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# AMINE ABSORPTION COLUMN DESIGN USING MASS TRANSFER RATE SIMULATION

Kh. Mohamadbigy, M. Bazmi, R. Behradi, R. Binesh

*Research Institute of Petroleum Industry, Tehran, IRAN*
*mohamadbeigy@ripi.ir*

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## Abstract

Amine treating is the most common system for gas sweetening that used in petroleum, gas and petrochemical industries. The solution to the dilemma of translating theoretical stages into actual trays and packed bed depths is to use detailed mass transfer, rate-based simulation. This completely new approach to simulating complex chemically reactive, non-ideal separations is particularly suited to amine columns. Comparisons with plant performance test data are used to evaluate this model. The results demonstrate benefits of modeling actual column internals using mass transfer rate-based process simulation. Also, a data bank has been prepared for providing the necessary information by using the most recent data or correlation available in the literatures.

***Key words:*** *Gas Absorption, Sweetening, Mass transfer, Simulation*

### Theoretical background

The removal of acid gas such as hydrogen sulfide ($H_2S$) and carbon dioxide ($CO_2$) from natural gas or natural gas liquid (NGL) is often necessary in gas plants and in oil refineries. The absorption process using aqueous solutions of alkanolamines is often used as a treatment technology.

The figure below illustrates process flow diagram of a typical amine-sweetening unit. The system consists of two major operations: absorption and regeneration.

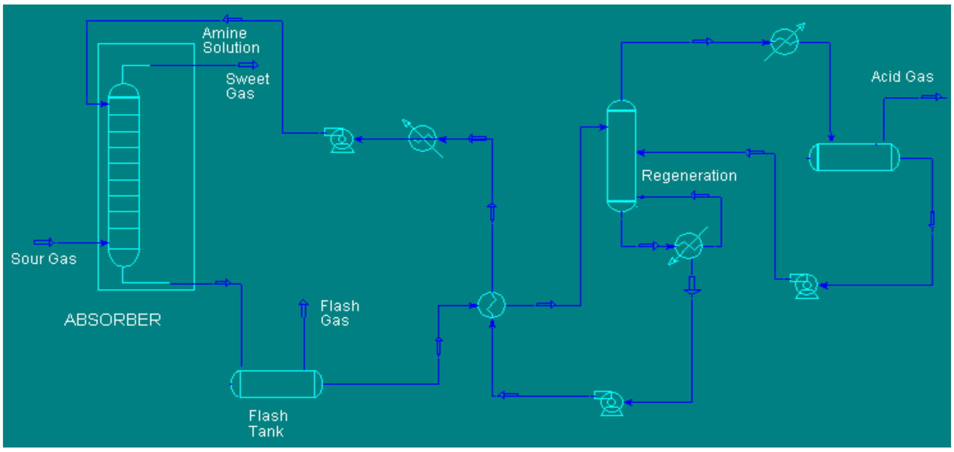

**Fig (1): Process Flow Diagram of amine-sweetening unit**

A natural gas stream containing acid gases ($H_2S$ and/or $CO_2$) is introduced into an absorber column where the stream is counter-currently contacted with an amine solution. The acid gas contents are removed through chemical reactions with the amine. After treatment, the natural gas becomes suitable for consumer use or further chemical processing. This process is often referred to as a gas sweetening process, and treated gas is called sweetened gas or liquid. After the absorption process, the amine solution, (referred to as rich amine solution after selectively absorbing the acid gases) requires regeneration before it can be used to sweeten sour gas again. The regeneration column serves the function of stripping absorbed acid gases from the rich amine solution. A flash tank is usually installed at the outlet of the absorber to permit the recovery of the dissolved and entrained hydrocarbons and to reduce the hydrocarbon contents of the acid gas product.

The flash gas from the flash tank and the stripped acid gas from the regenerator in amine units have the potential to emit hazardous air pollutants and volatile organic compounds.

In processes for total acid-gas removal, treated gas quality is completely determined by phase equilibrium, provided the column contains enough trays or packed depth. This is not the case in selective treating. Here, the extent to which each acid gas is removed is related directly to its mass transfer rate, as well as to the mass transfer rates of each of the other absorbing acid-gas species.

The separation is a rate process rather than one dominated by phase equilibrium. An appreciation of the fact that all alkaline solvents are thermodynamically selective for $CO_2$ but kinetically selective for $H_2S$ is vital to understanding the importance of mass transfer rates to contactor performance.

For a given lean-solvent acid-gas loadings, a high enough tray count or a deep enough packed bed guarantees that the treated gas leaves the contactor in equilibrium with the lean solvent (or for low solvent rates, that the rich solvent leaves in equilibrium with the sour gas). However, as the tray count is reduced (or the bed shortened) the treated gas becomes further and further removed from equilibrium. The thermodynamics of acid gas-amine systems is such that $CO_2$ is the preferred solute because it absorbs by forming a fairly stable chemical bond with the amine. However, the $CO_2$-amine reaction is of finite rate and, in fact, is quite slow in MDEA, for example. On the other hand, $H_2S$ ionizes instantaneously (to bisulfide ion); it does not react with the amine at all, it forms no chemical bonds, and the ionization reaction is immediately reversible. Thus, the chemical reaction kinetics is much faster for $H_2S$; therefore, $CO_2$ absorbs more slowly. At short contact times (read low interfacial areas, small tray counts, short packed beds) $H_2S$ absorbs at a higher rate than $CO_2$, and so $H_2S$ is preferentially absorbed. At long contact times (high interfacial areas, many trays, deep beds), $CO_2$ absorbs more completely, albeit more slowly, and $CO_2$ is preferentially absorbed. Thus, control over selectivity can be achieved by choosing an amine (or a multiple-amine mixture) with the right reactivity toward $CO_2$, allowing contact in a column with the right number of trays or the right depth of packing, and choosing the kind of column internals that favor either $CO_2$ or $H_2S$ absorption. Selectivity depends on rates-not just reaction rates, but mass transfer rates-which implies dependence on all the factors that affect the mass transfer characteristics and mass transfer performance of the actual physical hardware in which the process is carried out. Equilibrium stage models simply cannot capture these effects.

The currency of equilibrium stage models is the number of theoretical stages the currency of internals vendors and gas processors is actual tray counts, types, and passes and volumes and depths of packing of specified size, type and material. With ideal stages, translation between the two is forever an open question. A true mass transfer rate model, on the other hand, always deals in real trays and real packing there is never a question about how many trays are needed or what depth of packing to install. It is equally important to be able to model solvent regeneration accurately if for no other reason than the fact that the loading of the lean solvent produced by the stripper directly and significantly affects contactor performance. Not only does it affect its ability to meet treated gas specifications, but also the actual treated gas composition. Equilibrium stage models don't work very well here either because the reactions and the tower internals type and details affect mass transfer in just as important ways as in absorption. None of the trays in a stripper come even close to an equilibrium stage, and the desorption rate of each acid gas affects the rate of the other. From a technical standpoint, this mass transfer rate based stripper model treats regenerators every bit as rigorously as absorbers. It produces the best possible predictions of regenerator performance without the need for empirical adjustment. And when absorber and stripper models are tied together in a recycle flow sheet, the best possible prediction of treating-plant performance is obtained without applying user-supplied or internally generated empirical corrections of any kind. This complete freedom from empiricism allows the engineer to design and predict the Performance of new facilities for which absolutely no operating data or field experience exists.

## Mass Transfer Rate Simulation

First step in process simulation is system modeling and provide suitable function. In amine unit is occurred below Reactions:

$$RR'NH + H_2S \rightarrow RR'NH_2^{+} + HS^{-} \qquad (1)$$

$$2\,RR'NH + CO_2 \rightarrow RR'NH_2^{+} + RR'NCOO^{-} \qquad (2)$$

$$R_3N + H_2O + CO_2 \rightarrow R_3NH^{+} + HCO_3^{-} \qquad (3)$$

We are used this abbreviation for system modeling:

$H_2S$ : a
$CO_2$ : B
$RR'NH$ : R
$RR'NH_2^{+}$ : $P_1$
$HS^{-}$ : $P_2$
$RR'NCOO^{-}$ : $P_3$
$H_2O$ : $P_4$
$HCO_3^{-}$ : $P_5$

Fig 2 is shown a schematic of absorber tower that $WV_K$ and $WW_K$ is inlet and outlet Sid- stream related Tray NO.K, respectively.

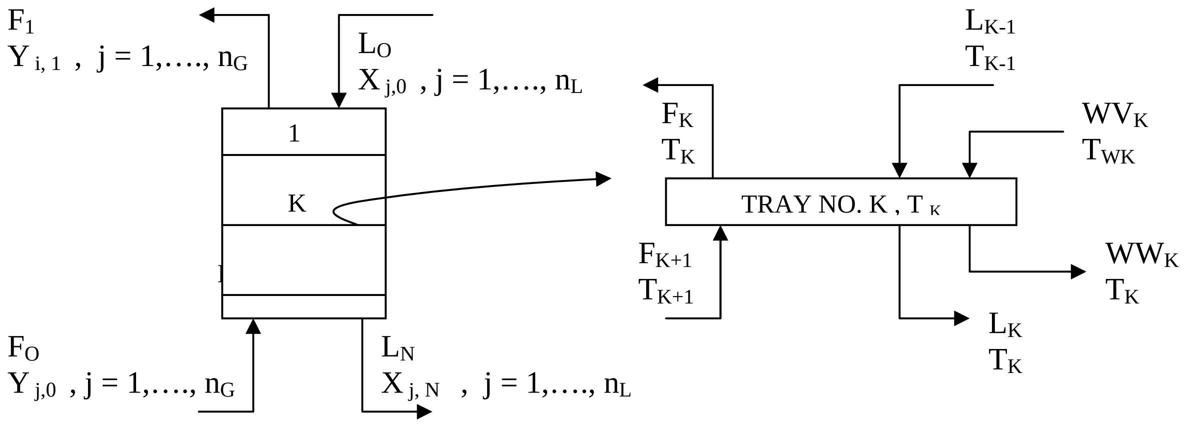

**Fig (2): Schematic of Absorber Tower**

We have written material balance in gas phase:

$$F\frac{dY_A}{dZ}=\{-N_A|_{x=0}+Y_A[N_A|_{x=0}+N_B|_{x=0}]\}APV\,A_a \qquad (4)$$

$$F\frac{dY_B}{dZ}=\{-NB|_{x=0}+Y_B[N_A|_{x=0}+N_B|_{x=0}]\}APV\,A_a \qquad (5)$$

$$\frac{dF}{dZ}=-[N_A|_{x=0}+N_B|_{x=0}]APV\,A_a \qquad (6)$$

Non-absorber material will have a constant contrition in tower, therefore will have

$$F\,Yj = \text{constant} \qquad (7)$$

And boundary Condition for above differential equation is according below:

at $Z = 0$ $\quad Y_{H2S} = Y_{H2S,K+1}$ $\quad Y_{CO2} = Y_{CO2,K+1}$ $\quad F = F_{K+1}$
at $Z = h_f$ (froth distance) $\quad Y_{H2S} = Y_{H2S,K}$ $\quad Y_{CO2} = Y_{CO2,K}$ $\quad F = F_K$

Then differential equation are solved and obtained gas component and flow rate. Mass transfer flux in gas-liquid interface is a function of gas component and is obtain from below equations.

$$N_A\big|_{x=0} = KG_A P_t [Y_A - H'_A (X_{A,K})_i] \qquad (8)$$

$$N_B\big|_{x=0} = KG_B P_t [Y_B - H'_B (X_{B,K})_i] \qquad (9)$$

That $(X_{j,k})_i$ is mole fraction of gas-liquid interface in liquid film, $H'_j = Hj\,(P_t)/\,C_k$ is Henry coefficient of j component and $C_k$ is liquid concentration.

H2S reaction is a equilibrium reaction therefore we will have:

$$X_{A,K} = (X_{A,K})\ \text{Equilibrium} \qquad (10)$$

And $CO_2$ is reacted rapid and $CO_2$ mole fraction in liquid bulk can be calculated from this equation

$$X_{B,K}(L_K + WW_K) = X_{B,K=1}L_{K-1} + X_{B,K-1}WV_K + N_B\big|_{x=0} APVA_t\, h_F - r_B(1 - A_V\, X_L)\ h_F\ \varepsilon_L \qquad (11)$$

That $N_B\big|_{x=x_L}$ is mass flux in the end of film that is obtain from below relation.

$$N_j\big|_{x=x_L} = DjC_K\ \frac{dx_i}{dx}\Big|_{x=xL} \qquad (12)$$

For mole fraction calculation of initial and product, we can used this equation:

$$(X_{R,K} - X_{A,K} - 2X_{B,K})(L_K + WW_K) = L_{K-1}(X_{R,K-1} - X_{A,K-1} - 2X_{B,K-1}) + WV_K \qquad (13)$$

$$(X_{WR,K} - X_{WA,K} - 2X_{WB,K}) - \{(F_{K+1}Y_{A,K+1} - F_K Y_{A,K}) + 2(F_{K+1}Y_{B,K+1} - F_K Y_{B,K})\} \qquad (14)$$

For Amine Type 3, coefficient 2 is changed to 1.

$$\begin{aligned}&(X_{P1,K} - X_{A,K} - 2X_{B,K})(L_K + WW_K) = L_{K-1}(X_{P1,K-1} - X_{A,K-1} - 2X_{B,K-1}) + \\ &+ WV_K(X_{WP1,K} - X_{WA,K} - 2X_{WB,K}) - \{(F_{K+1}Y_{A,K+1} - F_K Y_{A,K}) + 2(F_{K+1}Y_{B,K+1} - F_K Y_{B,K})\}\end{aligned} \qquad (15)$$

$$(X_{P2,K} + X_{A,K})(L_K + WW_K) = L_{K-1}(X_{P2,K-1} + X_{A,K-1}) + WV_K(X_{WP2,K} - X_{WA,K}) + (F_{K+1}Y_{A,K+1} - F_K Y_{B,K}) \qquad (16)$$

$$(X_{P3,K} + X_{A,K})(L_K + WW_K) = L_{K-1}(X_{P3,K-1} + X_{A,K-1}) + WV_K(X_{WP2,K} - X_{WA,K}) + (F_{K+1}Y_{A,K+1} - F_K Y_{B,K}) \qquad (17)$$

$$X_{P4,K}(L_K + WW_K) = L_{K-1}X_{P4,K-1} + WV_K X_{WP4,K} \qquad (18)$$

For Amine Type 3,

$$(X_{P5,K} + X_{B,K})(L_K + WW_K) = L_{K-1}(X_{P5,K-1} + X_{B,K-1}) + WV_K(X_{WP5,K} - X_{WB,K}) + (F_{K+1}Y_{B,K+1} - F_K Y_{B,K}) \qquad (19)$$

$$L_K = (\frac{1}{1-X_{B,k}})[\{1-X_{B,K-1}) + WV_K(1-X_{WB,K}) + (F_{K+1}Y_{A,K+1} - F_K Y_{A,K})] - WW_K \qquad (20)$$

We need mass transfer flux for mole fraction calculation in gas and liquid phase, therefore we used below differential equations:

$CO_2$ Reaction: $$D_B \frac{d^2[B]}{dx^2} + R_B = 0 \qquad (21)$$

$CO_2$ Material balance: $$D_B \frac{d^2[B]}{dx^2} + D_{P3} \frac{d^2[P3]}{dx^2} = 0 \qquad (22)$$

Sulfur material balance: $$D_A \frac{d^2[A]}{dx^2} + D_{P2} \frac{d^2[P2]}{dx^2} = 0 \qquad (23)$$

Amine material balance: $$D_R \frac{d^2[R]}{dx^2} + D_{P1} \frac{d^2[P1]}{dx^2} + D_{P3} \frac{d^2[P3]}{dx^2} = 0 \qquad (24)$$

Total acid balance: $$D_A \frac{d^2[A]}{dx^2} + D_B \frac{d^2[B]}{dx^2} + D_{P1} \frac{d^2[P1]}{dx^2} = 0 \qquad (25)$$

$H_2S$ material balance: $$Keq = \frac{[P1][P2]}{[A][R]} \qquad (26$$

For Amine type 3, equations 22, 24 will be changed as below:

$$D_B \frac{d^2[B]}{dx^2} + D_{P5} \frac{d^2[P5]}{dx^2} = 0 \qquad (27)$$

$$D_R \frac{d^2[R]}{dx^2} + D_{P1} \frac{d^2[P1]}{dx^2} = 0 \qquad (28)$$

Boundary condition for solving these equations is so:

X=0 XA= $X_{A,\text{ equilibrium}}$
X=$X_L$ $X_B$=$X_{B,K}$ $X_R$=$X_{R,K}$ $X_{P1}$=$X_{P1,K}$ $X_{P2}$=$X_{P2,K}$ $X_{P3}$=$X_{P3,K}$ $X_{P5}$=$X_{P5,K}$

We have written energy balance for determine of temperature profile:

$$\begin{aligned} &T_{K-1}L_{K-1}\sum_{j=1}^{nL} X_{j,K-1}CP_{L,j} - T_K[F_K\sum_{j=1}^{nG} Y_{j,K}CP_{G,j} + (WW_K + L_K)\sum_{j=1}^{nL} X_{j,K}CP_{L,j}] + \\ &T_{K+1}F_{K+1}\sum_{j=1}^{nG} Y_{j,K+1}CP_{G,J} + T_{WK}WV_K\sum_{j=1}^{nL} X_{Wj,K}CP_{L,j} = Q_K^C - \sum_{j=1}^{n} Q_{j,K}^R \end{aligned} \qquad (29)$$

That, heat reaction is calculated from below relation:

$$Q^R_{j,k} = (-\Delta H^R_j)\frac{1}{a_{i,j}}\{(F_{k+1}Y_{j,K+1} - F_{k1}Y_{j,K}) - [X_{j,k1}(L_K + WW_K) - (L_{K-1}\ X_{j,K-1} + WV_K X_{Wj,k})]\} \qquad (30)$$

## Solving Method and case study

We need a suitable method for solving these differential equations. For absorber tower simulation is presented an algorithm by Froment and Leye [5]. In this method, Differential equation in liquid and gas, also material balance equations are solved, therefore, we need a high try and error for obtain convergence boundary. But In our rapid, we are simultaneously solved equation; therefore the results will rapid converged. The algorithm in this method is presented suitable method for Amine tower Design (fig 3).

Mass transfer method in modeling and simulation of absorption columns has first been by L.D. Leye and G.F. Froment, but the reactions, which were studied by them, were not in agreement with amine absorption system. It is therefore the objective of this work to present a modified algorithm for simulation of model on a computer. The method of orthogonal collocation is used for solution of the nonlinear differential equations. Using modified Powell-Dogleg method solves the resulting algebraic equations, along with the nonlinear algebraic equations of the model. The computational algorithm used in this study is more efficient than that presented by Leye and Froment, since all material balance and mass transfer equations in the gas and liquid phases are solved simultaneously as opposed to the step-by-step method used by those authors.
This results in much less trial and error required, In addition, convergence is more easily achieved and there is no need for the assumption of linear concentration profile in the liquid film which has been used in some works.
We are programmed a simulation software for design and modeling of Amine absorber tower that is written in FORTRAN language. The results of this software are compared with PROII, which used equilibrium equations for amine absorption simulation.
Several case studies from operating plants have been used to check the validity and capability of the model. Mole fraction of sour gas and actual operating condition is shown in table 1 and 2, repressively.

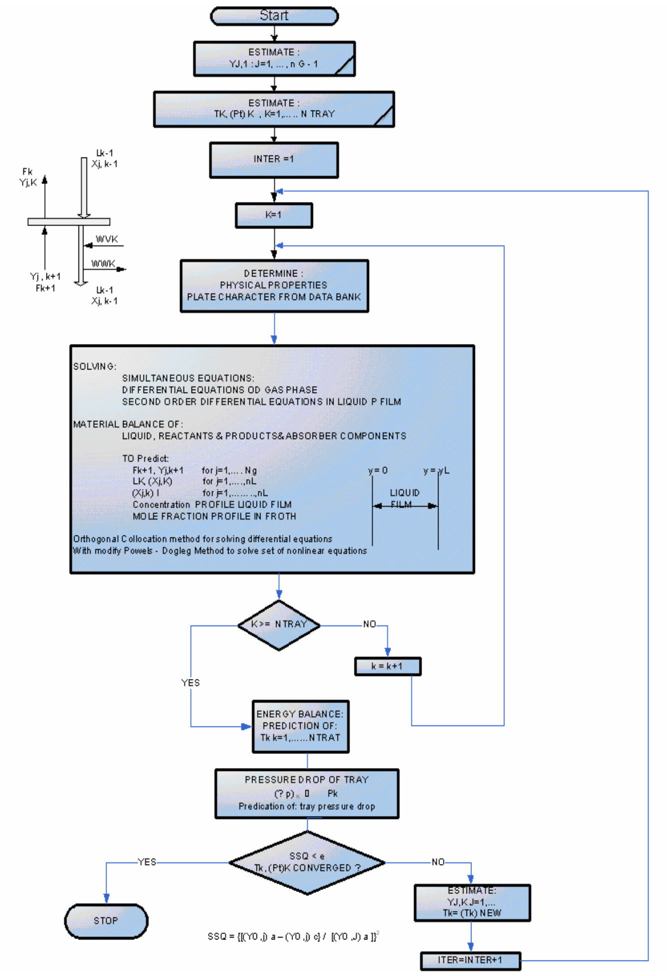

Fig (3): Suitable algorithm for equations solving

**Table (1): Mole fraction of Sour gas**

| **Component** | **Mole percent** | | | | |
|---|---|---|---|---|---|
| | **Case 1** | **Case 2** | **Case 3** | **Case 4** | **Case 5** |
| $H_2S$ | 0.0422 | 16.91 | 1.72 | 26.7 | 1.94 |
| $CO_2$ | 1.73 | 0 | 4.13 | 0 | 0.13 |
| $N_2$ | 5.7 | 1.62 | 0.16 | 0.35 | 0.2 |
| CO | 0 | 0.59 | 0 | 0 | 0.1 |
| $H_2$ | 0 | 20.64 | 0 | 9.98 | 7.6 |
| $H_2O$ | 0.0059 | 0 | 0.5 | 0.014 | 0 |
| $C_1$ | 86.20 | 22.64 | 86.92 | 22.33 | 44.17 |
| $C_2$ | 3.86 | 11.90 | 3.93 | 14.12 | 17.1 |
| $C_3$ | 1.9 | 13.05 | 0.93 | 16.57 | 17.0 |
| n-$C_4$ | 0.36 | 11.39 | 0.29 | 54.9 | 11.76 |
| i-$C_4$ | 0.25 | 0 | 0.26 | 1.2 | 0 |
| n-$C_5$ | 0.174 | 1.26 | 0.12 | 1.5 | 0 |
| i-$C_5$ | 0.175 | 0 | 0.14 | 0.9 | 0 |
| $C_6$ | 0.17 | 0 | 0.18 | 0.9 | 0 |
| $C_{7+}$ | 0.217 | 0 | 0 | 0 | 0 |

**Table (2): Actual operating condition**

| **Component** | **Mole percent** | | | | |
|---|---|---|---|---|---|
| | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
| Sour gas flow rate (kmol/hr) | 19555 | 240 | 1239.5 | 314.8 | 860 |
| Lean Amine (kmol/hr), Type (% wt) | 12864, DEA(32) | 2986.24, MEA(15) | 3084.42 DEA (26.5) | 1168.7 DGA (65) | 1494 DEA (20) |
| Temperature (° K) | 310 | 310.7 | 295 | 313 | 311 |
| Pressure (KPa) | 8100 | 1069 | 6879 | 570 | 845 |
| H2S content of sweet gas (ppm) | < 4ppm | 46 ppm | 1 ppm | 193 ppm | <30ppm |
| Tray number | 32 | 20 | 20 | 20 | 21 |

These cases are modeling with mass transfer method and Equilibrium method; the results are shown in table 3.

It is shown that this model is able to simulate the plants much better than simulation such as PRO/II that use equilibrium methods

**Table (3): Comparison ProII and ACS * simulation results**

| Parameter | | Mole percent | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Case 1 | | Case 2 | | Case 3 | | Case 4 | | Case 5 | |
| | | Pro II | ATSS | Pro II | ACS | Pro II | ACS | Pro II | ACS | Pro II | ACS |
| Sweet Gas | $H_2S$, ppm | 1.1 | 1.1 | 77 | 55 | 1.4 | 1 | 150 | 190 | 44 | 21 |
| | $CO_2$, ppm | 0.86 | 0.4 | 0 | 0 | 240 | 800 | 0 | 0 | 87 | 52 |
| | Flow rate (Kmol/hr) | 19192 | 19209 | 200.2 | 199.47 | 1165.2 | 1168.02 | 233.8 | 230.79 | 848.9 | 860 |
| | Temperature (° K) | 316 | 310.15 | 317 | 316.3 | 308 | 308 | 320 | 317 | 318.1 | 328.2 |
| Rich Amine (kmol/hr) | | 13227.5 | 12872.6 | 3026.1 | 2991.03 | 3158.8 | 3105 | 1247.8 | 1217.5 | 1508.1 | 1494 |
| **ACS: Amine Absorption Column Simulation Software, is programmed in Sharif University* | | | | | | | | | | | |

## Result

Tray columns are the most common systems for gas sweetening Ethanolamine are used for removal of $H_2S$ and $CO_2$ from natural gases in petroleum, gas and petrochemical industries. These solutions remove acidic gases ($H_2S$, $CO_2$) from natural gas in absorption column to sweeten the gases.

Modeling and simulation of amine absorption columns are often based on equilibrium models of Kent-Eisenberg. In This method each plate is assumed as an equilibrium stage and efficiencies of absorbing components are used for prediction of the number of actual plates. Due to the low efficiencies of these columns and lack of reliable methods for prediction of efficiency the results of such simulation models are not satisfactory. On the other hand the effect of variations of many system's parameters such as gas composition are not taken into account. Therefore, in this study, is presented a mathematical models based on mass transfer for simulation amine absorption columns. The differential equations for mass transfer in liquid and gas films along with chemical equilibrium equations and material and energy balances are used to predict the number of actual trays, compositions and tray temperatures.

## Reference

[1] J. Polasek, “Selecting Amine for Sweetening Units”, Energy Progress, Vol. 4, No.3, p. 146-150, 1984.
[2] R.N.Maddox, “Gas conditioning and processing”, 1985
[3] T.Ball, R.Weldman, “ Improve Gas Treating “, Chemical Engineering Progress, January, 1991.
[4] R.L.Kent, B.Einsenberg, “Better Data for Amine Treating”, Hydrocarbon Processing, feb.1974.
[5] L.D.Leye, G.F.Froment, “Rigorous Simulation and Design of Columns for Gas Absorption and Chemical Reaction II”, Computers &Chemical Engineering, Vol.10, no.5, 1986.
[6] Holmes, J. W., M. L. Spears and J. A. Bullin, "Sweetening LPGs with Amines," Chemical Engineering Progress, May 1984, p.47.
[7] Veldman, R., "How to Reduce Amine Losses”, Paper presented at Petroenergy 89, October 1989.
[8] Tse, J., and J. Santos, "The Evaluation and Design of LPG Treaters," Laurance Reid Gas Conditioning Conference proceedings, Norman, Oklahoma, 1993.
[9] D. H.MacKenzie, F. C. Prambil, C. A. Daniels and J. A. Bullin, "Design and Operation of a Selective Sweetening Plant Using MDEA," Energy Progress, 1987, p.31.
[10] Polasek, J. C., and J. A. Bullin, "Influence of Ammonia on Gas Sweetening Units Using Amine Solutions," AICHE Annual Meeting, 1993.