A New Method to Enhance Separation of Acid Gas from Natural Gas by Mixed Amine Solution

- Abolfazl Gharibi Kharaji

  Department of Chemical Engineering, Isfahan University, Isfahan , Iran
- Vahid Madadi Avergani* And Parviz Darvishi

  Department of Chemical Engineering, Yasouj University, Yasouj, Iran

  *(E-mail: v.madadi@yu.ac.ir)

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Abstract

Application of mixed amine solution in gas sweetening unit decreases the operation cost and corrosion rate. Also it increases the amount of sulfur in acid gas stream that exits from sweetening and enters to sulfur recovery units. Gas sweetening unit of Bidboland gas refinery (BGR) was simulated by Hysys software. Simulation of BGR had good agreement with industrial data. The parameters such as CS (carbon dioxide in sweet gas), SSRU (the amount of H2S in outlet acid gas stream from stripper to sulfur recovery unit), RAL (rich amine loading) and HPA (reboiler duty per amine circulation rate), were compared for ten blends of DEA (Diethanolamine) and MDEA (Methyl Diethanolamine). According to technical specified parameters, mixed amine with composition of 40 wt. % MDEA and 10 wt. % DEA identified as a good amine blend for gas sweetening unit in BGR. JOGPT. Because Photonics is produced in DOC, strict adherence to format

Keywords: Gas Sweetening, Bidboland Gas Refinery, Hysys, Mixed Amine, Hydrogen Sulfide

1. Introduction

Natural gas is the most important source after fuel gas because of its clean combustion and reduction of the atmosphere pollution. Natural gas contains impurities such as carbon dioxide, hydrogen sulfide and sometimes traces of Carbonyl sulfide, carbon disulfide and mercaptans.

MDEA selectively removes H_2S from natural gas streams while piperazine acts mainly as a corrosion inhibitor and surfactant. A corrosion inhibitor is a chemical compound which added in small concentration stops or slows down corrosion of metals and alloys. The slower rate of reaction of CO_2 with MDEA is compensated through the addition of small amounts of rate-promoting agents such as DEA or piperazine [1]. So blends of activating primary or secondary amines (such as DEA) can be improved with tertiary amines (such as MDEA) for the removal of carbon dioxide from natural gas [2]. MDEA is a compound that used in oil refinery industry to absorb and strip hydrogen sulfide and carbon dioxide. Due to technological or human malfunctions, MDEA may be found in process waters and afterwards transported to the wastewater treatment plant [3].

Several chemical solvents are available for gas sweetening processes, almost being based on alkanolamine products. Sour gas purifying facilities use the process of chemical absorption by alkanolamines to remove hydrogen sulfide and carbon dioxide from raw natural gas. Hydrogen sulfide must be removed from the gas before using due to its highly corrosively and toxicity. Aqueous solutions of alkanolamines absorb acid gas at lower temperatures and release the acid gases at higher temperatures. This process allows the separation of carbon dioxide and hydrogen sulfide from natural gases.[4] The main alkanolamine products used in the gas sweetening industries are Mononethanolamine (MEA), Diglycolamine (DGA), Diethanolamine (DEA) and Methyl Diethanolamine (MDEA). Advantages and disadvantages for amine types are mentioned in Table 1.

Table 1: Advantages and Disadvantages for Amine Solutions[5, 6]

Advantage	Disadvantage	Amine Type
• Non selective removal • Degrading by mercaptans • High vapor pressure • Needs reclaimer	• Rapidly reaction with acid gases • Largest carrying capacity for acid gases • Separates easily from acid gas • Less circulation rate	Primary Amine
• Less reactive than primary amine • Non selective removal	• Low degrading by mercaptans • High Chemically stable • Low vapor pressure	Secondary Amine
• Less reactive with acid gas • Low absorbing for CO_2	• Selective removal for H_2S • Highly stable • Use with high concentration • Energy saving	Tertiary mine

Recently attention has been focused on using amine blends for gas sweetening due to compensating single amine solution problems. A promising blend has a high capability for loading capacity, high reaction rate, low operating cost, low corrosive tendencies and high resistance to degradation [7]. MDEA is one component that used for the absorption and stripping of hydrogen sulfide and carbon dioxide, as well as and the removal of carbonyl sulfide (CS) from natural gas in natural gas sweetening processes [8, 9].

Compared to the most common alkanolamines, the tertiary amine (MDEA) is known for its lower regeneration cost, its thermal and chemical degradation resistance and lower corrosion rate. In addition, it has capability for selective H_2S removal in the presence of CO_2 and removal of both H_2S and CO_2 simultanously [10]. Glasscock et.al showed that MDEA interfere in DEA kinetics, in other hand increase DEA rate of reaction with addition MDEA [11]. Carbamate ions ($R_2NH^+COO^-$) produced during CO_2 absorptions with primary and secondary amines. While CO_2 absorptions with tertiary amines were accompanied with formation of carbonate and bicarbonate. Since reaction heat of carbamate is higher than carbonate, energy cost of primary and secondary amines expected higher than tertiary amines [12, 13] .

In this study, the effect of mixed amine concentrations were investigated on CO_2 mole fraction of sweet gas (CS), H_2S mole fraction of acid gas stream (SSRU), rich amine loading (RAL) and reboiler duty per amine circulation rate (HPA). RAL is summation of acid gas moles (CO_2+ H_2S) per amine moles and it's dimensionless. In order to define parameters, the best blend of amines was selected.

2. Simulation Description

2.1. Bidboland Gas Refinery (BGR)

Bidboland Gas refinery (BGR) which located in Khuzestan, state of I.R. Iran, is the first gas refinery in Middle East. Sour gas as a feed comes from Aghajari field & Asaluyeh region (Pars Special Energy Economic Zone) with the rate of 240 MMSCFD and maximum of 2.85% acid gas (Bidboland site). Sour gas was treated by four units and reach to pipeline specifications (i.e. less than 4ppm for H_2S). A portion of sweet gas will be sent to IGAT I (Iranian gas transmission pipeline I) and another part goes to NGL (Natural Gas Liquids) plants. For sweetening gas need to be passed through an amine solution. Amine solution at BGR firstly was MEA and after a while due to MEA degradation and high steam consuming need to be regenerated , DEA was replaced and recently sour gas replaced by activated MDEA for a unit.

2.2. Gas sweetening unit

Sour gas that contains CO_2 and H_2S firstly enters scrubber to remove its free liquids, solid materials and any contaminations. The gas from scrubber enters the bottom of absorber and flows upward through column with counter-current contact with aqueous amine solution (Lean Amine) that comes from top of absorber. Chemical reactions between amine and acid gas occurs and amine solution absorbs the acid gas according to the following equations to [6, 14];

(1) $H_2S + R_2NH \rightleftharpoons R_2NH_2^+ + HS^-$

(2) $CO_2 + 2R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCOO^-$

(3) $CO_2 + H_2O \rightleftharpoons H_2CO_3$

(4) $H_2CO_3 + R_2NH \rightleftharpoons R_2NH_2^+ + CO_3H^-$

Reaction is exothermic so the gas temperature increases and sweet gas leaves the top of absorber column and the amine solution with acid gases (Rich Amine) leaves the bottom of the absorber. Absorber in the BGR is packed column with 30 and 3 meters height and diameter respectively, and operates at pressure of 45-60 kg/cm^2. Temperature of lean amine solution is 5-10°C higher than sour gas temperature to prevent forming condensate in absorber column. To regenerate and recycling amine solution, temperature of rich amine must be increased and pressure will be decreased.

In flash drum with suppressing amine pressure to 3-4 kg/cm^2 a part of acid gas removes from rich amine solution and then rich amine passes through tube side of amine/amine heat-exchanger. The rich solution is heated

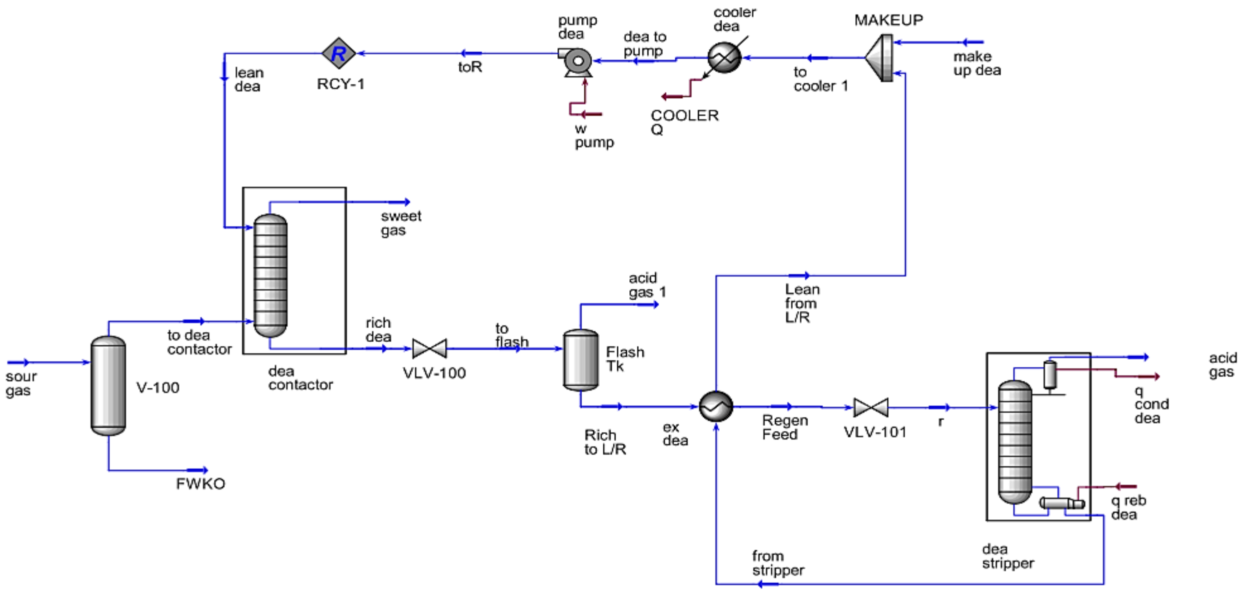

Figure 1: PFD of simulated gas sweetening unit

by regenerated solution (Lean amine) which comes from bottom of regenerator column, so rich amine enters. The regenerator column with 25 and 4 meters for height and diameter respectively which operate at the pressure of 0.4 kg/cm^2 with 19 trays. In regenerator column, rich amine became free from acid gas by heat it up. Temperature of reboiler maintain between 110-116°C by steam flow.

The lean amine drains from bottom of regenerator and release heats at amine/amine heat-exchanger drain and will mix with makes up of water and DEA in order to maintain amine concentration constant and their pressure will increase by pumps and finally will enter to the tops of absorber column. Figure 1 indicates simulated process flow diagram for gas sweetening by DEA solution.

Simulation of gas sweetening unit was performed by Hysys software that equipped with Amine package. Figure 1 indicates process flow diagram for sweetening. First of all, the sour gas was saturated by water stream and then sent to scrubber. The required information for running the program was used by Bidboland data. Flow for makes up was obtained by performing mass balance around the sweetening unit.

3. Results and Discussions

Table 2 clearly showed that results for simulation were compatible with industrial data and had a good agreement with less than 2% relative error. Relative error was calculated by given Equation. Results also showed that H_2S reached to pipeline specification with concentration of 2.1 ppm.

$$Relative\ Error = \frac{|Real\ data - Simulated\ data|}{Real\ data} \quad (5)$$

By comparison of simulation and industrial data, it can be concluded that simulation results were valid, so blends of MDEA and DEA with different mass fractions were used. Results show, while amine concentration increased, energy consumption decreased (discuss later); so the maximum possible mixed amine concentration was used. Typical concentration range for DEA and MDEA are 25-35% and 30-50% by weight in the aqueous solution, respectively [6, 14]. Table 3 shows the high concentration mixed amine solutions that satisfy amine concentration

Table 2: Composition of major components in sour and sweet gas and relative errors with industrial data

Components	Mole fraction of Sour gas in industrial	Mole fraction of Sweet gas in industrial	Mole fraction of Sweet gas in simulation	Relative Error
CO_2	2.17E-02	4.20E-03	4.24E-03	9.64E-03
H_2S	3.30E-03	2.10E-06	2.11E-06	3.54E-03
Methane	8.62E-01	8.81E-01	8.80E-01	1.07E-03
Ethane	6.17E-02	6.29E-02	6.30E-02	1.90E-03
Propane	1.25E-02	1.27E-02	1.27E-02	1.08E-03
i-Butane	1.24E-03	1.25E-03	1.27E-03	1.40E-02
n-Butane	1.78E-03	1.78E-03	1.82E-03	2.22E-02
n-C_4+	3.58E-02	3.62E-02	3.70E-02	2.21E-02

ranges.

The effect of mixed amine concentrations were investigated on CO_2 mole fraction of sweet gas (CS), H_2S mole fraction of acid gas stream (SSRU), amount of energy consumed per amine circulation rate (HPA) and rich amine loading (RAL) which is significant index for corrosion in unit .

Table 3: Different mixed amines that used in simulation

Total mixed amine used in 50 wt. %	Total mixed amine used in 40 wt. %
40% MDEA, 10% DEA	30% MDEA, 10% DEA
35% MDEA, 15% DEA	25% MDEA, 15% DEA
30% MDEA, 20% DEA	20% MDEA, 20% DEA
25% MDEA, 25% DEA	15% MDEA, 25% DEA
20% MDEA, 30% DEA	10% MDEA, 30% DEA
50% MDEA	40% MDEA

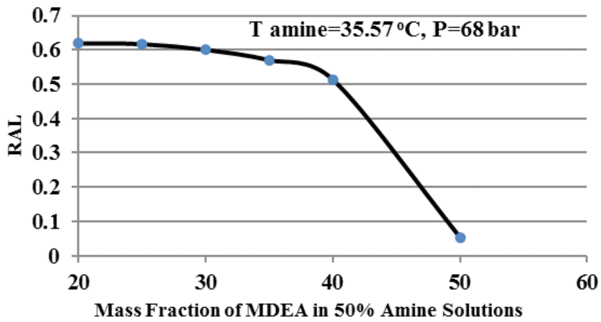

Figure 2: The effect of MDEA concentration on RAL for 50% wt. amine solution

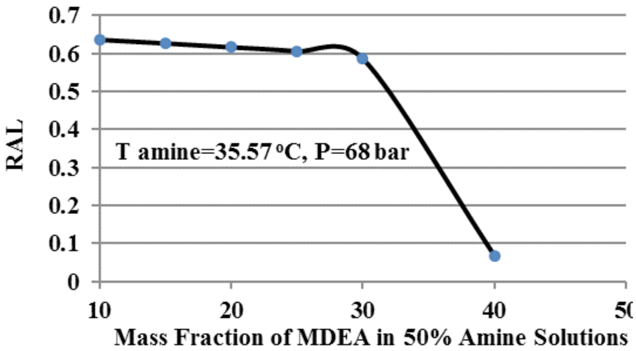

Figure 3: The effect of MDEA concentration on RAL for 40% wt. amine solution

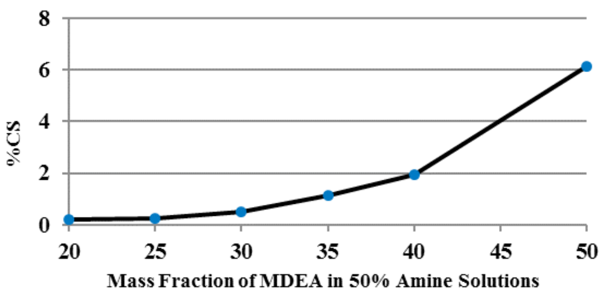

Figure 4: The effect of MDEA concentration on CS for 40% wt. amine solution

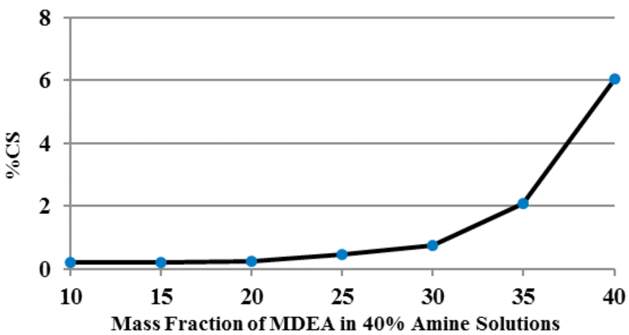

Figure 5: The effect of MDEA concentration on CS for 40% wt. amine solution

The effect of MDEA concentration on rich amine loading, RAL, was shown in figure 2 and 3. Results showed that by increasing in MDEA concentration in two 40 and 50% mixed amine solutions, the amount of RAL decreases.

The results also indicated SSRU and CS parameters were decreased with increase of DEA in amine solution (figure 4 to 7). That behaviors caused from selective removal of H_2S by MDEA, so mass fraction of MDEA was increasable while amount of CS not passing from allowance. With adds up DEA in MDEA solution, order of CS gone down and CS approached to the industrial data. Increase of DEA in MDEA solution greater than 10% wt. had no obvious change in CS parameter, so solution of 10% wt. DEA and 40% wt. MDEA was selected as the best amine blend.

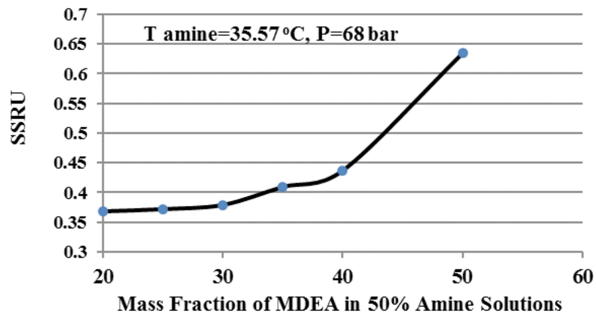

Figure 6: The effect of MDEA concentration on CS for 40% wt. amine solution

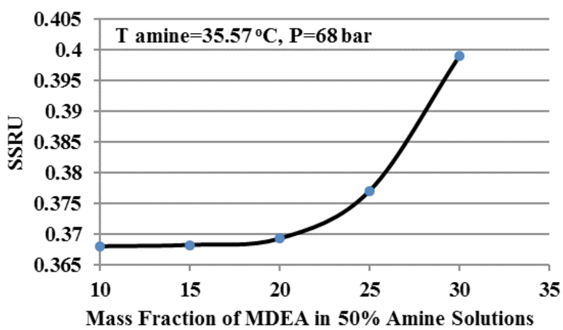

Figure 7: The effect of MDEA concentration on CS for 40% wt. amine solution

HPA parameter was compared for 40 and 50% wt. amine solutions; it was found that HPA for 40% wt. at any blends were greater than 50% wt. with same DEA concentration and amine flow circulation rate. As further work 40% wt. amine solutions were eliminated and results were analyzed for 50% wt. amine solutions. It

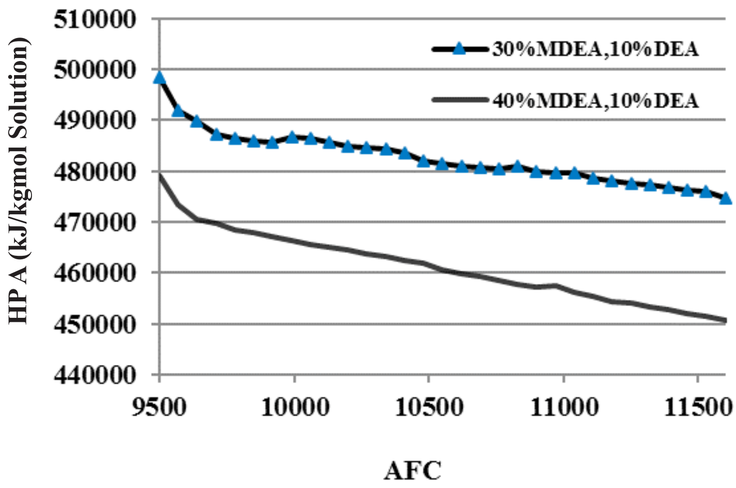

Figure 8: The effect of Amine Flow Circulation on HPA

is necessary to say that HPA represented factor of process economic, unit will be inefficiently while HPA became greater. The figure 8 shows these results. HPA parameter was investigated for mixed amine solution (10% wt. DEA, 40% wt. MDEA) and DEA solution, according to results, for any amine flow rate (AFC) HPA of blend amine was lower than industrial condition (DEA solution). HPA expressed energy consumption in gas sweetening unit and with decrease in HPA process became more economically.

As the results shown in figure 8, in each flow circulation rate, the magnitude of HPA for 50% wt. mixed amine solution is less than 40% wt. Therefore 50% wt. mixed amine by 10% wt. DEA is the best belnd solution for gas sweetening unit in BGR.

Major parameters for real and amine blend solutions were compared in Table 4. Results reveals that replacing of mixed amine with DEA solution, the operation of gas sweetening unit will improve. Investigating of adding MDEA to DEA solution showed that SSRU, RAL and HPA were improved. Expressed parameters had positive effect on SRU efficiency, amount of corrosion and operation costs respectively. While increase of MDEA have no significant effect on CS and SS and sweet gas specifications satisfied allowance, so it can be concluded that mixed amine increased amount of sulfur to SRU and reduced corrosion and operation costs. According to figure 8 and Table 4, blend of 40% MDEA-10% DEA was recommended to BGR to improve the performance of unit.

4. Conclusion

When large amounts of CO_2 are being passed through to the sweet gas at relatively low

Table 4: Comparison of industrial data against offered mixed amine solution

Amine solution	SSRU	CS	RAL	HPA (MJ/m^3)
Real solution	0.157118	4.24E-03	0.470629	217.3832
40% wt. MDEA, 10% wt. DEA	0.160447	4.79E-03	0.257535	146.2427

pressures, it becomes difficult for MDEA to reach pipeline specification for H_2S if the inlet gas contains more than about 1000 ppm H_2S. At these lower pressures, the addition of a more reactive amine clearly enhances the solution ability to remove CO_2. Thus, in situation where MDEA cannot meet the residual gas requirements, the use of amine mixtures can be usually improved the plant performance. At this study, the effect of mixed amine concentrations were studied on CS, SSRU, RAL and HPA parameters in a gas sweetening unit of BGR. According to defined parameters, 40% MDEA-10% DEA such as best blend of amines was selected to reach high amount of SSRU, low RAL and HPA parameters in unit. So this blend was recommended to BGR due to approach the conditions to optimum values in terms of energy consuming, corrosion amount in unit and SRU efficiency.

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یک روش جدید برای افزایش جداسازی اسید گازی از گاز طبیعی با استفاده از مخلوط محلول‌های آمینی

- ابولفضل غریبی خراجی

دانشجوی دکتری مهندسی شیمی، دانشکده فنی و مهندسی، دانشگاه اصفهان، اصفهان، ایران

- وحید مددی اورگانی*

* نویسنده مسئول، استادیار گروه مهندسی شیمی، دانشکده فنی و مهندسی، دانشگاه یاسوج، کد پستی: ۸۱۹۵۷-۱۳۸۴۷، یاسوج، ایران

(ایمیل نویسنده مسئول: **v.madadi@yu.ac.ir**)

- پرویز درویشی

استادیار گروه مهندسی شیمی، دانشکده فنی و مهندسی، دانشگاه یاسوج، کد پستی: ۸۱۹۵۷-۱۳۸۴۷، یاسوج، ایران

چکیـــــــده

استفاده از مخلوط محلول‌های آمینی در واحد شیرین‌سازی گاز هزینه‌های عملیاتی و نرخ خوردگی را کاهش می‌دهد. این در حالی است که این مخلوط‌ها مقدار گوگرد در جریان گاز خروجی از واحد شیرین‌سازی را افزایش می‌دهد و وارد واحد بازیافت گوگرد می‌شود. واحد شیرین‌سازی گاز پالایشگاه گازی بیدبلند با نرم‌افزار Hysys شبیه‌سازی شده است. نتایج حاصل از این شبیه‌سازی تطابق خوبی با داده‌های صنعتی موجود از این واحد دارد. پارامترهایی مانند مقدار دی‌اکسید کربن در گاز شیرین، مقدار گاز سولفید هیدروژن در جریان گاز خروجی از واحد دفع و ورودی به واحد احیاء گوگرد، مقدار محلول آمین غنی‌شده و بار حرارتی بازجوشاننده به ازای نرخ گردش محلول آمین برای ده نمونه مخلوط آمینی متشکل از دی‌اتانول آمین و متیل دی‌اتانول آمین مقایسه شده است. مطابق با پارامترهای خاص تکنیکال، مخلوط آمینی با درصد اجزاء ۴۰ درصد وزنی متیل دی‌اتانول آمین و ۱۰ درصد وزنی دی‌اتانول آمین به عنوان بهترین مخلوط آمینی جهت شیرین‌سازی گاز در پالایشگاه گاز بیدبلند بدست آمده است.

واژگان کلیدی: واحد شیرین‌سازی، پالایشگاه گاز بیدبلند، نرم‌افزار **Hysys**، مخلوط آمینی، سولفید هیدروژن