CFD Simulation of a Wetted-Wall Column for Natural Gas Sweetening Using DEA Solution

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Abstract
Natural gas usually contains significant amounts of acid gases when it is extracted from underground reservoirs. Therefore, it must be treated by appropriate processes to remove these acidic components. In this study, the simultaneous absorption of carbon dioxide and hydrogen sulfide from natural gas into diethanol amine solution was simulated using CFD. Absorption process was performed in a wetted-wall column with counter-current gas-liquid flow. A two-dimensional simulation based on the volume of fluid model was used. To investigate the hydrodynamics of the flow in the column, distribution of the volume fraction of phases along the column, the formation of liquid film and velocity profiles were studied. To validate the results for predicting the liquid film thickness, the column was simulated at different flow rates of water and air in laminar flow regime. Then by considering the mass transfer from the gas phase to liquid phase based on Higbie’s penetration theory, the concentration distribution of components in gas and liquid phases was calculated. The effect of temperature on absorption of CO₂ and H₂S was also studied. The comparison of simulation results with the experimental data for the outlet concentrations in the gas phase showed that there was a good agreement between them. The developed model can also be used in further studies to determine the effective parameters on simultaneous absorption of CO₂ and H₂S in a wetted-wall column. This helps to optimize the performance of the sweetening process in gas refineries.

Keywords
Natural gas sweetening; Carbon dioxide; Hydrogen sulfide; CFD; DEA

1. Introduction
Natural gas is the most important and the most common fossil fuels in the current age and future. In the world today, natural gas is widely used in household, industries and transportation. Since natural gas is located in deep underground reservoirs, it may contain several non-hydrocarbon components such as carbon dioxide and hydrogen sulfide so it is called sour gas. Gas sweetening is the separation of acid gases from sour gas. Acid gases in the sour gas are undesirable compounds, which cause several problems such as corrosion and environmental pollutions without any thermal value. Therefore, before using natural gas, acid gases should be removed by sweetening processes in the treatment units (Abdulrahman & Sebastine, 2013; Rahimpour, Saidi, Baniadam, & Parhoudeh, 2013). Due to the presence of impurities such as acid gases in natural gas and the problems caused by them, separation processes to remove these gases have always been an important issue. The increasing importance and application of natural gas as an energy source lead to challenges related to the design of separation and purification processes. The utilization of natural gas extracted from natural resources is limited because of high corrosion and environmental problems caused by acid gases. Gas sweetening is usually done in tray towers, packed towers, venturi and spray scrubbers, bubble columns and wetted wall columns (Baniadam, Fathikalajahi, & Rahimpour, 2009; Keshavarz, Fathikalajahi, & Ayatollahi, 2008). Wetted
Alkanolamines are widely used for acidic components removal from natural gas (Baniadam et al., 2009). Monoethanolamine (MEA), Diethanolamine (DEA), Diisopropanolamine (DIPA) and N-Methyldiethanolamine (MDEA) are the most commonly used amines for removal of CO₂ and H₂S (Mandal & Bandyopadhyay, 2006). MEA and DEA are widely used for simultaneous absorption of CO₂ and H₂S from sour gas and industrial gas streams but MDEA is often used for selective removal of H₂S from gas streams containing both CO₂ and H₂S (Mandal & Bandyopadhyay, 2005). Many efforts have been done in the field of natural gas sweetening and finding new ways to increase the efficiency of acid gases removal during the past years.

Yih and Sun (1986) worked on simultaneous absorption of CO₂ and H₂S using potassium carbonate and amine-promoted potassium carbonate solutions in a 183 cm long wetted wall column of outside diameter of 2.72 cm. The influences of gas and liquid flow rate, temperature, solvent concentration, promoter type and concentration on absorption rate, mass transfer coefficient and selectivity factor were studied. It was observed that DEA was a more effective promoter for absorption of CO₂ and H₂S.

Mandal and Bandyopadhyay (2005) studied the simultaneous absorption of CO₂ and H₂S into aqueous blends of 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA) in their theoretical and experimental investigations. The effects of contact time, amine concentration and temperature on the absorption rate and the selectivity were investigated by absorption experiments in a wetted wall column at atmospheric pressure with a constant feed gas ratio. The diffusion–reaction processes for CO₂ and H₂S mass transfer in blended amines were modelled according to Higbie’s penetration theory with the assumption of reversible reactions. It was observed that the blended amine solvent was an efficient mixture solvent for simultaneous absorption of CO₂ and H₂S and by varying the relative amounts of AMP and DEA, the solvent selectivity for absorption of CO₂ and H₂S can be changed.

Mandal and Bandyopadhyay (2006) also studied the simultaneous absorption of CO₂ and H₂S into aqueous blends of DEA and MDEA in their theoretical and experimental investigations. The effect of contact time, temperature and amine concentration on the rate of absorption and the selectivity were investigated by absorption experiments in a wetted wall column at atmospheric pressure and constant feed gas ratio. The diffusion–reaction processes for CO₂ and H₂S mass transfer in blended amines were modelled according to Higbie’s penetration theory with the assumption that all reactions are reversible. Model results based on the kinetics-equilibrium-mass transfer coupled model were found to be in good agreement with the experimental data for absorption rates of CO₂ and H₂S into (MDEA + DEA + H₂O).

Baniadam et al. (2007) developed a 2D mathematical model for acid gases (i.e. CO₂ and H₂S) removal in a commercial sieve tray column using MDEA. The velocity profile in the liquid phase in both radial and axial directions was calculated using computational fluid dynamics. Mass and energy equations also were derived and numerically solved in order to define the concentration and temperature profiles in radial and axial directions. The model was based on two film theory.

Xu, Paschke, Repke, Yuan, & Wozny (2009) studied the mechanism of absorption and momentum transfer in a laminar, counter current gas and liquid film flow on a plate in a three-dimensional model using computational fluid dynamics. The volume of fluid (VOF) model was used to investigate the hydrodynamics and mass transfer between gas and liquid phases based on penetration theory. Experiments and simulations were done for a system of propane and toluene. The irregular surface of the liquid film, velocity profiles in gas and liquid phases, concentration profiles and output concentrations were studied. There was a good agreement between simulation results and experimental data.

Rezakazemi et al. (2010) studied the chemical absorption of CO₂ and H₂S in a hollow fibre membrane contactor (HFMC) theoretically and experimentally. A 2D mathematical model was developed for simultaneous absorption of CO₂ and H₂S in a HFMC using MDEA solution. The radial and axial diffusion were considered in that model. The effects of convection and chemical
reactions were also considered in both the shell and tube. Computational fluid dynamics (CFD) was used to solve the equations of continuity and momentum. The experimental data confirmed the model predictions and good agreement was observed between simulation results and experimental data for different values of gas and liquid velocity. The simulation results showed that \( \text{H}_2\text{S} \) removal using MDEA solution was very high and \( \text{H}_2\text{S} \) was almost completely removed. Their results showed that the membrane used for removal of small amounts of \( \text{H}_2\text{S} \) was very effective in high gas to liquid ratios. The model was able to predict the absorption performance of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) in the HFMC.

In order to screen different amine solvents for \( \text{CO}_2 \) capture, Chen, Closmann, and Rochelle (2011) used a wetted-wall column to measure \( \text{CO}_2 \) equilibrium partial pressure and absorption/desorption rates at various \( \text{CO}_2 \) loading from 40 to 100°C. The heat of absorption, \( \text{CO}_2 \) capacity and liquid film mass transfer coefficients were also determined in this study. The results showed that primary amines used in this research (DGA, MAPA and MEA) had low \( \text{CO}_2 \) capacity, low absorption rates and high heat of absorption. AMP had a high \( \text{CO}_2 \) capacity but suffered from low absorption rate. MDEA blended with PZ showed high \( \text{CO}_2 \) capacity and absorption rate with a lower heat of absorption in comparison to primary amines.

Rahimpur et al. (2013) developed a mathematical model based on computational fluid dynamics for absorption of acid gases into amine solution in a structured packing with corrugated sheets. 2D mass and energy equations with chemical reactions between acid gases and amine solution were derived for cylindrical coordinate since corrugated plates placed in a way that channels were created along the bed. The temperature and concentration profiles were obtained over the bed in the gas and liquid by solving the governing equations based on mass and energy conservation equations.

Rodriguez-Flores, Mello, Salvagnini, and de Paiva (2013) studied \( \text{CO}_2 \) absorption into MEA, AMP and their respective blend to evaluate the absorption process and determine a design parameter for a single-amine absorption system. A wetted-wall column with a film promoter, a thin stainless steel woven, was used for experimental tests which were carried out in counter-current flow at 298 K, atmospheric pressure, a constant gas load (10% \( \text{CO}_2 \)) and three different liquid loads. It was concluded that the interfacial area was influenced by increasing the liquid load which means an increase in the effective interfacial area between liquid and gas phase. The values of \( K_a \) related to MEA and the blend based on it were higher in comparison to AMP and the results showed that \( K_a \) value for MEA: AMP mixtures increased by increasing the MEA proportion in the blend.

Hosseini, Alizadeh, Fatehifar, and Alizadehdakhel (2014) studied the chemical absorption of \( \text{CO}_2 \) into the monoethanolamine solution in a wetted wire column consisting of one wire. The two-phase flow, mass transfer and chemical reaction were simulated using computational fluid dynamics method with applying volume of fluid model. The simulation results were in good agreement with experimental data. Their simulation results showed that by increasing the gas and liquid flow rates, the diameter and intervals of liquid beads increased. The beads velocity also increased by increasing the liquid flow rate and decreasing the mass fraction of MEA in the liquid phase and mass transfer resistance in the liquid phase reduced by formation of the beads. Finally, they concluded that their model was able to predict the effect of physical and operating parameters on the investigated chemical absorption process.

Taheri, Mohebbi, Hashemipour, and Rashidi (2016) employed a wetted-wall column to study the simultaneous removal of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) from natural gas using a nanofluid containing SiO\(_2\) and \( \text{Al}_2\text{O}_3 \) nanoparticles and nanoporous graphene in Diethanolamine. The effects of concentration and particle types on absorption of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) were studied. The experiments were done at 298 K and with two different inlet gas compositions. The results showed that SiO\(_2\)-DEA nanofluid had deteriorating effects on \( \text{H}_2\text{S} \) removal while \( \text{Al}_2\text{O}_3\)-DEA improved \( \text{H}_2\text{S} \) absorption. It was also observed that \( \text{CO}_2 \) absorption rate was enhanced with both \( \text{Al}_2\text{O}_3\)-DEA and SiO\(_2\)-DEA nanofluids but SiO\(_2\) was found to be a more effective candidate for \( \text{CO}_2 \) absorption. It was also found that the presence of nanoporous graphene in DEA solution had a significant effect on absorption of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) in comparison to DEA.

Karlsson and Svensson (2017) investigated \( \text{CO}_2 \) absorption rate using a wetted-wall column with two different solvents, MEA and mixture of AMP in the NMP. Experiments were carried out for various concentrations of amine solutions and the results showed a higher flux and higher liquid side mass...
transfer of CO₂ for the mixture of AMP in NMP compared to aqueous MEA.

Lillia, Bonalumi, Fosbøl, Thomsen, and Valenti (2018) studied the absorption of CO₂ into NH₃ using a wetted-wall column in order to investigate the effect of solvent condition on the rate of reaction. The experimental tests were done at different temperatures, various NH₃ concentrations and different CO₂ loadings. They presented the raw data and also the final value of the overall mass transfer coefficient as a result of the raw data treatment.

Wang, Xu, Lai, and Sun (2018) developed a multiphase computational fluid dynamics (CFD) model in order to determine the CO₂ mass transfer coefficient in solvent-based CO₂ capture using a wetted-wall column. A volume of fluid model was used to model the hydrodynamics and the diffusive and reactive mass transfer between the two phases was modelled by applying a one-fluid formulation. The results for the mass transfer coefficients were compared with the standard two-film theory (STFT).

The aim of this study was the simulation of a counter-current wetted-wall column for simultaneous removal of CO₂ and H₂S from natural gas using computational fluid dynamics. The solvent of absorption process was DEA. A 2D simulation based on the volume of fluid (VOF) model was developed. After studying the hydrodynamics of the column, mole fractions of CO₂ and H₂S were calculated in the gas output considering mass transfer from the gas phase to the liquid phase (i.e. absorption of acid gases into the amine solution) and simulation results were compared with the experimental data.

2. Simulation Procedure

2.1. Geometry

The structure of the wetted wall column used in this simulation is based on the experimental set up in the Sarkhoon and Qeshm gas Refinery Company for CO₂ and H₂S removal from natural gas. The wetted wall column is made up of two concentric tubes. The inner one is 8 cm long stainless steel wetted-wall tube with an outer diameter of 0.635 cm and thickness of 0.1 cm. The outer tube is 8.5 cm long pyrex tube with an inner diameter of 2.54 cm. Due to the symmetrical geometry of the column, a two-dimensional axisymmetric model was selected for simulation of the two-phase flow in the column. Dimensions of the column are shown in Fig. 1.

2.2. Governing Equations

2.2.1. Conservation Equations

Conservation equations are used for obtaining the main equations of the laminar fluid flow. For all kind of flows, FLUENT solves the conservation equations of mass and momentum. By writing the mass and momentum balances around a small element of fluid, Navier-Stokes and continuity equations are derived. The velocity and pressure distribution of the fluid are obtained from solving these equations (Fluent 6.3.26 users guide, 2006; Hosseini, 2013).

The general form of the continuity equation is shown in Eq. (1) (Fluent 6.3.26 users guide, 2006):

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0$$  \hspace{1cm} (1)

where \(\rho\) and \(\vec{v}\) are density and the velocity vector respectively.

The conservation equation of momentum in the inertial coordinate system is as follows (Fluent 6.3.26 users guide, 2006):

$$\frac{\partial}{\partial t} (\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{v}) = -\nabla p + \nabla \cdot (\vec{f}) + \rho \vec{g} + \vec{f}$$  \hspace{1cm} (2)

Here \(p\) is the static pressure, \(\vec{f}\) is the stress tensor, \(\rho \vec{g}\) and \(\vec{f}\) are the gravitational and external body forces respectively. By substituting the equation of stress tensor in
2.2.2. Volume Fraction Equations

In a two-phase flow in which the two fluids are immiscible, VOF model is used to track the interface between the two phases. In this model, the volume fraction of each phase is defined as a variable (Hosseini et al., 2014). The total volume fraction of phases is one in each control volume. The equation of volume fraction for liquid phase is shown in Eq. (4) (Ho et al., 2011).

\[
\frac{\partial}{\partial t}(\alpha_l \rho_l) + \nabla \cdot (\alpha_l \rho_l \vec{v}_l) = 0
\]  

(4)

This equation is derived from the conservation of mass in the liquid phase. Since the sum of volume fraction of phases is equal to 1, the gas volume fraction \( \alpha_g \) is calculated from Eq. (5) (Ho et al., 2011).

\[
\alpha_l + \alpha_g = 1
\]  

(5)

The volume averaged density and viscosity are estimated using the following equations (Ho et al., 2011).

\[
\rho = \alpha_l \rho_l + (1 - \alpha_l) \rho_g
\]  

(6)

\[
\mu = \alpha_l \mu_l + (1 - \alpha_l) \mu_g
\]  

(7)

In Fluent software, the effect of surface tension along the interface of phases is considered by using the continuum surface force (CSF) model. In this model, by applying the surface tension to the VOF calculations, a source term appears in the momentum equation. The source term is as follows (Hosseini et al., 2014):

\[
\vec{F} = \sigma \frac{\rho K a_i}{\tau (\rho_l + \rho_g)}
\]  

(8)

where \( K \) is the interface curvature and is computed from the gradients of the unit normal \( \hat{n} \) at the interface (Hosseini, 2013; Hosseini et al., 2014).

\[
K = \nabla \cdot \hat{n}
\]  

(9)

Here \( \hat{n} \) is as follows:

\[
\hat{n} = \frac{\nabla a}{|\nabla a|}
\]  

(10)

In Fluent, the effect of contact angle between the wall and the fluid is applied by a boundary condition. Near the wall, the contact angle is defined as a measure of adhesion. This boundary condition is applied to the cells near the wall and adjusts the curvature of the interface in these cells. \( \theta_c \) is the contact angle between the fluid and the wall, so the surface normal vector in the cell next to the wall is calculated from Eq. (11).

\[
\hat{n} = \hat{n}_w \cos \theta_c + \hat{t}_w \sin \theta_c
\]  

(11)

where \( \hat{n}_w \) and \( \hat{t}_w \) are the unit normal and tangent vectors to the wall (Ho et al., 2011). So, the defined surface curvature for cells is used for the surface tension calculations (Chen et al., 2011).

2.2.3. Mass Transfer

The fluid flow in the wetted wall column for simultaneous absorption of carbon dioxide and hydrogen sulfide is along with mass transfer between two phases and also chemical reaction. Species transport equation is derived by solving the conservation equation of chemical species in the multiphase flows. The equation of species transport is as follows (Fluent 6.3.26 users guide, 2006):

\[
\frac{\partial}{\partial t}(\rho \alpha_i Y_i^q) + \nabla \cdot (\rho \alpha_i \vec{v}_i Y_i^q) = -\nabla \cdot (\vec{F}_i) + R_i^q + \sum_{j=1}^{n} (\vec{m}_{ip} - \vec{m}_{pj})
\]  

(12)

where \( \alpha_i^q \) is the volume fraction of phase q, \( Y_i^q \) is the mass fraction of component i in the phase q, \( \vec{F}_i \) is the vector of mass transfer flux for component i in the phase q, \( R_i^q \) is the production rate of component i by chemical reaction in the phase q and \( \vec{m}_{ip} \) is the mass transfer rate between components i and j from phase q to the phase p.

2.2.4. Mass Transfer Equation at the Interface

Mass transfer rate at the gas-liquid interface is calculated from the equation based on the two-film theory (Hosseini et al., 2014).

\[
\vec{m}_{lg,n} = E k_a a_s M^n C_n (x_n^i - y_n^i) = k_s a_s M^n C_n (y_n^i - y_n^g)
\]  

(13)

where \( x_n^i \) and \( y_n^i \) are the mole fraction of component n at the interface of liquid and gas phases, \( x_n^g \) and \( y_n^g \) are the mole fraction of component n in the bulk liquid and gas phases, \( a_s \) is the specific area, \( M^n \) is the molecular weight of component n, C is the total concentration of each phase, \( k_1 \) and \( k_g \) are the
mass transfer coefficients in liquid phase and gas phase respectively and $E$ is the enhancement factor for considering the effect of chemical reaction. Using the two- film theory and the assumption of equilibrium at the gas- liquid interface, the relationship between $x_i^g$ and $y_i^l$ is obtained by Henry's law.

$$C_i x_i^g H_e = p y_i^l$$  \hspace{1cm} (14)

In the equation (14), the unit of Henry's constant is $\frac{kmol}{m^3}$.

Using the penetration theory, mass transfer coefficients in gas and liquid phases are calculated as follows (Hosseini, 2013):

$$k_g = 2 \frac{D_{n_i,g}}{\tau T_g}$$  \hspace{1cm} (15)

$$k_l = 2 \frac{D_{n_i,l}}{\tau T_l}$$  \hspace{1cm} (16)

The contact time at the interface of the two phases is the same and is calculated as follows (Hosseini, 2013):

$$\tau_g = \tau_l = \frac{L_t}{w_i^x}$$  \hspace{1cm} (17)

where $L_t$ is the length of each cell along the flow for numerical simulation and $w_i^x$ is the interface velocity along the flow.

Because of chemical reaction between CO$_2$ and amines, the molecular diffusion coefficient of CO$_2$ cannot be measured directly. So, the N$_2$O analogy can be used to estimate the diffusion coefficient of carbon dioxide into amine solutions. Based on this analogy, due to the similarities between CO$_2$ and N$_2$O molecular structures, diffusion coefficient of CO$_2$ into amine solutions is proportional to the diffusion coefficient of N$_2$O into amine solutions. This analogy is shown by Eq. (18).

$$D_{CO_2,m} = D_{N_2O,m} \frac{D_{CO_2,w}}{D_{N_2O,w}}$$  \hspace{1cm} (18)

Where $D_{CO_2,w}$ and $D_{N_2O,w}$ are the diffusion coefficients of CO$_2$ and N$_2$O into water and are calculated as follows:

$$D_{CO_2,w} = 2.35 \times 10^{-6} \exp(- \frac{2119}{T})$$  \hspace{1cm} (19)

$$D_{N_2O,w} = 5.07 \times 10^{-6} \exp(- \frac{2371}{T})$$  \hspace{1cm} (20)

and Eq. (21) is used to calculate the diffusion coefficient of N$_2$O into DEA solution (Ko, Tsai, Lin, Wang, & Li, 2001).

$$D_{N_2O,m} = (5.07 \times 10^{-6} + 2.17 \times 10^{-6} \times C_{DEA} + 2.29 \times 10^{-6} \times C_{DEA}) \times \exp(- \frac{2371 - 2.92 \times 10^6 \times C_{DEA}}{T})$$  \hspace{1cm} (21)

where $C_{DEA}$ is the concentration of DEA solution in terms of $kmol/m^3$.

The diffusion coefficient of $H_2S$ into amine solution is calculated by the modified equation of Stokes- Einstein as follows (Hosseini, 2013):

$$D_{H_2S,w} = D_{N_2S,w} \left( \frac{T_w}{T} \right)^{0.6} \left( \frac{\mu_w}{\mu} \right)$$  \hspace{1cm} (22)

where $\mu_w$ is the viscosity of water and $D_{H_2S,w}$ is the diffusion coefficient of H$_2$S into water at $T_w$.

The N$_2$O analogy is also used to determine Henry’s constant of CO$_2$ for absorption of it into DEA solution. The Eq. (23) shows this analogy (Penttilä, Dell’Era, Uusi-Kyyny, & Alopaeus, 2011).

$$H_{CO_2,m} = H_{N_2O,m} \left( \frac{H_{CO_2,w}}{H_{N_2O,w}} \right)$$  \hspace{1cm} (23)

The Henry’s constants for dissolution of CO$_2$ and N$_2$O in water are defined as follows (Penttilä et al., 2011):

$$H_{CO_2,w} = \exp(145.369 - \frac{8172.355}{T} - 19.303lnT)$$  \hspace{1cm} (24)

$$H_{N_2O,w} = \exp(158.245 - \frac{9048.596}{T} - 20.860lnT - 0.00252T)$$  \hspace{1cm} (25)

The Henry’s constant for dissolution of N$_2$O into pure DEA is calculated by the Eq. (26) (Penttilä et al., 2011).

$$H_{N_2O,DEA} = -11958 + 50.478T$$  \hspace{1cm} (26)

Equation (27) is used to calculate Henry’s constant for dissolution of N$_2$O in DEA solution (Penttilä et al., 2011).

$$H_{N_2O,DEA} = \sum_{i=1}^{2} H_{N_2O,i} x_i$$

$$+ 4899600 \times 0.015 \left[ x_i^0 x_s^0 \right] \left[ 1 - \frac{T}{362.079} \exp(-15.809 x_s) \right]$$  \hspace{1cm} (27)

Here $x_i$ is the mole fraction of component i in the solvent. 1 refers to the water and 2 refers to the DEA. In the above equations, the Henry’s constant is in terms of $\frac{kmol}{m^3}$ and temperature is in term of K.
The Henry's constant for dissolution of \(H_2S\) in water is calculated from the following equation (Carey, Hermes, & Rochelle, 1991):

\[
H_{H_2S,w} = \frac{\exp(342.595 + 0.0595651 \times T - 55.0551 \ln T - \frac{15236.8}{T})}{\rho_w}
\]

(28)

where \(H_{H_2S,w}\) is in terms of \(\text{atm} \cdot m^3/\text{mole}\).

When two gases are simultaneously absorbed in a solution containing a component which can react with both of the gases, the absorption rate of each gas would be affected by the other one. The reaction of \(H_2S\) with primary and secondary amines can be considered as an instantaneous reaction. An instantaneous reaction is limited by diffusion. Since the reaction is very fast, the reactant and the absorbed gas in the liquid phase cannot simultaneously exist in the same area of the liquid. The reaction of \(CO_2\) with primary and secondary amines is very slower than the reaction of \(H_2S\) and often can be considered the second order. In this research, the simultaneous absorption of two gases into the liquid containing a component that reacts with both of the gases is simulated based on Higbie’s penetration theory. The reaction of \(H_2S\) with DEA is instantaneous and the reaction of \(CO_2\) with DEA is considered second order (Haimour & Sandall, 1983).

Because of chemical reaction in the liquid phase, \(R_t\) in Eq. (12) should be substituted with the kinetics of reaction. Equation (29) gives the mechanism of reaction between \(H_2S\) and DEA.

\[
R'R'NH + H_2S \leftrightarrow R'R'NH_2^+ + HS^- 
\]

(29)

Since this reaction is so fast, it can be considered as an instantaneous reaction. The mechanism of reaction between \(CO_2\) and DEA is also given by Eq. (30) (Versteeg, Van Dijck, Van Swaaij, 1996).

\[
R'R'NH + CO_2 \leftrightarrow R'R'NCOO^- + H^+ 
\]

(30)

Here \(R'R'NH\) is DEA and \(R' = CH_2CH_2OH\). Equation (31) shows the rate of the reaction between \(CO_2\) and DEA using the reaction constant developed by Blanc and Demarais (Versteeg et al., 1981).

\[
R_{CO_2} = 2.81 \times 10^7 \exp(-\frac{5237}{T})[CO_2][DEA] 
\]

(31)

in which \(T\) is in term of K and concentrations are in terms of \(\text{mol} / \text{m}^3\).

2.3. Solution Method

Due to the dynamic nature of the two-phase flow, unsteady state calculations were chosen for the solution of the equations with a time step of \(10^{-5}\) s and the residual amount of the parameters was considered 0.001. The SIMPLE algorithm was used for pressure-velocity coupling calculations. The PRESTO! method was selected for discretization of the pressure equation and a second order upwind calculation method was applied for discretization of momentum, volume fraction and species equations. The equations of mass transfer rate between two phases were defined using the user-defined function (UDF).

2.3.1. Initial and Boundary Conditions

Uniform velocity inlet and atmospheric pressure outlet were used as boundary conditions for inlet and outlet of the phases respectively. At the walls of the column, no-slip boundary condition was applied. At time zero, gas and liquid velocity magnitudes and volume fraction of liquid phase were set to zero as initial conditions.

Table 1 shows the compositions, volume flow rates and inlet velocities for both gas and liquid phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Volume flow rate (\left(L/min\right))</th>
<th>Inlet velocity (\left(m/s\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>10 % wt DEA</td>
<td>0.055</td>
<td>0.0617</td>
</tr>
<tr>
<td></td>
<td>90 % wt water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23 ppm (H_2S)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>1 %mol (CO_2)</td>
<td>0.5592</td>
<td>0.01962</td>
</tr>
<tr>
<td></td>
<td>(CH_4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Results and Discussion

In this section, the results of CFD simulation for VOF profile and liquid film formation with time, pressure, velocity and concentration profiles are presented. Simulation results for mole fractions of CO₂ and H₂S in output gas are compared with experimental data. Then the concentration distribution in gas and liquid phases and the effect of temperature on absorption process are investigated.

Figure 2 shows the geometry generated in Gambit software for liquid film formation. After the complete formation of the liquid film, since the effective length for absorption process is $x=0$ to $x=8$ cm, the geometry shown in Fig. 3 was used for mass transfer simulation.

In order to reduce the calculations time and also less precision required in the gas phase, smaller and larger grid sizes were used for liquid and gas regions respectively. The grid independency was checked by using three different mesh sizes with a total number of 116850, 121000 and 142750 cells. The results of these three cases were close together for the average thickness of the liquid film. Therefore the grid with 121000 numbers of cells was selected as the suitable grid.

3.1. Validation of Simulation Results for Liquid Film Thickness

In order to validate the simulation results for liquid film thickness, as respects the liquid film thickness for 10% DEA solution has not been measured experimentally, the column is simulated for different flow rates of water-air flows in laminar flow regime. The results of these simulations for the film thickness are compared with the experimental data published by Yih and Hsu (1985) and also Zhou, Gambaryan-Roisman, and Stephan (2009) in laminar flow regime. Table 2 gives the results of these comparisons. As it is observed, by increasing the Reynolds number, the average film thickness increases and there is a good agreement between simulation results and the experimental data. So it is concluded that the developed model can determine the liquid film thickness in laminar flow regime and does not need to guess an initial value for film thickness unlike similar works previously done.

3.2. VOF Profile

To determine the volume fraction of each phase, VOF equation with mass conservation (continuity) and conservation of momentum (Navier-Stokes) equations were solved. Figure 4 shows the formation of the liquid film with time. In this figure, red colour refers to the presence of DEA solution and the dark blue refers to the presence of natural gas ($\text{CH}_4+\text{CO}_2+\text{H}_2\text{S}$). As it can be seen, after the liquid overflows, a thin film streams down on the wall and finally exits the column. It takes about 48 seconds to form a stable liquid film.
Table 2. Comparison of simulation results and experimental data for liquid film thickness in two different Reynolds numbers of liquid.

<table>
<thead>
<tr>
<th>$Re_l$</th>
<th>$\delta_{simulation}$ (mm)</th>
<th>$\delta_{experimental}$ (mm) (Yih &amp; Hsu, 1985)</th>
<th>$\delta_{experimental}$ (mm) (Zhou et al., 2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.2850</td>
<td>0.2928</td>
<td>0.300</td>
</tr>
<tr>
<td>600</td>
<td>0.3288</td>
<td>0.3149</td>
<td>0.320</td>
</tr>
</tbody>
</table>

Figure 4. Contours of liquid volume fraction for aqueous DEA solution (10-wt% DEA) with the passage of time.
3.3. Velocity Profile

Obtaining the correct distribution of velocity is very important in order to simulate the counter current gas-liquid flow in the column. The simulation results for velocity magnitudes are shown in Figs. 5 and 6. As one can see, the velocity magnitude is zero on the wall due to applying a no-slip condition on this wall.

The profile of velocity magnitude at x = 4 cm is clearly shown in Fig. 6. As can be seen, the velocity magnitude is zero on the walls (r = 0.3175 cm and r = 1.27 cm) due to the no-slip condition. Because of the counter current gas-liquid flow, the mixture velocity tends to zero at r = 0.64 cm.

Figure 7 shows the axial velocity contour so that the negative values refer to the liquid film flow in the opposite direction of gas flow. The profile of axial velocity at x = 4 cm is shown in Fig. 8. The gas-liquid counter current flow is clearly shown by negative values for downward liquid flow and positive values for upward gas flow in the column.

![Figure 5](image5.png)

*Figure 5. Contour of velocity magnitude for counter current gas-liquid flow in the wetted-wall column*

![Figure 6](image6.png)

*Figure 6. Profile of velocity magnitude (m/s) at x=4 cm*
Figure 7. Axial velocity contour for counter current gas-liquid flow in the wetted-wall column

Figure 8. Profile of axial velocity (m/s) at x=4 cm

Figure 9. Comparison of axial velocity profiles in different heights of the column
In Fig. 9 axial velocity profiles in different heights of the column are compared together. As can be seen, the velocity profiles are completely coincident so that both liquid and gas flow in the column can be considered fully developed after x= 2 cm.

In Fig. 10 the counter-current flow of gas and liquid is clearly shown by using the vector form of axial velocity. As can be seen the liquid moves downward and the gas flow direction is upward.

3.4. Validation of the Simulation Results

In order to validate the applied model, simulation results for outlet concentrations of acid gases were compared with experimental data obtained in Sarkhoon and Qeshm gas refinery laboratory at 25, 30 and 35°C. Tables 3 and 4 show a good agreement between the simulation results and the experimental data. As the simulation results show, CO₂ and H₂S output mole fractions increased as the temperature increased. When the temperature increased from 25 °C to 30 °C, CO₂ output mole fraction rose from 0.00701 to 0.00736 which is 4.99 % increase and H₂S output mole fraction increased from 6.04 ppm to 6.61 ppm which showed a rise of 9.44 %. At 35 °C, CO₂ and H₂S output mole fractions increased 0.68 % and 11.8 % respectively toward 30 °C. So, it can be concluded that H₂S was more sensitive to temperature changes.

Table 3. Comparison of simulation results and experimental data for CO₂ mole fraction in the column gas outlet

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mole fraction of CO₂ in the gas outlet</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Simulation results</td>
<td>Experimental data</td>
</tr>
<tr>
<td>25</td>
<td>0.00701</td>
<td>0.0075</td>
</tr>
<tr>
<td>30</td>
<td>0.00736</td>
<td>0.0071</td>
</tr>
<tr>
<td>35</td>
<td>0.00741</td>
<td>0.0073</td>
</tr>
</tbody>
</table>
Table 4. Comparison of simulation results and experimental data for \( \text{H}_2\text{S} \) mole fraction in the column gas outlet

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mole fraction of ( \text{H}_2\text{S} ) in the gas outlet (ppm)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Simulation Results 6.04</td>
<td>Experimental data 6</td>
</tr>
<tr>
<td>30</td>
<td>6.61</td>
<td>7</td>
</tr>
<tr>
<td>35</td>
<td>7.39</td>
<td>7</td>
</tr>
</tbody>
</table>

For obtaining the concentration distribution in the column, the species transport equations were solved with other equations simultaneously. The UDF was also applied for considering the mass transfer between two phases.

Mole fraction changes for \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) in the gas phase are shown in Figs. 11 and 12 respectively. As expected, with the upward flow of the gas, the acid component mole fractions are decreased and in the upper part of the column due to the gas contact with fresh amine, more changes are observed for \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) concentrations. As the solvent goes downward, the amount of absorbed acid gases is increased. Thus, fewer changes are observed in the acid gas concentrations in the lower part of the column.

![Figure 11](image1.png)

**Figure 11.** Contour of \( \text{CO}_2 \) mole fraction in the gas phase

![Figure 12](image2.png)

**Figure 12.** Contour of \( \text{H}_2\text{S} \) mole fraction in the gas phase

Figure 13 shows the changes of \( \text{CO}_2 \) mole fraction in radial direction at three different sections \( x = 2 \text{ cm}, x = 5 \text{ cm} \) and \( x = 7 \text{ cm} \). As one can see, the mole fraction of \( \text{CO}_2 \) in the bulk gas is more than the gas interface and at the liquid interface is more than the \( \text{CO}_2 \) mole fraction in the bulk liquid. In the upper sections of the column, more concentration changes are observed in the gas phase due to the gas contact with fresh amine solution. Figure 14 compares the changes of radial \( \text{CO}_2 \) concentration profiles in the gas phase at different sections of the column. As it is shown, in the lower part of the column where the gas has just entered the column \( (x=2 \text{ cm}) \), \( \text{CO}_2 \) concentration in the gas is high but with upward flow and absorption of \( \text{CO}_2 \) in the solvent, \( \text{CO}_2 \) concentration in the gas phase decreases in the upper part of the column \( (x=7 \text{ cm}) \).
Figure 13. CO₂ mole fraction profiles at three different sections of the column
(a) x=2cm (b) x=5cm (c) x=7cm
Figure 14. Comparison of CO\textsubscript{2} mole fraction profiles in the gas phase at different sections of the column

Figure 15. H\textsubscript{2}S mole fraction profiles at three different sections of the column (a) x=2cm (b) x=5cm (c) x=7cm
Figures 15 and 16 also show H$_2$S concentration profiles. The changes of H$_2$S mole fraction in both gas and liquid phases at different heights of the column are shown in Fig. 15. As it is shown in Fig. 16, the mole fraction of H$_2$S in the gas phase decreases with upward flow and absorption of H$_2$S in the solvent. Figure 16 shows the changes of H$_2$S concentration profiles in the gas phase at different heights clearly. As the gas flows upward through the column, H$_2$S is absorbed in the amine solution, so more changes are observed in H$_2$S concentration in the gas phase at upper parts of the column.

When CO$_2$ is transferred from the gas to the liquid phase, it reacts with DEA in the solution and is consumed. Figure 17 shows the reaction rate in the liquid phase. As can be seen, CO$_2$ in the liquid phase is consumed according to a second-order reaction at the liquid interface and the reaction only occurs at the interface.

In a gas absorption process using a wetted wall column, the fresh solvent enters from the top of the column (x=8 cm). CO$_2$ and H$_2$S mole fractions in the solvent increase in the flow direction with downward flow and absorption of acid gases in the solvent. Also, due to the reaction between CO$_2$ and DEA in the liquid phase, the mole fraction of reaction products increase as the liquid moves downward. Figure 18 shows the changes of CO$_2$ and H$_2$S mole fractions and Fig. 19 shows the changes of reaction products mole fractions in the liquid phase.

![Figure 16. Comparison of H$_2$S mole fraction profiles in the gas phase at different sections of the column](image1)

![Figure 17. Reaction rate of CO$_2$ in the liquid phase in terms of (kgmol/m$^2$.s)](image2)
Figure 18. Changes in acid gases mole fractions in the solvent (a) CO$_2$ (b) H$_2$S

Figure 19. Changes of reaction products mole fractions in the solvent (a) R’R’NCDO$^-$ (b) H$^+$
3.5. The Effect of Temperature on the Absorption of Acid Gases

In order to evaluate the effect of temperature on the absorption of CO₂ and H₂S, the process was simulated at 25, 30 and 35°C. The results of CO₂ and H₂S mole fractions in the output gas are shown in Table 5. As can be seen, the mole fraction of acid gases increased with increasing temperature, which means the absorption amount is decreased as the temperature increased and this is completely explainable due to the exothermic absorption reaction.

4. Conclusions

The simultaneous absorption of carbon dioxide and hydrogen sulfide from natural gas into DEA solution in a wetted wall column was simulated using computational fluid dynamics (CFD). The volume of fluid (VOF) model was applied for simulating the gas-liquid two-phase flow. In order to study the hydrodynamics of the process, volume fraction distribution of the phases, liquid film formation and its thickness and velocity profiles were investigated and it was observed that the developed model was applicable to predict the liquid film thickness carefully in a wetted wall column and in
comparison with previous works there is no need to determine an initial value for liquid film thickness. Then by considering mass transfer from the gas phase to the liquid phase, absorption of CO₂ and H₂S into the solvent was simulated and concentration distribution of the components in the column was obtained. In order to study the effect of temperature on absorption of CO₂ and H₂S, the absorption process was simulated at 25, 30 and 35°C. It was observed that by increasing temperature, the absorption of acid gases was decreased. The simulation results were compared with the experimental data for output concentration of acid components in the gas and a good agreement was observed between them. In conclusion, the effects of different parameters on absorption process can be studied using these numerical simulations without the need for costly research experiments.

Acknowledgments
The authors acknowledge Sarkhoon & Qeshm gas treating company for providing us with the experimental data.

Note: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

List of Symbols
\begin{itemize}
\item \( A \): Area (m²)
\item \( a_e \): Specific area (\( \frac{m^2}{m^3} \))
\item \( C \): Concentration (\( \frac{mol}{m^3} \))
\item \( D \): Diffusion coefficient (\( \frac{m^2}{s} \))
\item \( E \): Enhancement factor
\item \( \vec{F} \): Force (N)
\item \( \vec{g} \): Gravity acceleration (\( \frac{m}{s^2} \))
\item \( He \): Henry’s constant (\( \frac{m^3}{mol \cdot atm} \))
\item \( J \): Diffusion flux (\( \frac{kg}{m^2 \cdot s} \))
\item \( K \): Interface curvature
\item \( k \): Mass transfer coefficient (\( \frac{mol}{s \cdot m^2} \))
\item \( L \): Length (m)
\item \( \dot{m} \): Mass flow rate (\( \frac{kg}{s} \))
\item \( M \): Molecular weight (\( \frac{kg}{mol} \))
\item \( \hat{n} \): Unit normal vector
\item \( p \): Pressure (Pa)
\item \( R_i \): Production rate of component \( i \) in the chemical reaction (\( \frac{kg}{m^3 \cdot s} \))
\item \( Re \): Reynolds number
\item \( t \): Time (s)
\item \( T \): Temperature (K)
\item \( \vec{v} \): Velocity vector (\( \frac{m}{s} \))
\item \( x \): Species mole fraction in liquid phase
\item \( y \): Species mole fraction in gas phase
\item \( Y \): Species mass fraction
\end{itemize}

Greek Symbols
\begin{itemize}
\item \( \alpha \): Volume fraction
\item \( \delta \): Liquid film thickness (m)
\item \( \mu \): Viscosity (\( \frac{N}{m^2} \))
\item \( \rho \): Density (\( \frac{kg}{m^3} \))
\item \( \sigma \): Surface tension (\( \frac{N}{m} \))
\end{itemize}

Superscripts and Subscripts
\begin{itemize}
\item \( g \): Gas phase
\item \( i \): Interface
\item \( l \): Liquid phase
\item \( m \): Amine solution
\item \( n \): The \( n \)th component
\item \( w \): Water
\end{itemize}

References


Lillia, S., Bonalumi, D., Fosbal, P. L., Thomsen, K., & Valenti, G. (2018). Experimental data of the aqueous NH₃ and CO₂ absorption at temperatures from 15 °C to 35°C, NH₃ concentrations from 5% to 15% and CO₂ loadings from 0.2 to 0.6 measured with the Wetted Wall Column. *Datain Brief, 17*, 1240-1244.


