# Removal of CO2 and H2S using Aqueous Alkanolamine Solusions

Zare Aliabad, H., and Mirzaei, S.

*Abstract*—This work presents a theoretical investigation of the simultaneous absorption of $CO_2$ and $H_2S$ into aqueous solutions of MDEA and DEA. In this process the acid components react with the basic alkanolamine solution via an exothermic, reversible reaction in a gas/liquid absorber. The use of amine solvents for gas sweetening has been investigated using process simulation programs called HYSYS and ASPEN. We use Electrolyte NRTL and Amine Package and Amines (experimental) equation of state. The effects of temperature and circulation rate and amine concentration and packed column and murphree efficiency on the rate of absorption were studied. When lean amine flow and concentration increase, $CO_2$ and $H_2S$ absorption increase too. With the improvement of inlet amine temperature in absorber, $CO_2$ and $H_2S$ penetrate to upper stages of absorber and absorption of acid gases in absorber decreases. The $CO_2$ concentration in the clean gas can be greatly influenced by the packing height, whereas for the $H_2S$ concentration in the clean gas the packing height plays a minor role. HYSYS software can not estimate murphree efficiency correctly and it applies the same contributions in all diagrams for HYSYS software. By improvement in murphree efficiency, maximum temperature of absorber decrease and the location of reaction transfer to the stages of bottoms absorber and the absorption of acid gases increase.
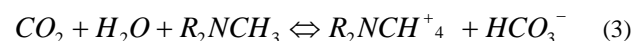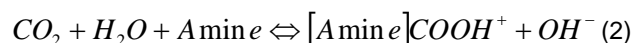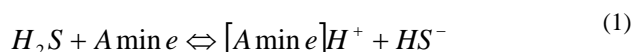
*Keywords*—Absorber, DEA, MDEA, Simulation.

## I. INTRODUCTION

ACID gases like $CO_2$, $H_2S$ and other sulphuric components are usually to some extent present in natural gas and industrial gases. They may have to be removed (selectively) from these gas streams for operational, economical or environmental reasons. One of the most commonly used processes for the removal of acid components is absorption in alkanolamine based solvents. In this process the acidic components react with an alkanolamine absorption liquid via an exothermic, reversible reaction in a gas/liquid contactor. In a following process step the acidic components are removed from the solvent in a regenerator, usually at low pressure and/or high temperature [2]. Industrially important alkanol amines for this operation are monoethanol amine (MEA), diethanol amine (DEA), di-isopropanol amine(DIPA) and N-methyl diethanol amine (MDEA) [3].

Authors are with Chemical Engineering Department, Islamic Azad University, Shahroud Branch, Shahroud, Iran (e-mail: H_a_zare@yahoo.com).

Aqueous di-ethanol amine (DEA) is a common chemical absorbent used in refineries to remove $H_2S$ from refinery off gases. Aqueous MDEA is used to accomplish selective removal of $H_2S$ [5]. Besides MDEA, di-isopropanol amine (DIPA) has also been reported to have a greater selectivity for $H_2S$ over $CO_2$ than either MEA or DEA [3]. The removal of $H_2S$ from the gas is termed the sweetening process. The sweet gas specification is ¼ grain $H_2S$ /100 SCF [1].
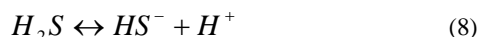
## II. PROCESS CHEMISTRY

$$H_2S + A\min e \Leftrightarrow [A\min e]H^+ + HS^- \qquad (1)$$

$$CO_2 + H_2O + A\min e \Leftrightarrow [A\min e]COOH^+ + OH^- \quad (2)$$

$$CO_2 + H_2O + R_2NCH_3 \Leftrightarrow R_2NCH^+_4 + HCO_3^- \qquad (3)$$
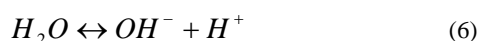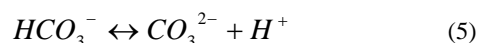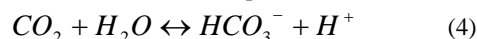
In number (1) reaction $H_2S$ is thought to react almost instantaneously with the amines by proton transfer.

In number (2) $CO_2$ is thought to react with primary and secondary amines to form a carbamate.

Since MDEA is a tertiary amine and does not have hydrogen attached to the nitrogen, the $CO_2$ reaction can only occur after the $CO_2$ dissolves in the water to form a bicarbonate ion [1, 3, 6, 7, 8, and 9].

The following chemical reactions occur in an aqueous MDEA solution when $CO_2$ and $H_2S$ are present:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (4)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (5)$$

$$H_2O \leftrightarrow OH^- + H^+ \qquad (6)$$

$$RR'R'NH^+ \leftrightarrow RR'R'N + H^+ \qquad (7)$$

$$H_2S \leftrightarrow HS^- + H^+ \qquad (8)$$

$$HS^- \leftrightarrow S^{2-} + H^+ \qquad (9)$$

Where: R corresponds to a methyl group and $R'$ to an ethanol group [2].

Reactions which tack place in the liquid phase can be divided in principle into two groups. Reactions equilibrium controlled and reactions kinetically determined. The chemical reactions determine the composition of the different ion species in the liquid phase and, therefore, the enhancement of the mass transfer. Equilibrium reactions are fast enough to assume chemical equilibrium throughout the entire liquid phase. This assumption is fulfilled if reaction kinetics is significantly faster than mass transport in the phase. A certain number of equilibrium reactions occur within the system $CO_2$ –$H_2S$-Alkanol amines [11].

## III. PROCESS OPERATING PARAMETERS

Several operating parameters must be carefully examined to yield the optimum design for each application. Of course, the sweet gas requirements will strongly influence the operating parameters. These may easily range, for $H_2S$, from 3.5 ppm pipeline specification to higher values in fuel gas systems or hydro cracker recycles and, for $CO_2$, from 2% for pipeline specification down to less than 100 ppm for feed to some LP-gas separation facilities. Depending on the feed gas composition, temperature and pressure along with the sweet gas requirements, the most sensitive operating parameters include:

### A. Lean Amine Temperature

Usually the only parameter available for control of the column temperature is the lean amine temperature. Since the $CO_2$ reaction with MDEA is kinetically controlled; a hotter column increases the reaction rate. However, once the lean amine temperature reaches about 135 to 140 ∘ F, the decrease in solubility of the $CO_2$ in the amine solution will usually become the overriding factor and the net $CO_2$ pickup will begin to decrease.

### B. Circulation Rate

When the circulation rate is increased for any given column, the $CO_2$ pickup will increase. This usually holds true for MDEA in a column of fixed diameter even through the liquid residence time on a tray will decrease with increased circulation.

### C. Steam Stripping Rate

For any given situation, as the steam stripping rate is increased, a leaner amine will be produced which will result in lower $H_2S$ and $CO_2$ in the sweet gas.

### D. Liquid Residence Time on Tray

Since the $CO_2$ reaction rate with MDEA is slow, the column diameter and weir height must be adjusted to give sufficient time for the reaction to occur. The usual range of weir heights are from 2 to 4 in. resulting in residence times from about 2 to 5 sec [6]. The operating data of amine-acid gas absorber are given in Table I.

## IV. RESULTS AND DISCUSSION

We use Electrolyte NRTL and Amine Package and Amines (experimental) equation of state. The Electrolyte-NRTL model was originally proposed by Chen et al. [10, 11].For the aqueous electrolyte systems. It was later extended to mixed solvent electrolyte systems [11, 12].

Simulation results of amine-acid gas absorber are given in Table II and Table III.

TABLE I
TYPICAL OPERATING DATA OF AMINE-ACID GAS ABSORBER

| Parameter | Value (MDEA) | Value (DEA) |
|---|---|---|
| Inlet gas flow rate (SCMH) | 173000 | 173000 |
| Inlet liquid flow rate (M3/HR) | 350 | 405 |
| Inlet gas temperature © | 58 | 58 |
| Inlet liquid temperature © | 58 | 58 |
| Amine Concentration(%wt) | 45 | 34 |
| Gas in press.(PSIA) | 1063 | 1063 |
| L. Amine in press.(PSIA) | 1100 | 1100 |
| $H_2S$ inlet gas composition (%mole) | 3.588 | 3.588 |
| $CO_2$ inlet gas composition (%mole) | 6.459 | 6.459 |

TABLE II
SIMULATION RESULTS OF AMINE-ACID GAS ABSORBER IN HYSYS SOFTWARE

| Parameter | MDEA | DEA |
|---|---|---|
| Outlet gas flow rate (kgmol/hr) | 6687 | 6567 |
| Outlet liquid flow rate (kgmol/hr) | 1.283e+4 | 1.737e+4 |
| Outlet gas temperature© | 58.5 | 58.14 |
| Outlet liquid temperature© | 82.05 | 87.01 |
| $CO_2$ Outlet gas composition(%mole) | 1.7376e-2 | 4.3e-5 |
| $H_2S$ Outlet gas composition(%mole) | 7.376908e-9 | 2.031665e-8 |
| No. of stages | 20 | 20 |

TABLE III
SIMULATION RESULTS OF AMINE-ACID GAS ABSORBER IN ASPEN SOFTWARE

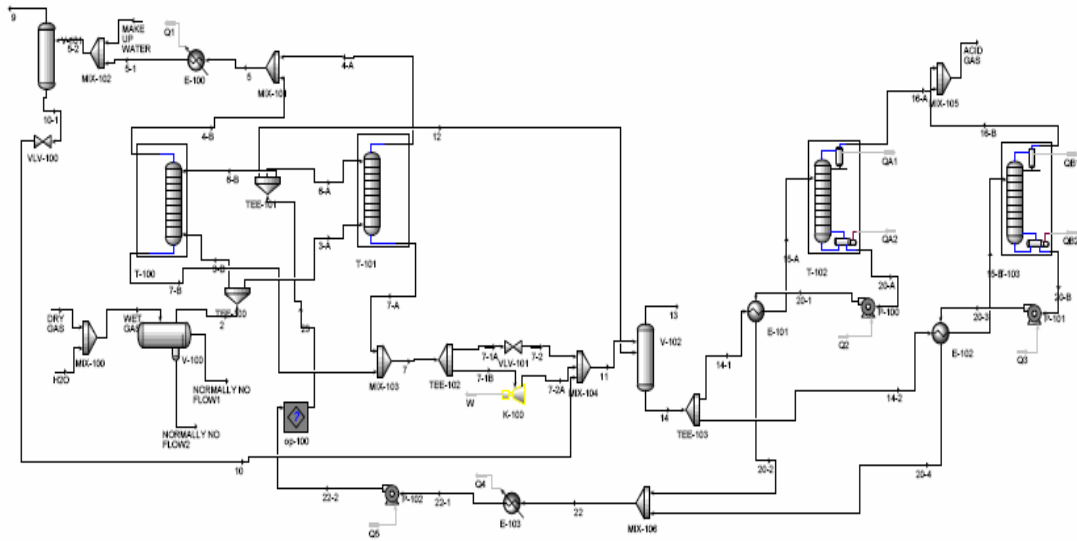| Parameter | MDEA | DEA |
|---|---|---|
| Outlet gas flow rate (kgmol/hr) | 6597.1692 | 6577.2 |
| Outlet liquid flow rate (kgmol/hr) | 12938.94 | 19276.6068 |
| Outlet gas temperature© | 34.27 | 58.16 |
| Outlet liquid temperature© | 61.79 | 82.07 |
| $CO_2$ Outlet gas composition (%mole) | 1.44981e-2 | 2.75279e-5 |
| $H_2S$ Outlet gas composition (%mole) | 1.84811e-9 | 2.07944e-9 |
| No. of stages | 20 | 20 |

Fig. 1 Schematic of gas sweetening process by HYSYS software
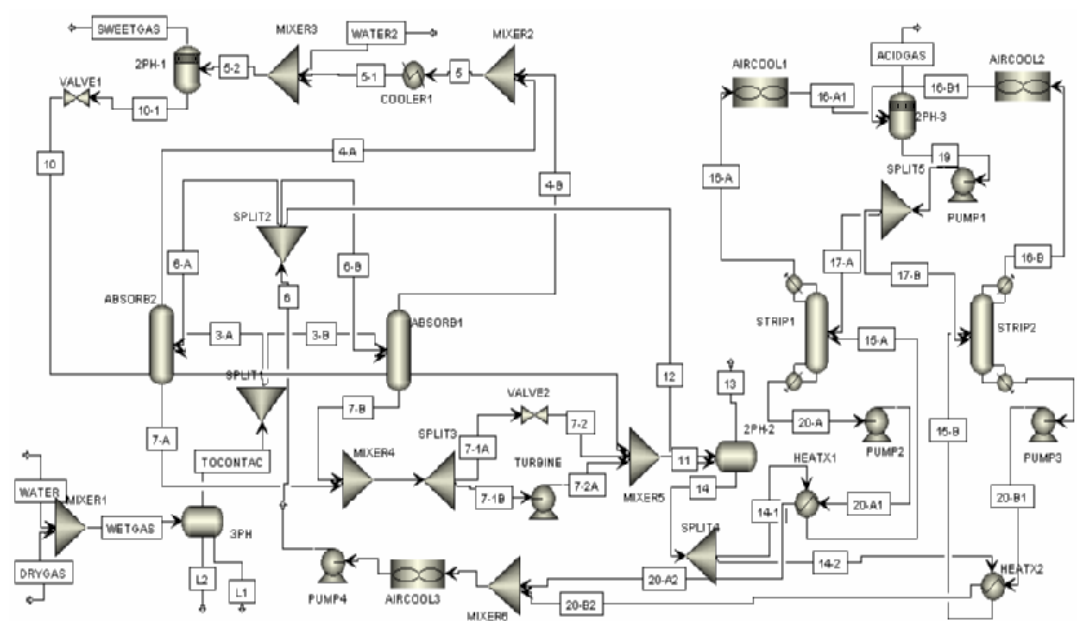


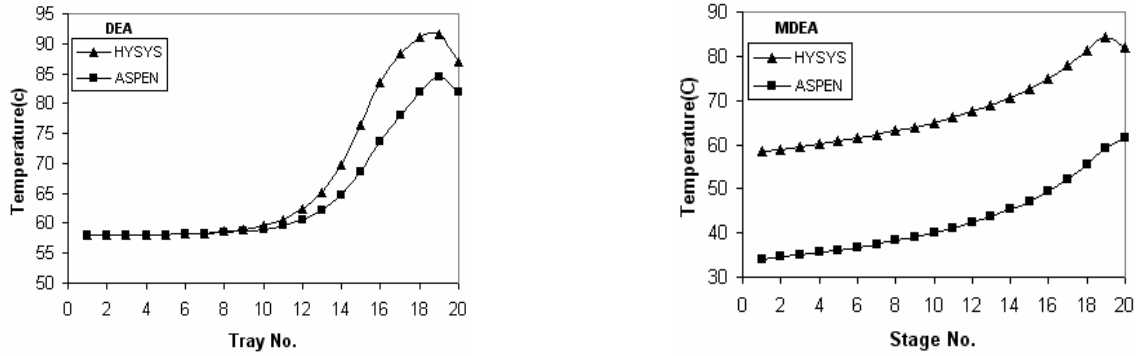Fig. 2 Schematic of gas sweetening process by ASPEN software

Fig. 3 Absorber temperature profile

From these profiles (Fig. 3), it can be noticed that a temperature bulge occurs. This temperature bulge may be explained as follows. As the liquid flows down the tower, it continues to absorb acid gas. This absorption is accompanied by a heat of reaction, which causes the temperature of the liquid to continue to rise. The temperature drop at the bottom of the tower results from the cold gas entering the bottom and contacting the hot liquid flowing downwards. The cold gas absorbs heat from the hot liquid causing its temperature to decrease. This results in a temperature bulge at bottom of the tower. The heat of reaction for MDEA is less so temperature bulge is less.
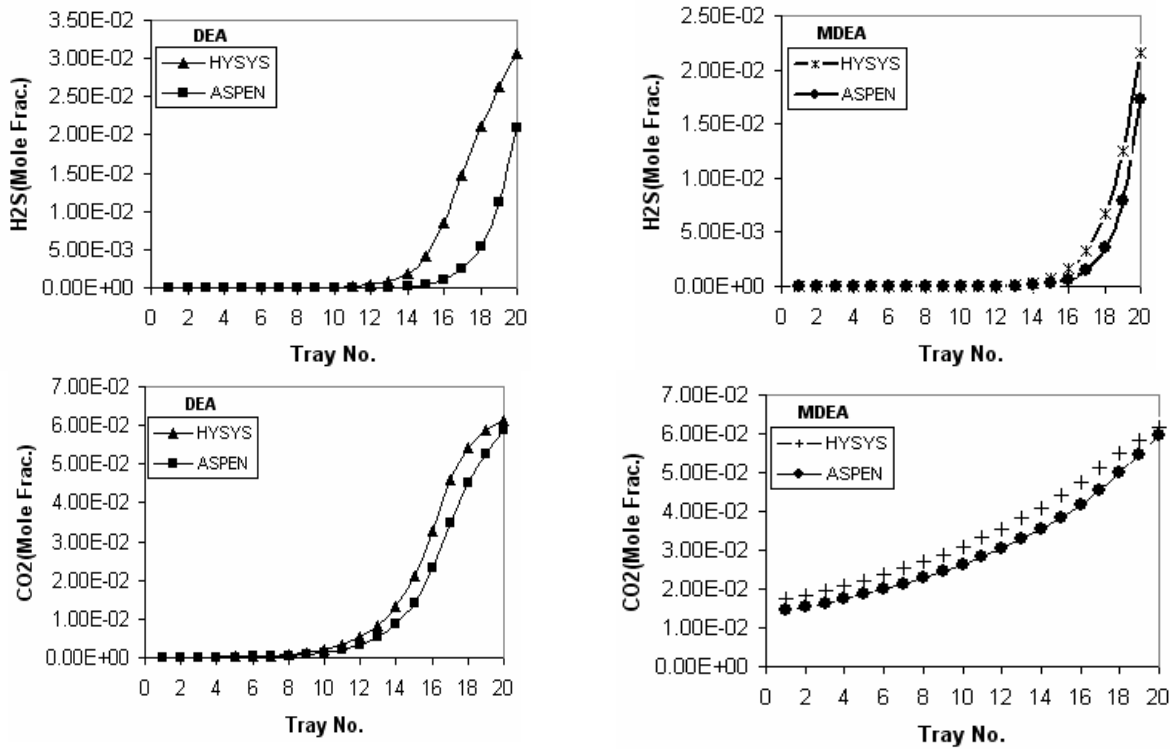


Fig. 4 Stage number vs. $CO_2$ and $H_2S$ vapor composition profiles in the absorber

The less $CO_2$ will be absorbed by the MDEA solvent because aqueous MDEA is used very often for selective removal of $H_2S$ from gas streams containing both $CO_2$ and $H_2S$. As can be seen (Fig. 4), the concentration of $H_2S$ drops down to almost zero at about stage 11(HYSYS software) and 14(ASPEN software) for DEA as compared to stage13 (HYSYS software) and 15(ASPEN software) for MDEA.
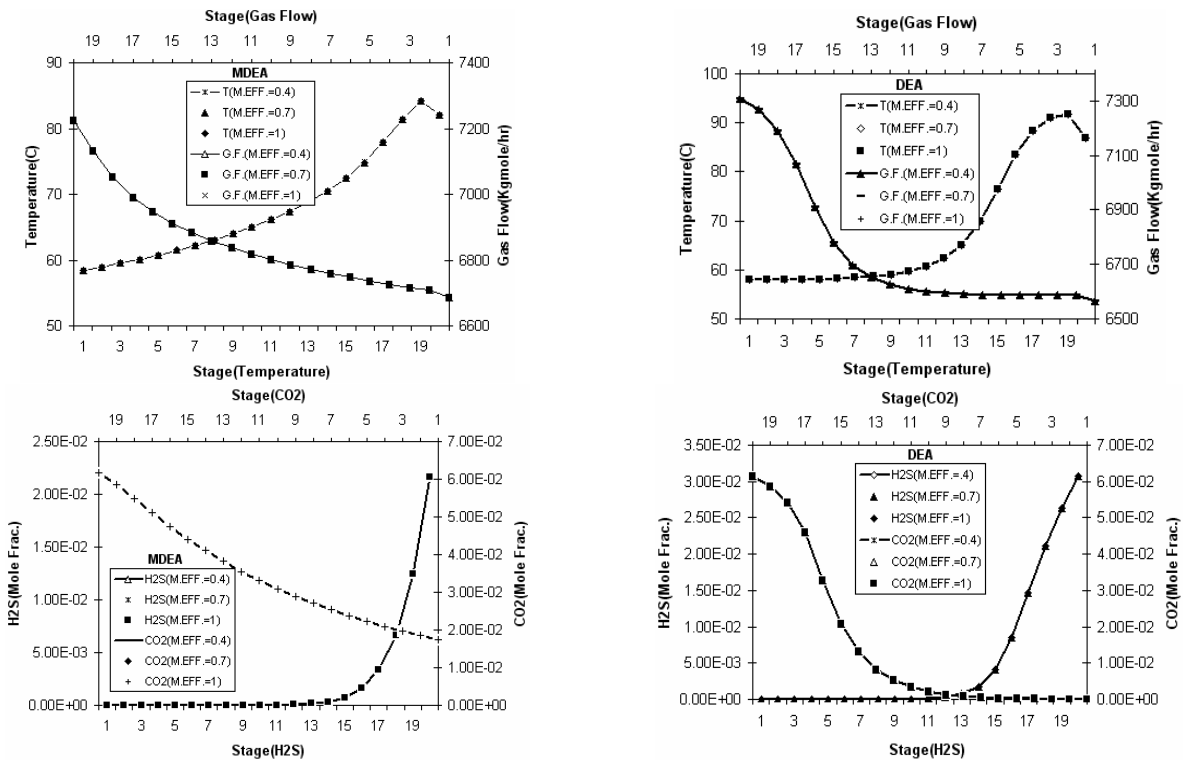


Fig. 5 Effect of murphree efficiency on temperature and gas flow and $CO_2$ and $H_2S$ vapor composition in absorber in HYSYS software
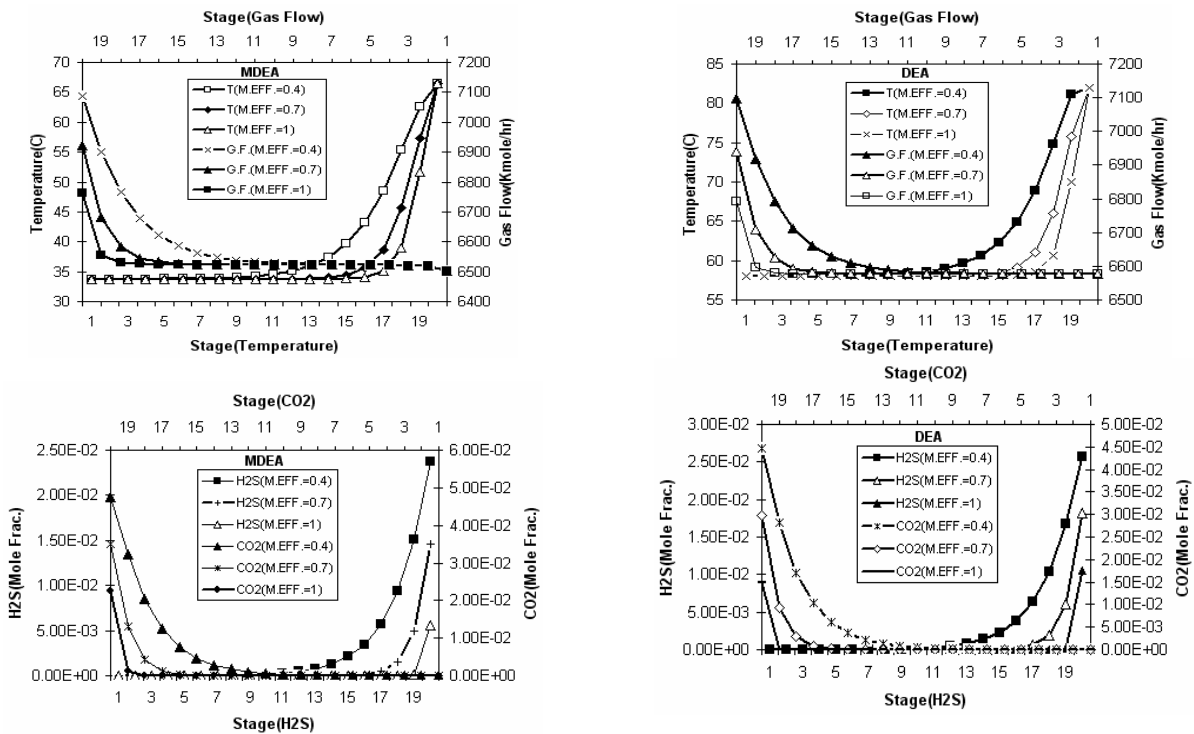


Fig. 6 Effect of murphree efficiency on temperature and gas flow and $CO_2$ and $H_2S$ vapor composition in absorber in ASPEN software
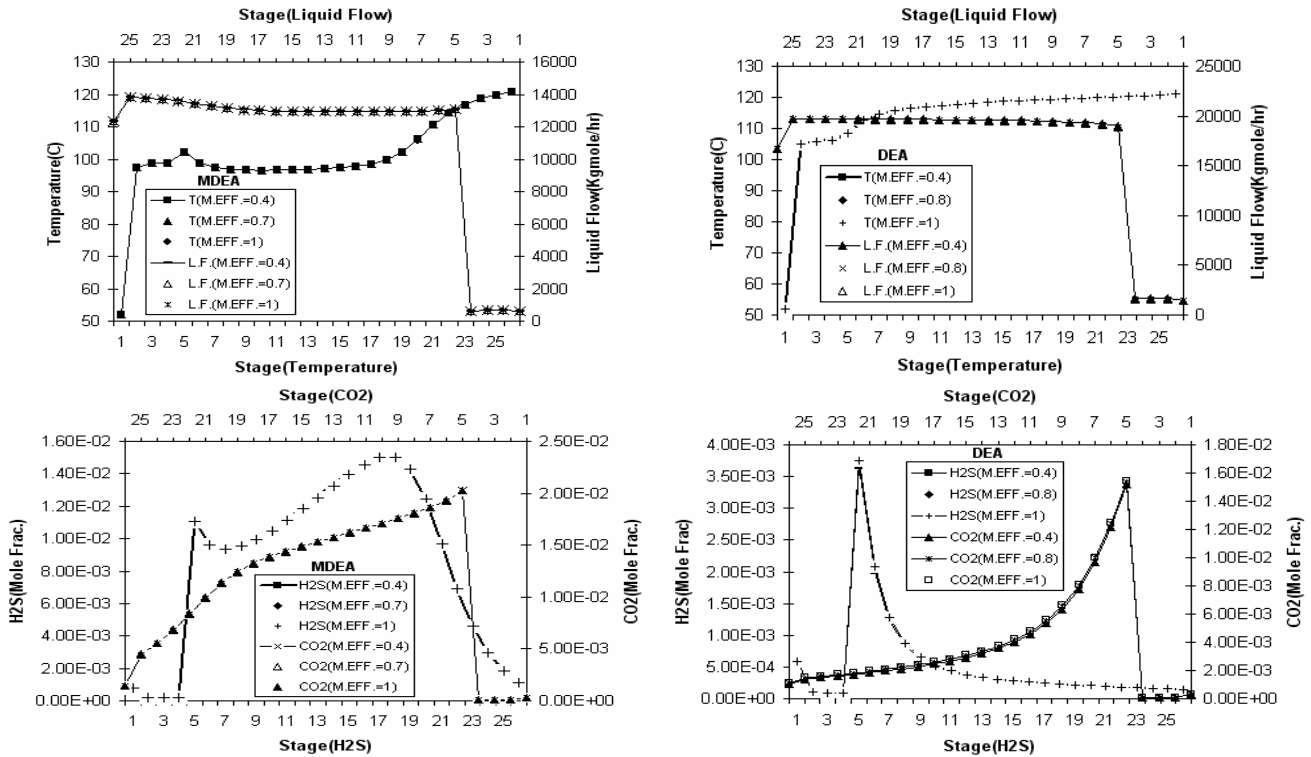
Fig. 7 Effect of murphree efficiency on temperature and liquid flow and $CO_2$ and $H_2S$ liquid composition in stripper in HYSYS software
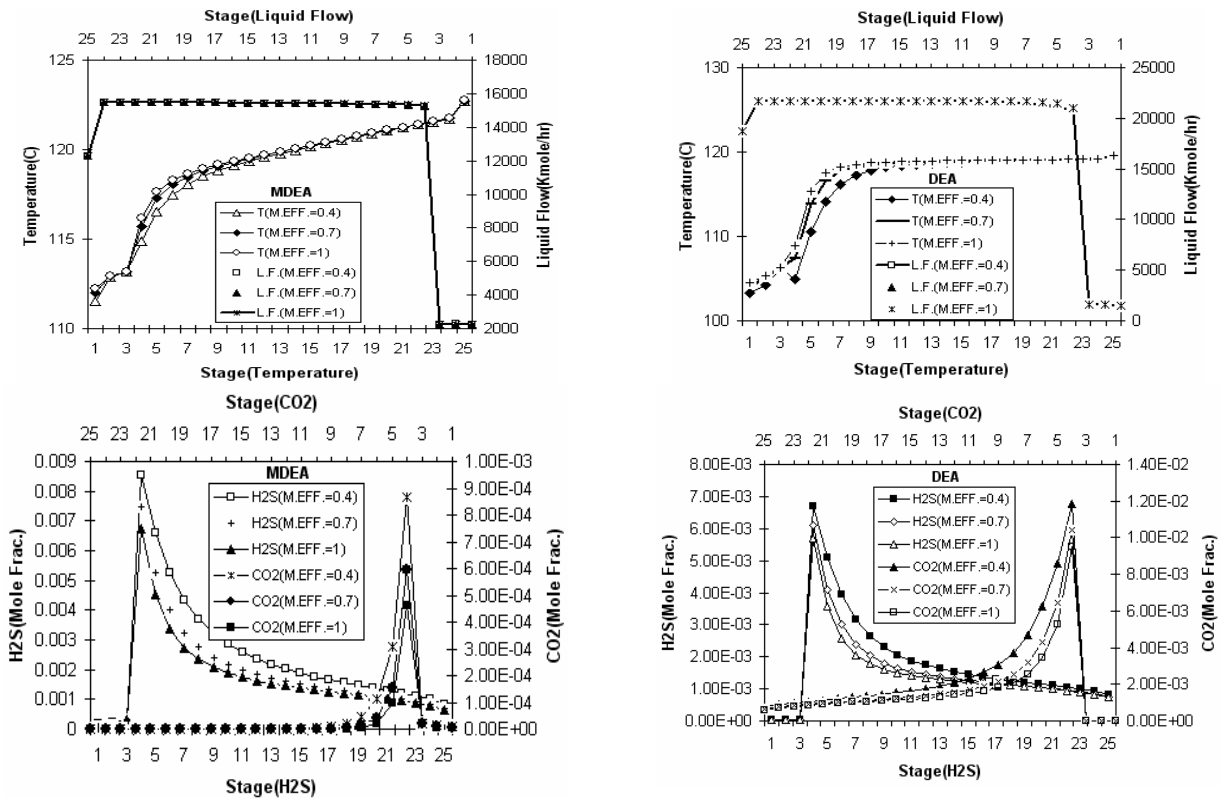


Fig. 8 Effect of murphree efficiency on temperature and liquid flow and $CO_2$ and $H_2S$ liquid composition in stripper in ASPEN software

HYSYS software can not estimate murphree efficiency correctly and it apply the same contributions so in all diagrams related to HYSYS software, all the figures depending on variant efficiencies match to each other and in all cases efficiency of condenser and reboiler processes equals one. By improvement in murphree efficiency, maximum temperature of absorber decrease and the location of reaction transfer to the stages of bottom absorber and the absorption of acid gases increase. In stripper when murphree efficiency increase, the maximum temperature increases too and therefore the repel of acid gases increase.

The Figures 9 and 10 show that when lean amine flow and concentration increase, $CO_2$ and $H_2S$ absorption increase too. The Figure 11 shows that with the improvement of inlet amine temperature in absorber, $CO_2$ and $H_2S$ penetrate to upper stages of absorber and the location of reaction will be transfer to the upper column and finally absorption of acid gases in absorber decreases.
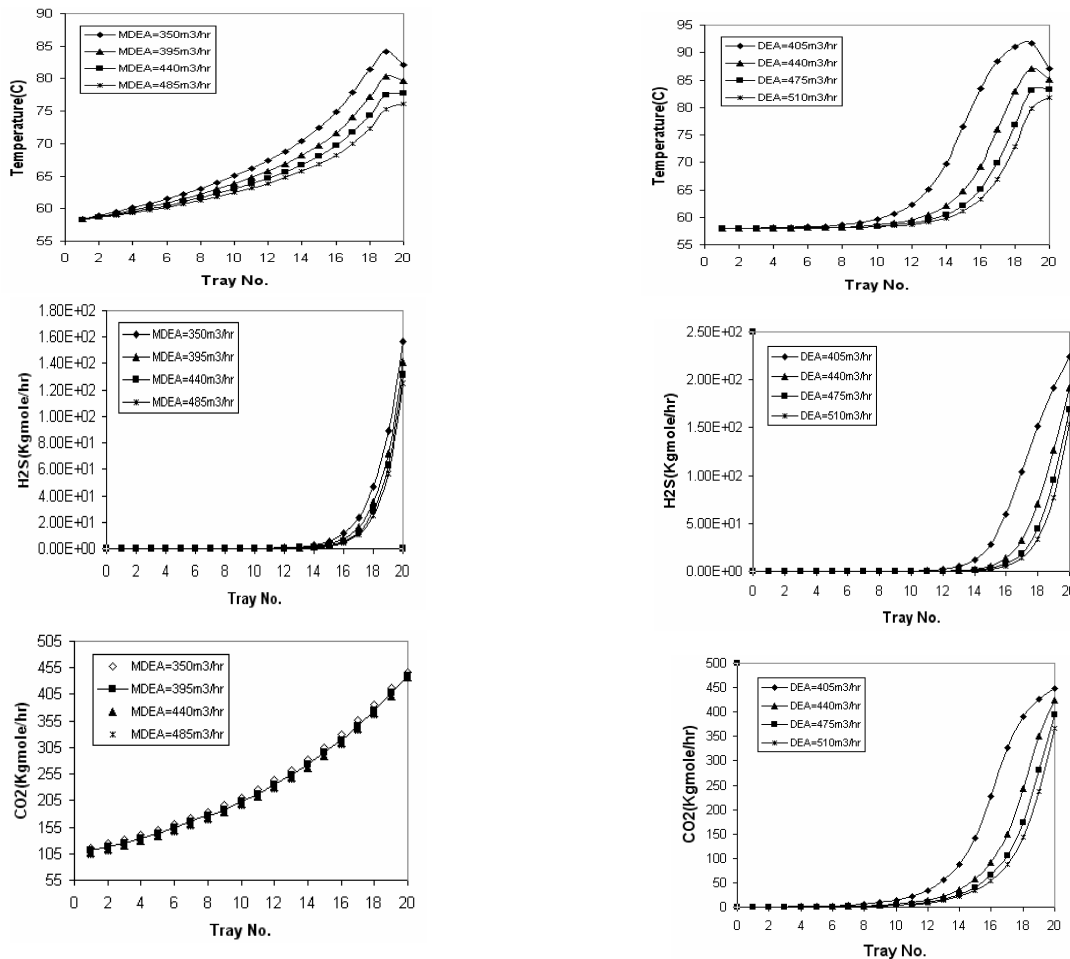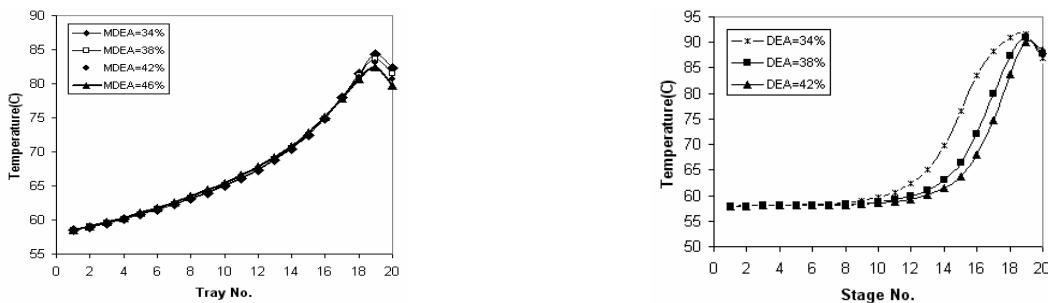


Fig. 9 Effect of lean amine flow on $CO_2$ and $H_2S$ vapor composition and temperature in absorber in HYSYS software
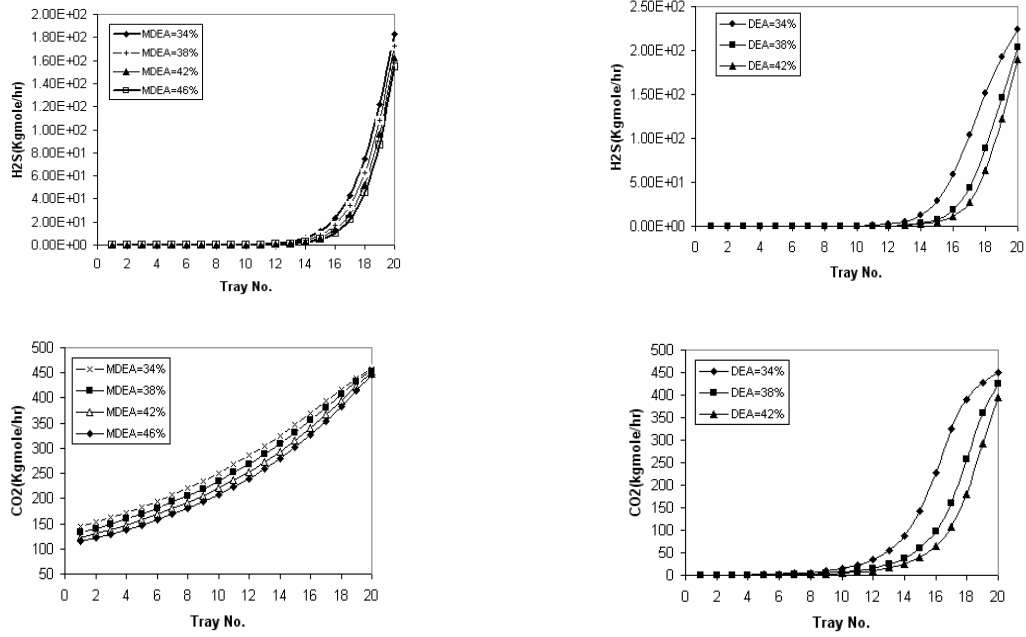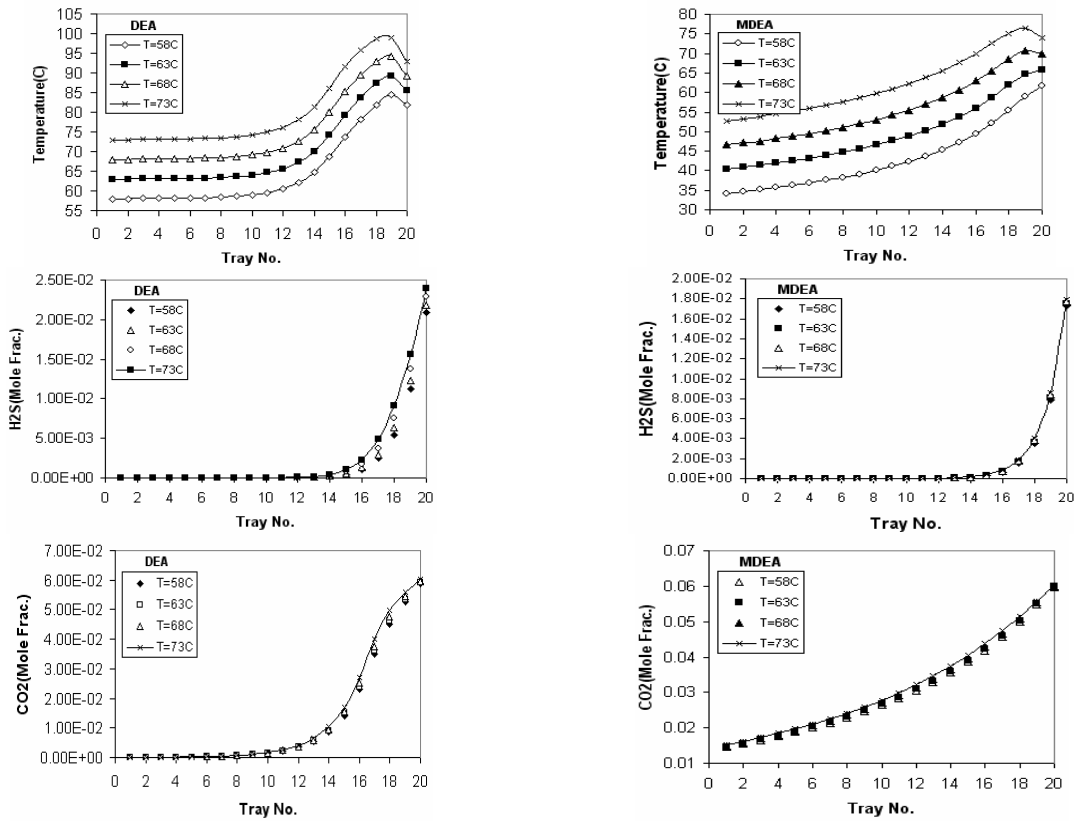
Fig. 10 Effect of lean amine concentration on $CO_2$ and $H_2S$ vapor composition and temperature in absorber in HYSYS software
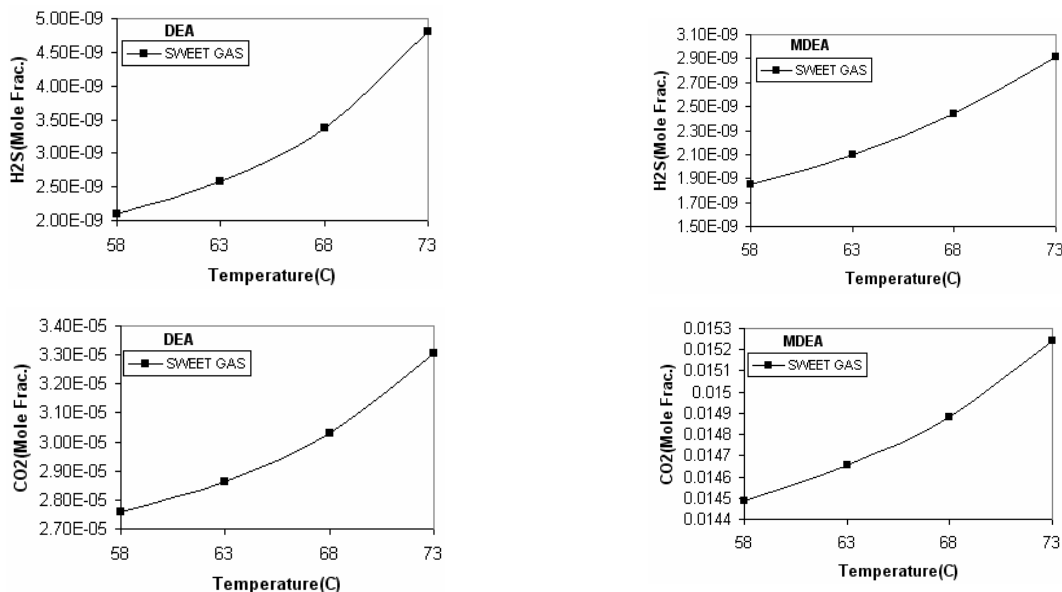
Fig. 11 Effect of lean amine temperature on $CO_2$ and $H_2S$ vapor composition in absorber in ASPEN software

In Fig. 12 the calculated vapor mole fractions concentration profiles of $CO_2$ and $H_2S$ over the packing height for two software are given. The difference between the absorption of $H_2S$ and $CO_2$ can be seen clearly. $CO_2$ which has to dissolve first before reacting with MDEA, has a nearly constant absorption gradient over the whole pac king, whereas $H_2S$ shows the typically bend chemical reactive absorption profile. It can be generally stated that all simulation programs predict a better cleaned gas in case of $H_2S$ for all measurements. For $CO_2$ this general trend can not be seen, but the relative deviation of the calculated values is much lower. In can be clearly seen that the $CO_2$ concentration in the clean gas can be greatly influenced by the packing height, whereas for the $H_2S$ concentration in the clean gas the packing height plays a minor role.
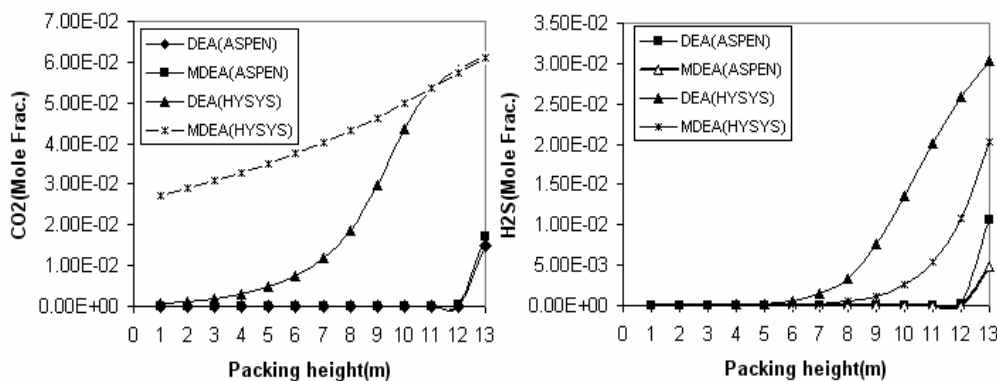


Fig. 12 Effect of packed column (absorber) on $CO_2$ and $H_2S$ vapor composition

## V. RESULTS

A comparison of the temperature profiles for DEA and MDEA shows, maximum temperature for MDEA is less because absorption reaction is an exothermic reaction and MDEA has less reaction heat.

A comparison of the $CO_2$ and $H_2S$ vapor composition profiles in absorber for DEA and MDEA shows, $CO_2$ absorption for MDEA is less.

HYSYS software can not estimate murphree efficiency correctly and it applies the same contributions in all diagrams. By improvement in murphree efficiency, maximum temperature of absorber decrease and the location of reaction transfer to the stages of bottom absorber and the absorption of

acid gases increase. When lean amine concentration and flow increase, $CO_2$ and $H_2S$ absorption increase too.

With the improvement of inlet amine temperature in absorber, $CO_2$ and $H_2S$ penetrate to upper stages of absorber and the location of reaction will be transfer to the upper column and finally absorption of acid gases in absorber decreases and the $CO_2$ and $H_2S$ concentration in sweet gas (clean gas) increase.

The $CO_2$ concentration in the clean gas can be greatly influenced by the packing height, whereas for the $H_2S$ concentration in the clean gas the packing height plays a minor role.

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