S1 P cond Delta P Delta P Dyenhead Outlets S1 P cond Stages P reb 190.0 kPa Reboiler Energy Stream n Delta P Delta P Reboiler Energy Stream Delta P Bottoms Liguid Outlet R A P cond Delta P Delta P De
Design Param		
Delete	Column Environment Run	Reset Converged Vpdate Outlets I Ignored

Figure: Shows the simulation regenerator tower manger.

Figure: Shows the material stream for acid gases that were emitted from amine regenerator unit.

Material Stream: A	Acid Gases St		
Worksheet Conditions Properties Composition Oil & Gas Feed Petroleum Assay K Value User Variables Notes Cost Parameters Normalized Yield:	Nitrogen H2S CO2 Methane Ethane Propane i-Butane n-Pentane n-Pentane n-Pentane H2O DEAmine ◀	Mass Flows 0.0000 12762.7109 6008.8034 10.5249 6.0589 1.5970 0.0000 0.0078 0.0000 0.0073 0.0000 1100.7442 0.0000 ► 390.45435 kg/h	
4	Edit View Prop	erties Basjs	
Worksheet Attachments Dynamics			
Delete	Define from Other Stream 💠 🜩		