COMPUTER SIMULATION OF GAS TREATING UNIT AND COMPARISON WITH PLANT DATA

M. Moshfeghian[1], R.N. Maddox [2], A.H. Johannes[2]
S. Amiri[3] and H. Sh. Saremi[3]

1 Computer Simulation, University of Sydney, Sydney, Australia.
2 Oklahoma State University, Stillwater, OK, USA.
3 Shahid Hasheminejad Gas Treating Plant, Serakhs, Iran.

ABSTRACT

Predicting the performance of an industrial plant using computer simulation is becoming a common practice. Confirming the effectiveness of computer packages is not so common. The Shahid Hasheminejad Gas Treating Unit (GTU) in north east Iran provided an opportunity to test two different commercially available computer program packages. The GTU, consists of an amine contactor and a stripping column.

The programs use different techniques for correlating/predicting equilibrium concentrations in the acid gas ethanolamine system. Comparing the calculated temperature profiles, liquid phase acid gas loadings and sweet gas purity with operating plant data shows that the results for both simulation packages agree well with plant data. This gives the engineer confidence that the plant is operating effectively and that the computer packages can be used with confidence to predict plant performance and to size plant equipment for final plant design.

NOMENCLATURE

D	:	Stripper overhead product, mols/time
H_{CO2}	:	Henry's law constant for CO_2, Bar. $(Mol/liter)^{-1}$
H_{H2S}	:	Henry's law constant for H_2S, Bar. $(Mol/liter)^{-1}$
L_0	:	Reflux to top tray of stripper, mols/time
M	:	Molarity, mol/liter
P	:	Pressure, Bar
P_{CO2}	:	Partial pressure of CO_2, Bar
P_{H2S}	:	Partial pressure of H_2S, Bar

T : Temperature, °C

[i] : Concentration of species i, mol/liter

α_{CO2} : CO_2 liquid loading, mole H_2S/mole DEA, defined by Eq. 11

α_{H2S} : H_2S liquid loading, mole H_2S/mole DEA defined by Eq. 10

INTRODUCTION

Hydrogen sulfide and carbon dioxide are the principal objectionable acid gas constituents often present in natural gas, synthetic gas, and various refinery gas streams. These acid gas constituents must be removed for corrosion prevention in gas pipelines and process equipment and for health and safety reasons. Maddox (1985) provides the current acceptable concentration levels for these acid gases in gas streams. Hydrogen sulfide removal is also often important for production of sulfur needed for sulfuric acid and fertilizers.

In natural gas treating, there are several processes available for removing the acid gases. Aqueous solutions of alkanolamines are the most widely used, Maddox (1985). The alkanolamine process is characterized as "mass transfer enhanced by chemical reaction" in which the acid gases either react directly or react through an acid-base buffer mechanism with an alkanolamine to form nonvolatile ionic species.

A typical simplified process flow diagram for removal of acid gases from a natural gas stream is shown in Figure (1). The numbers in boxes represent the stream number. The sour gas stream, usually at high pressure and a temperature slightly above the hydrocarbon dew point of the gas enters the bottom of the contactor. The lean amine enters at the top of the column and is also at a temperature above the gas hydrocarbon dew point. In the contactor, the acid gases dissolve in the liquid phase and react with the alkanolamine to form nonvolatile salts (in ionic species form). Gas leaving the top tray of the contactor contains only a very low concentration of the acid gases. The warm, rich (in acid gases) amine from the bottom tray of the contactor undergoes heat exchange with the hot lean amine from the bottom of the stripper and then enters the top of the stripper. In the stripper, which is slightly above atmospheric pressure and at higher than ambient temperature, the reactions reverse causing the nonvolatile salts to dissociate, releasing the acid gases and regenerating the alkanolamine for re-use in the contactor. The released acid gases in the overhead product of the stripper are sent to a sulfur recovery unit or burned by a flare. The hot lean amine from the bottom of the stripper is cooled by heat exchange with the rich amine, then is further cooled by air or water and pumped back to the top of the contactor.
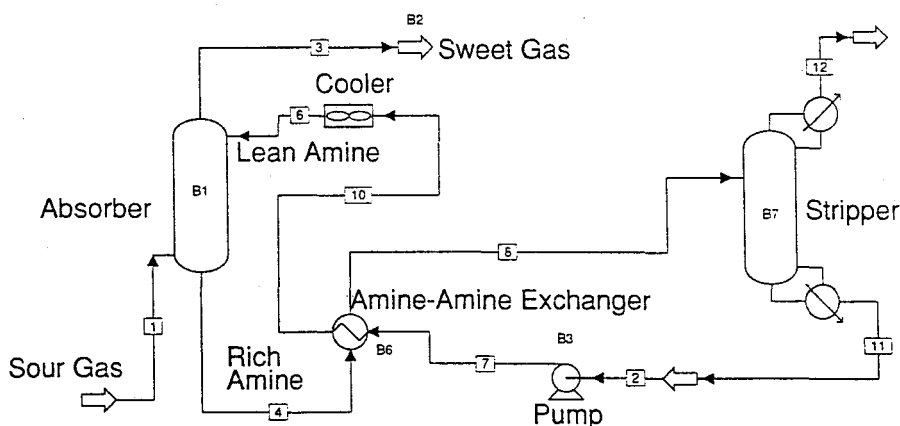
Fig. 1. A simplified flowsheet of the gas sweetening process

Design of such a gas-treating unit is complex and often tedious if carried out by hand, because mass transfer takes place with phase change in an aqueous electrolyte system. Both chemical-reaction-equilibrium and vapor-liquid-equilibrium must be considered. Maddox (1985) and Kohl and Reisenfeld (1979) present procedures and example calculations for alkanolamine processes using short cut methods suitable for hand calculation. Because of the low concentrations that must be achieved in the sweet gas, and the high operating cost of alkanolamine treating facilities, determination of optimum operating conditions is nearly always desirable. For accurate design and simulation of alkanolamine processes computer packages necessarily come into their use.

The objective of this study was to evaluate the accuracy and reliability of two available simulation packages and compare their calculated results with the plant operating data. The first of these programs is ASPEN PLUS™ by Aspen Technology, Inc (1995), and the second is APSIM™ by Chemical Engineering Consultants, Inc (1995). The ASPEN PLUS package is a general purpose flowsheet simulation package for various chemical engineering unit operations. By proper choice of options and selection of equilibrium calculation procedures, ASPEN PLUS can be used to model almost any refinery, natural gas or chemical plant process. It is in widespread use by companies around the world. The APSIM package is designed specifically for use in gas treating units using the alkanolamine process. Equilibrium calculations are possible only for aqueous solutions of monoethanolamine diethanolamine or methyl-diethanolamine. It is in widespread use by companies involved in sweetening natural gas streams. Operating data for the Shahid Hasheminejad Gas Treating Unit was used for evaluating these two computer programs.

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COMPUTER SIMULATION

A computer simulation package, such as ASPEN PLUS or APSIM, provides for the design or plant operating engineer a tool to predict the behavior of a process using basic engineering relationships, such as mass and energy balances and physical and chemical equilibrium. Given reliable thermodynamic data, realistic operating conditions, and rigorous equipment models, one can simulate plant behavior. With such programs the engineering user can run many cases, conduct "what if" analyses, and perform sensitivity studies and optimization runs. Through intelligent use of process simulation, the engineer can design better plants and increase profitability in existing plants. Process simulation is useful throughout the entire life cycle of a process, from research and development through process design to production.

ASPEN PLUS

ASPEN PLUS is a robust general-purpose flow sheet simulator. It is a powerful tool for simulation and optimization of a process, whether conceptual or already built and operating. The following options were selected for simulating the Shahid Hasheminejad GTU. ASPEN PLUS, release 9.2-1, version AXP-OSF1 was used in this study:

Property option set	:	SYSOP15M ELECTROLYTE NRTL / RKS
Henry-compounds ID	:	KDEA
Chemistry ID	:	KDEA - true species
Reaction chemistry ID	:	DEA-ACI
Algorithm option	:	Newton (in absorber) and Standard (in stripper)
H_2S tray efficiency	:	40% in absorber and 70% in stripper
CO_2 tray efficiency	:	40% in absorber and 70% in stripper

In addition to the above parameters, the temperature, pressure, stream compositions and flow rates were specified. The alkanolamine (DEA) circulation rate was fixed, as was the number of trays in the absorber and regenerator. The Electrolyte-NRTL model available in ASPEN PLUS and was used in this study.

Austgen, et al. (1989 and 1991) proposed a model for equilibrium calculation of aqueous acid gas-alkanolamine systems using the Electrolyte-NRTL equation. They developed a thermodynamically consistent model for representing vapor liquid equilibrium in the acid gas-alkanolamine-water system. Their model accounts for chemical equilibrium in a rigorous manner. Activity coefficients are represented,

with the Electrolyte-NRTL equation treating both long-range ion-ion interaction and local interactions between all liquid-phase species. They treated both water and alkanolamines as solvents.
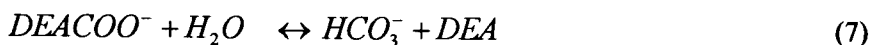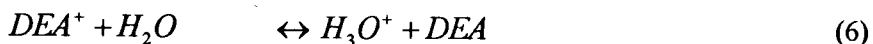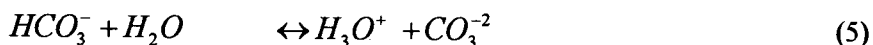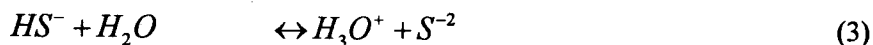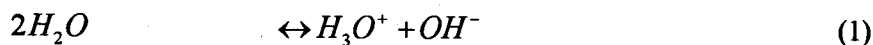
APSIM

The APSIM program is specifically developed for simulation of gas sweetening processes by ethanolamine solutions. Since it is developed especially for simulation of gas sweetening processes, the program is easy to work with and requires less input information than does ASPEN. A typical amine process simulation runs in much less time when using APSIM. In addition to the feed stream temperature, pressure, compositions and flow rates, tray efficiencies for H_2S and CO_2 similar to the ones used in the ASPEN PLUS calculations were specified. In this case, the unit operation parameters were also defined in the same manner as in ASPEN PLUS. However, the reaction equilibrium model chosen is that suggested by Kent & Eisenberg (1976) with the parameters optimized and reported by Moshfeghian and Maddox (1991).

Vapor Liquid Equilibrium (VLE) Models

Design of a gas treating unit requires knowledge of the vapor-liquid equilibrium (VLE) of the acid-gas aqueous alkanolamine system. Fortunately, there is available a large body of experimental VLE data for acid gas-aqueous alkanolamine systems. From this several correlations and models have been developed. Kent and Eisenberg (1976) were the first to present a practical semi-theoretical model with acceptable accuracy for industrial applications. The Kent and Eisenberg approach was to treat the alkanolamine solution as a weak electrolyte and write the chemical reactions occuring between acid gases, water and amine in that solution in ionic form as shown below. Kent and Eisenberg employed equilibrium constants reported in the literature for all reactions in the system except amine protonation and carbamate reversion. For these reactions, equilibrium constants as a function of temperature were determined by fitting the published equilibrium partial pressure data for the ternary systems alkanolamine-H_2S-H_2O and alkanolamine-CO_2-H_2O. Moshfeghian and Maddox (1991) used the widest available ranges of published experimental data and fitted simultaneously alkanolamine-H_2S-CO_2-H_2O data to chemical equilibrium constants. In this way they determined the equilibrium constants for the amine protonation and carbamate reversion reactions with better accuracy and covering wider ranges of operating conditions. Their data were used in APSIM for the work reported here.

The chemical reactions between alkanolamine in water solution and acis gas constituents can be written in terms of chemical dissociation reactions. Using this technique the reactions of H_2S and CO_2 with DEA (diethanolamine) are:

$$2H_2O \qquad \leftrightarrow H_3O^+ + OH^- \tag{1}$$

$$H_2S + H_2O \qquad \leftrightarrow H_3O^+ + HS^- \tag{2}$$

$$HS^- + H_2O \qquad \leftrightarrow H_3O^+ + S^{-2} \tag{3}$$

$$2H_2O + CO_2 \qquad \leftrightarrow H_3O^+ + HCO_3^- \tag{4}$$

$$HCO_3^- + H_2O \qquad \leftrightarrow H_3O^+ + CO_3^{-2} \tag{5}$$

$$DEA^+ + H_2O \qquad \leftrightarrow H_3O^+ + DEA \tag{6}$$

$$DEACOO^- + H_2O \leftrightarrow HCO_3^- + DEA \tag{7}$$

At a constant value of the equilibrium partial pressures for CO_2 and H_2S the presence of DEA enhances the solubility of hydrogen sulfide and carbon dioxide in the aqueous phase.

THE GOVERNING EQUATIONS

The system defined by reactions 1 through 7 contains thirteen unknown quantities. The thirteen unknowns are [H_2S], [CO_2], [DEA], [H_3O^+], [OH], [DEA^+], [DEACOO], [HS], [S^{-2}], [HCO_3^-], [CO_3^{-2}], P_{H2S} and P_{CO2}. These thirteen unknowns require thirteen independent relationships for correct solution. The thirteen independent relationships are the equilibrium constants for reactions 1 through 7; gas solubility described by Henry's law for both H_2S and CO_2:

$$P_{H_2S} = H_{H_2S}[H_2S] \tag{8}$$

$$P_{CO_2} = H_{CO_2}[CO_2] \tag{9}$$

the three component material balances for H_2S, CO_2 and diethanolamine :

$$[H_2S]+[HS^-]+[S^{-2}]=M\alpha_{H_2S} \qquad (10)$$

$$[CO_2]+[HCO_3^-]+[CO_3^{-2}]+[DEACOO^-]=M\alpha_{CO_2} \qquad (11)$$

$$[DEA]+[DEACOO^-]+[DEA^-]=M \qquad (12)$$

and finally, the charge balance for neutrality of aqueous solution:

$$[H_3O^+]+[DEA^+]=[HS^-]+2[S^{-2}]+[OH^-]+2[CO_3^{-2}]$$
$$+[HCO_3^-]+[DEACOO^-] \qquad (13)$$

Equations (1) through (13) are the governing equations that provide a unique solution for the thirteen unknowns in the system for a given set of temperature-pressure conditions. The necessary known variables include a fixed temperature T, the Henry's law constants for H_2S and CO_2, the H_2S liquid loading in the solution (α_{H2S}), the CO_2 liquid loading in the solution (α_{CO2}), and the molarity of the amine solution (M). Moshfeghian, Bell and Maddox (1977) developed a computer program for solution of this set of non-linear equations. Integration of these equations with the overall energy and material balances on each tray form the basic governing equations for rigorous tray-by-tray calculations in an absorber or stripping column, Moshfeghian (1988).

SHAHID HASHEMINEJAD GAS TREATING UNIT

The Shahid Hasheminejad gas treating unit chosen for the basis of this study is located in the north east part of Iran. At the time plant data were taken, it was processing 7.2 MMSCM/D of sour natural gas. The sour gas contained 6.55 mole % CO_2, 3.39 mol % H_2S, 88.9 mole % CH_4, 1.1 mole % C_2H6 with the remaining 1.1 mol % propane plus. It is designed and operated to reduce the H_2S content of the sweet gas below 4 PPMV. The contactor contains 20 actual plates and the stripper contains 24 plates. The lean amine solution is 29.5 weight percent diethanolamine (DEA). The hot rich amine enters the stripper column on the fourth plate from the top at 104.5 °C. The bottom and top pressures of the stripper column are 1.931 and 1.724 bar, respectively. The lean amine flowing from the stripper column is at 120°C. After cooling, the lean amine enters on the top plate of the contactor at 58.6 °C. The sour gas pressure is 73 bar and its temperature is 54.8 °C. It enters below

the bottom plate of the contactor. The lean amine circulation rate is 792000 kg/hr. A simplified flowsheet for this unit is shown in Figure (1).

SIMULATION RESULTS

The Shahid Hasheminejad Gas Treating Unit was simulated using both ASPEN PLUS and APSIM. The same unit parameters were specified in both cases so comparison could be made on the same basis. The computer simulation by the two packages generates a large amount of information such as vapor and liquid flow rates, stream compositions, temperature and pressure on each tray in both the contactor and the stripper. Operating numbers are not available for direct comparison with all of these calculated values. Where operating values are not available, calculated values from the two different procedures are compared.

The acid gas loading in the rich liquid amine is shown Table (1). The two calculations give almost the same value, and both are slightly above the measured value. The lean amine acid gas loading is shown in Table (2). The results by APSIM are slightly higher than for ASPEN PLUS. Table (3) shows condenser duties for the stripper. ASPEN PLUS calculates a reboiler duty which is about 7 % less than that calculated by APSIM. There are also some differences in calculated reflux ratio, but there is good agreement between the calculated condenser temperatures.

Table 1. Acid Gas Liquid Loading in Rich Amine (Stream 4)

Liquid Phase Loading	APSIM	ASPEN PLUS	Plant Data
Mole CO_2/ Mol DEA	0.3686	0.3608	N/A
Mole H_2S/Mole DEA	0.1850	0.1868	N/A
Total Mole H_2S+CO_2/Mole DEA	0.5536	0.5476	0.5150

Table 2. Acid Gas Liquid Loading in Lean Amine (Stream 11)

Liquid Phase Loading	APSIM	ASPEN PLUS	Plant Data
Mole CO_2/ Mol DEA	0.0261	0.0137	N/A
Mole H_2S/Mole DEA	0.0065	0.0007	N/A
Total Mole H_2S+CO_2/Mole DEA	0.0325	0.0144	N/A

Table 3. Cooling and Heating Loads, Reflux Ratio and Condenser
Temperature of Stripping Column

Item	APSIM	ASPEN PLUS	Plant Data
Condenser duty, MMkcal/hr	-20.3585	-21.1804	N/A
Reboiler duty, MMkcal/hr	53.1564	49.5461	N/A
Reflux ratio, L_O/D	1.55	1.43	N/A
Condenser temperature, °C	47.0	47.5	49.0

The temperature profiles in both columns are shown in Tables (4) and (5). The calculated temperature profiles are shown as are plant-measured temperatures for selected trays. Tables (4) and (5) indicate that the calculated temperature profiles are in good agreement with the measured stage temperatures.

Table 4. Temperature (°C) Profile in the Absorber Column

Try No.	APSIM	ASPEN PLUS	Plant Data
1	58.6	58.6	59.0
2	58.6	58.6	
3	58.6	58.6	
4	58.6	58.7	
5	58.6	58.7	59.5
6	58.6	58.7	
7	58.7	58.7	
8	58.7	58.7	
9	58.8	58.8	
10	58.9	58.9	60.5
11	59.0	59.1	
12	59.3	59.4	
13	59.8	60.0	
14	60.5	60.8	
15	61.8	62.3	71.4*
16	63.9	64.8	
17	67.3	68.9	
18	72.4	75.4	
19	78.5	83.1	
20	79.9	84.7	81.7

* It seems that this temperature reading is not correct.

Table 5. Temperature (°C) Profile in the Absorber Column

Try No.	APSIM	ASPEN PLUS	Plant Data
1	103.8	101.2	101.0
2	111.6	102.3	
3	114.8	102.5	
4	116.2	107.0	
5	116.9	111.7	
6	117.3	114.4	107.0
7	117.7	116.0	
8	117.9	116.9	
9	118.1	117.6	
10	118.3	118.0	
11	118.5	118.4	
12	118.7	118.7	117.0
13	118.9	119.0	
14	119.1	119.2	
15	119.3	119.4	
16	119.4	119.7	
17	119.6	119.9	
18	119.7	120.1	119.0
19	119.9	120.3	
20	120.1	120.4	
21	120.3	120.6	
22	120.4	120.8	
23	120.8	121.1	
24	121.3	121.4	119.0

CONCLUSIONS

The Shahid Hasheminejad Gas Treating Unit has been simulated with two commercial computer packages and the results of simulation calculations have been compared with plant operating data. Based on this study, both ASPEN and APSIM give results which are very close to each other and are in good agreement with the plant data. Due to its generality, ASPEN PLUS requires more input data and greater care in selection of proper design options and parameters. Being specific for gas sweetening by amine, APSIM requires less input information and less run time to perform a given calculation.

This paper demonstrates that the two commercial packages are able to predict the current duties and operating conditions of the plant. It also suggests that the plant is operating well. If this were not the case, the simulation packages could be used to determine more nearly optimum operating conditions.

ACKNOWLEDGMENTS

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