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## Application of Conservation of Mass on Modeling of a Dynamic Non-Isothermal Dehydrator of Natural Gas using Diethylene Glycol

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**Abstract** Using the principle of conservation of mass, mathematical models of the absorber of a Diethyleneglycol dehydration facility was developed. A model that could predict the variation of the water content of gas in mole fraction across the column height was developed. The models developed contain contributions from bulk and diffusion flows, and the effect of diffusion on the process occurring in the dehydrator was studied. The model developed were integrated numerically using the backward and forward difference methods and incorporated into the MATLAB code, an algorithm and flow chart for the solution of the models are also presented herein. The model was then validated using the initial conditions in the plant data from an SPDC DEG unit in Soku Gas Plant to ascertain if the outlet conditions predicted by the models meet the plant data outlet requirements. The results obtained showed that the effect of diffusion was noticed between  $z=0$  and  $z=0.004\text{m}$ . A deviation from plant data of 0% was observed for the gas water content at a residence time of 20 seconds, at  $z=0.004\text{m}$ . A valid conclusion to draw from this study is that the effect of diffusion on absorption of a flow process is negligible compared to the effect of bulk flow.

**Keywords** Modeling, Gas dehydration, Diethylene glycol, conservation of mass

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### 1. Introduction

Natural gas to be transported by pipeline must meet certain specifications. In addition to specifications regarding delivery pressure, rate and possibly temperature, other specifications include maximum water content (water dew point), maximum condensable hydrocarbon content (hydrocarbon dew point) and allowable concentrations of contaminants such as  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , mercaptans, gross heating value/maximum heating value, and cleanness (allowable solid contents) [1].

Water vapour is probably the most common undesirable component found in untreated natural gas. The main reason for removing water vapour from natural gas is that water vapour becomes liquid water under low temperature and/or high pressure conditions. Specifically, water content can affect long-distance transmission of natural gas due to the following facts:

- Liquid water and natural gas can form hydrates that may plug the pipeline and other equipment
- Natural gas containing  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  is corrosive when liquid water is present
- Liquid water in a natural gas pipeline potentially causes slugging flow conditions resulting in lower flow efficiency of the pipeline
- Water content decreases the heating value of natural gas being transported.

Ice formation is only a problem when the temperatures are adequately low for ice to form. Ice is especially a problem in process equipment and valves, where the ice can create blockages. Ice is mainly a problem in low temperature gas treatment like NGL recovery and gas liquefaction. When low temperature gas treatment is



utilized ultralow water contents are required, making the requirements for the dehydration process more stringent. Although ice is a problem, gas hydrates are often more troublesome.

Gas hydrates are crystals of natural gas and water which can appear far above ice formation temperature; typical temperature is 20 °C. Because the gas hydrate crystals are similar to ice crystals, the problems with gas hydrates are similar to those with ice, although gas hydrates are more troublesome because of higher formation temperature. Large amounts of hydrates can be in the gas simultaneously; this can create plugs and cause corrosion in the pipeline. Because of the potential dangers from gas hydrates they must be prevented by one of the following methods: (i) Gas dehydration (ii) Raising the temperature (iii) reducing the pressure (iv) adding inhibitors.

Inhibitors acts as antifreeze in the gas, the usual inhibitors are alcohols and glycols. Methanol and mono-ethylene glycol (MEG) are the most commonly used inhibitors, low doses are often injected continuously in pipeline where hydrate formation is a problem. Higher doses of especially methanol are used temporally to dissolve hydrate plugs. MEG is more viscous than methanol, but has the advantage of being easier to regenerate from the gas than methanol, because methanol regeneration is usually not feasible. MEG is the most commonly used glycol, because it is more efficient at a given mass concentration than di-ethylene- glycol (DEG). DEG may nevertheless be used as inhibitor in the pipeline, but only if DEG also is the glycol used in the dehydration process afterwards. In the industry there exist different methods of dehydrating natural gas. The most popular of these are liquid desiccant (glycol) dehydration and solid desiccant dehydration [2-3]. In all these processes of gas dehydration, absorption is the best separation method applied; in this process water vapour in the gas stream is absorbed in a liquid solvent stream. Glycols are the commonly used absorption liquids due to their properties that meet commercial application criteria [4-5]. Several glycols have been found suitable for commercial application such as Mono-ethylene glycol, di-ethylene glycol (DEG), tri-ethylene glycol (TEG) and tetra-ethylene glycol (TREG) are the most commonly used for absorbents. Triethylene glycol (TEG) is by far the most common liquid desiccant used in natural gas dehydration as it exhibits most of the desirable criteria of commercial suitability [6]. Higher polymers than TREG are usually not used for dehydration because they become too viscous compared to the smaller polymers. The important values are the normal boiling point, vapor pressure, viscosity, maximum recommended regeneration temperature

**Table 1:** Properties for MEG, DEG, TEG, TREG and water [7]

	MEG	DEG	TEG	TREG	WATER
Formula	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>	C <sub>6</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>18</sub> O <sub>5</sub>	H <sub>2</sub> O
Molar Mass (Kg/Kmol)	62.07	106.12	150.17	194.23	18.015
Normal Boiling Point °C	197.1	245.3	288.0	329.7	100.0
VapourPres @ 25°C (Pa)	12.24	0.27	0.05	0.007	3170
Density @ 25°C (Kg/m <sup>3</sup> )	1110	1115	1122	1122	55.56
Viscosity @ 25°C (cP)	17.71	30.21	36.73	42.71	0.894
Viscosity @ 60°C (cP)	5.22	7.87	9.89	10.63	0.469
Maximum recommended regeneration temperature (°C)	163	177	204	224	-
Onset decomposition (°C)	-	240	240	240	-

In order to Optimize the glycol dehydration unit of a natural gas plant, it is generally aimed at developing a suitable mathematical model which when tested with plant data, will help in choosing the best operating conditions required to reduce natural gas water content to the standard pipeline specification of less than 7lbH<sub>2</sub>O/MMSCF of gas [8]. Several works has been done on modeling and simulation of this unit [9], simulated an active absorption system for the absorption of CO<sub>2</sub> in a packed column using methyl diethanolamine (MDEA) as the solvent. Steady state conditions and plug flow were assumed for the gas phase, leading to a set of ordinary differential equations. Richardson et al., [10] generated a mathematical model for the wet scrubbing of CO<sub>2</sub> using chilled ammonia. In the study, diffusion and conduction terms were included in the development of the unsteady state models. These models predict the variation of the concentration of the reactants and products with time across the packed height, as well as the variation of the temperature of the system with time across the packed height. The partial differential equations developed were solved using the numerical technique of MATLAB by applying the Robin, Neumann, and Dirichlet boundary conditions (BC) [11]. Ahmed et al., [12]



studied CO<sub>2</sub> absorption using a highly concentrated monoethanolamine (MEA). Kenneth and Jackson [13] simulated the absorber unit of gas dehydration using TEG, in their models a functional industrial absorber was presented. And the results from the models were compared with data obtained from functional full-scale industrial absorber plant. In this paper the modeling of gas dehydrator was carried out in this case Diethylene glycol was used in place of Triethylene glycol

## 2. Methodology

The most common method for dehydration in the natural gas industry is the use of a liquid desiccant contactor (dehydrator) process. In this process, the wet gas is contacted with lean solvent Di-ethylene glycol as the absorbent). The water in the gas is absorbed in the lean solvent, producing a rich solvent stream and a dry gas which leaves at the top of the column.

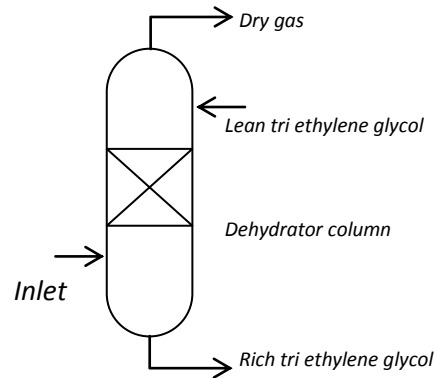


Figure 1: Schematic of the dehydrator

The approach wet gas enters the bottom of the dehydrator, and flows up counter currently with the lean diethylene glycol, which enters at the top of the dehydrator. The Diethylene glycol absorbs water vapour from the wet gas as it flows down the column and leaves the bottom of the column rich in water, whereas dry gas leaves from the top of the dehydrator. Therefore, the mass diffusion principles governing this operation will be used in developing the mathematical models for the dehydrator. The models would be developed using the principle of conservation of mass and energy to predict the variation of water content in the gas also the variation of temperature of the gas and diethylene glycol across the height of the dehydrator.

The following assumptions are made to develop the model:

- Since the column requirement is a diameter  $\leq 0.65\text{m}$  and a packing height of  $\leq 6\text{m}$  and the fluid is corrosive coupled with a minimum pressure drop cross the column, packed column is preferred to plate column [14].
- The dehydrator is well lagged, hence the heat losses is negligible.
- Since the water vapour in the wet gas is the only diffusing component, no diffusing term would be considered for the liquid phase.
- The effect of change in total molar flow rate is ignored, an average value is assumed constant [15].
- Vapour-liquid equilibrium relationship is described using Raoult's law and Antoine's equation used for calculation of vapour pressure [16].

### 2.1. Model Development

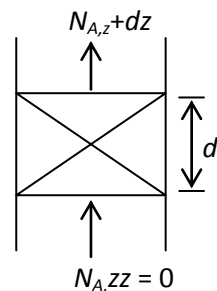


Figure 2: Elemental Packed Volume



Consider a homogeneous medium consisting of wet gas (A) and non-diffusive diethylene glycol (B); Let the packed bed be stationary (i.e. the molar average velocity is of the mixture is zero), the mass transfer may occur only by diffusion. Now consider a differential control volume  $dx dy dz$ .

## 2.2. Mass balance

A general equation can be derived for a binary mixture of wet gas and non-diffusive diethylene glycol for diffusion and convection that also includes terms for unsteady-state diffusion and chemical reaction. Making the material balance on the wet gas on an element of  $dx, dy, dz$  fixed in space and shown in Fig. 2.

The general material balance of the wet gas diffusing through the control volume in the stationary median (diethylene glycol) is given by along the x-direction;

Mass influx in the x-direction

$$= N_{A,x} dy dz \quad (1)$$

Mass efflux in the x-direction

$$\begin{aligned} &= N_{A,x} + dx dy dz \\ &= N_{A,x} dy dz + \frac{\partial}{\partial x} [N_{A,x} dy dz] dx \\ &= \left[ N_{A,x} + \frac{\partial}{\partial x} (N_{A,x}) dx \right] dy dz \end{aligned} \quad (2)$$

The difference between the mass influx and mass efflux gives the accumulation of mass of the wet gas in the control volume due to its mass diffusion in the x-direction.

Therefore, the mass of the wet gas accumulated / stored, due to diffusion, within the control volume.

$$\begin{aligned} &= N_{A,x} dy dz - \left[ N_{A,x} + \frac{\partial}{\partial x} (N_{A,x}) dx \right] dy dz \\ &= - \frac{\partial}{\partial x} (N_{A,x}) dx dy dz \end{aligned} \quad (3)$$

Similarly, the mass accumulation/stored due to diffusion along y and z direction is given by:

Along y-direction

$$= - \frac{\partial}{\partial y} (N_{A,y}) dx dy dz \quad (4)$$

Along z-direction

$$= - \frac{\partial}{\partial z} (N_{A,z}) dx dy dz \quad (5)$$

Therefore, net accumulation of mass of wet gas is given by

$$- \frac{\partial}{\partial x} (N_{A,y}) + \frac{\partial}{\partial y} (N_{A,y}) + \frac{\partial}{\partial z} (N_{A,z}) dx dy dz \quad (6)$$

The rate of accumulation of the wet gas within the control volume is given by:

$$\frac{\partial C_A}{\partial t} \cdot dx dy dz \quad (7)$$

Since the chemical reaction term is not considered, the general relation for a molar balance of the net gas for the control volume may be stated as:

$$\begin{aligned} &- \frac{\partial}{\partial x} (N_{A,y}) + \frac{\partial}{\partial y} (N_{A,y}) + \frac{\partial}{\partial z} (N_{A,z}) dx dy dz \\ &= \frac{\partial C_A}{\partial t} \cdot dx dy dz \end{aligned} \quad (8)$$

Dividing both sides of equations 8 by  $dx dy dz$  we get:

$$- \left[ \frac{\partial}{\partial x} (N_{A,x}) + \frac{\partial}{\partial y} (N_{A,y}) + \frac{\partial}{\partial z} (N_{A,z}) \right] = \frac{\partial C_A}{\partial t} \quad (9)$$

For a packed column i.e. stationary median, applying Fick's law, equation 9 reduces to

$$- \left[ \frac{\partial}{\partial x} \left( D_{AB} \frac{\partial C_A}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{AB} \frac{\partial C_A}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_{AB} \frac{\partial C_A}{\partial z} \right) \right] = \frac{\partial C_A}{\partial t} \quad (10)$$



If  $D_{AB}$  and  $C$  are constant, Eq. 10 becomes

$$-\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right] = \frac{1}{D_{AB}} \frac{\partial C_A}{\partial t} \quad (11)$$

Since the dehydrator is in vertical position;

$$-\frac{d^2 C_A}{\partial x^2} = \frac{\partial^2 C_A}{\partial y^2} = 0 \quad (12)$$

Equation 3.11 now becomes

$$\frac{\partial^2 C_A}{\partial z^2} = \frac{1}{D_{AB}} \frac{\partial C_A}{\partial t} \quad (13)$$

But

$$C_A = C_{AO} (1 - y_A) \quad (14)$$

Differentiating Equation 14

$$\begin{aligned} dC_A &= -C_{AO} dy_A \\ d^2 C_A &= -C_{AO}^2 d^2 y_A \end{aligned} \quad (15)$$

Substituting equation 15 and Equation 14 into equation 13 gives:

$$\begin{aligned} &= \left[-C_{AO}^2 \frac{\partial^2 y_A}{\partial t^2}\right] = \frac{1}{D_{AB}} C_{AO}^2 \frac{\partial y_A}{\partial t} \\ C_{AO} \frac{\partial^2 y_A}{\partial t^2} &= \frac{1}{D_{AB}} \frac{\partial y_A}{\partial t} \end{aligned} \quad (16)$$

$$\frac{\partial y_A}{\partial t} = D_{AB} C_{AO} \frac{\partial^2 y_A}{\partial z^2} \quad (17)$$

The model equation 17 can be used to predict the variation of water content of gas along the column height at different residence time.

### 2.3. Solution Techniques

#### 2.3.1. Numerical Solution to Gas Water Content Model Based on Finite Divided Difference Scheme

Given the condensed model as:

$$\frac{\partial y_A}{\partial t} = D_A \frac{\partial^2 y_A}{\partial z^2} \quad (18)$$

For  $t_0 \leq t \leq t_m$  &  $z_0 \leq z \leq z_n$

Assuming  $M = \{(z, t): z_0 \leq z \leq z_n, t_0 \leq t \leq t_m\}$  is sub-divided into  $n-1$  by  $m-1$  rectangles with sides  $\Delta z$  &  $\Delta t$  as shown in Fig. 5 below:

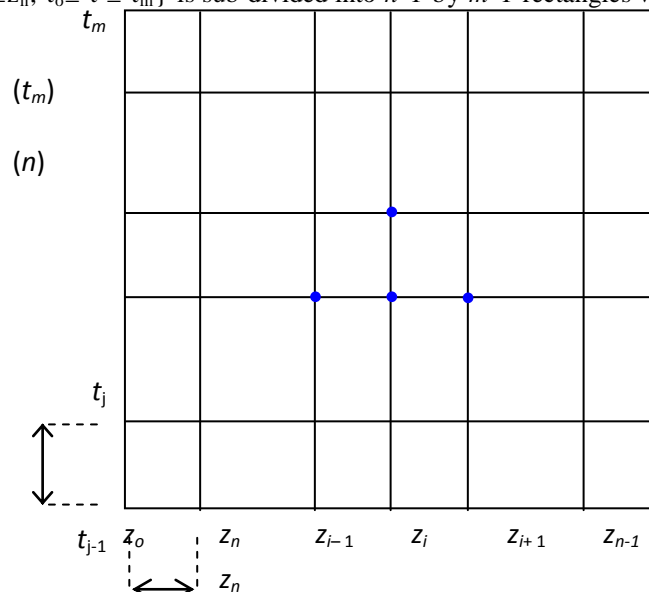


Figure 3: The grid for solving the guard PDWE over  $M$ .



Using the Taylor series, the 1<sup>st</sup> BFDD and 2<sup>nd</sup> CFDD are as follows:

$$f'(x) = \frac{f(x_i) - f(x_{i-1})}{h} \quad (19)$$

$$\& \quad f''(x) = \frac{f(x_{i-1}) - 2f(x_i) + f(x_{i+1}))}{h^2} \quad (20)$$

Applying the above eqn (19) and (20) into (18), we get:

$$\frac{y_{Ai}^j - y_{Ai}^{j-1}}{\Delta t} = D_A \frac{y_{Ai-1}^{j-1} - 2y_{Ai}^{j-1} + y_{Ai+1}^{j-1}}{\Delta z^2} \quad (21)$$

Re-arranging (34) yields:

$$y_{Ai}^j - y_{Ai}^{j-1} = \frac{D_A \Delta t}{\Delta z^2} (y_{Ai-1}^{j-1} - 2y_{Ai}^{j-1} + y_{Ai+1}^{j-1})$$

$$y_{Ai}^j = \frac{D_A \Delta t}{\Delta z^2} (y_{Ai-1}^{j-1} - 2y_{Ai}^{j-1} + y_{Ai+1}^{j-1}) + y_{Ai}^{j-1}$$

$$\text{Let } S = \frac{D_A \Delta t}{\Delta z^2}$$

$$\therefore y_{Ai}^j = S y_{Ai-1}^{j-1} - 2S y_{Ai}^{j-1} + S y_{Ai+1}^{j-1} + y_{Ai}^{j-1}$$

$$y_{Ai}^j = S y_{Ai-1}^{j-1} + (1 - 2S) y_{Ai}^{j-1} + S y_{Ai+1}^{j-1} \quad (22)$$

Equation (23) is employed to create the  $(j - 1)$  throw across the grid, assuming that approximations in the  $j^{\text{th}}$  rows are known. Notice that the formula explicitly gives the value  $y_{Ai}$ ,  $j$  in terms of  $y_{A(i-1, j-1)}$ ,  $y_{A(i, j-1)}$  and  $y_{A(i+1, j-1)}$

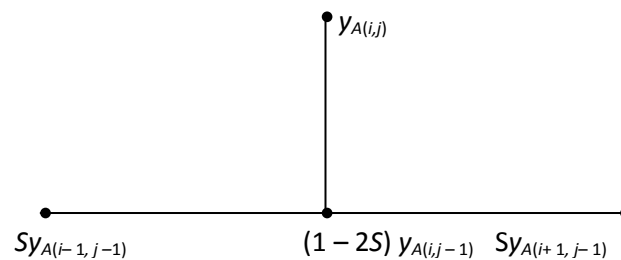


Figure 4: The forward difference stencil for  $y_A$  variations

More so, the Boundary conditions along the edges of the plate are specified by “Dirichlet B. C.”, where temperature at the boundary is set at fixed value.

$$y_A(z_o, t) = y_{Ao}, \text{ i.e. for } z = z_o = O, 0 \leq t \leq t_m$$

$$y_A(z_n, t) = y_{Af}, \text{ i.e. for } z = z_n = H, 0 \leq t \leq t_m \quad (23)$$

where  $Y_{Ao}$  &  $Y_{Af}$  are initial and final water content in gas stream respectively.

The initial condition s as follows:

$$y_A(z, t_o) = D_A \frac{\partial^2 y_A}{\partial z^2} = f(x); \text{ i.e. for } t = t_o = 0, 0 \leq z \leq H$$

Employing the 2<sup>nd</sup> CFDD to the RHS yields:

$$f(x) = \frac{D_A}{\Delta z^2} (y_{Ai-1}^{j-1} - 2y_{Ai}^{j-1} + y_{Ai+1}^{j-1})$$

However, assuming uniform  $y_A$  distribution across the first elemental packing height:  $\frac{\partial^2 y_A}{\partial z^2} = 0$

$$\therefore \text{I. C.} = 0 \quad (24)$$



### 3. Results and Discussion

The dehydrator performance was simulated based on the mathematical model equations 17 using computer programs (MATLAB 7.5 codes)

The results generated here will show the following variations of gas water content with time and axial height of packing in the column; and variation of gas water content across column height at different mass diffusivities

**Table 5:** Comparison between Plant and Predicted Process Parameters

Process Parameter	Model Prediction	Plant Data	% Deviation
Final Gas water content	7.92673E-07	7.92594E-07	0.01

#### 3.1. Variation of water content of gas with column height at different residence time

It can be deduced from the Fig.5 that the water content of the gas reduces as the gas moves from the bottom of the column to the top. It can also be deduced that the greater the residence times of the gas in the column, the higher the rate of removal of the water vapour from the gas. This holds true since a relatively smaller time is needed to establish equilibrium between the water vapour in the gas and that in the liquid phase. This means that as the residence time increases, say to 200 seconds, the water vapour returns to the vapour phase again implying that the water content in gas increases. It can also be deduced from Fig. 5 that at a height of approximately 7m and above, the gas water content variation becomes steady.

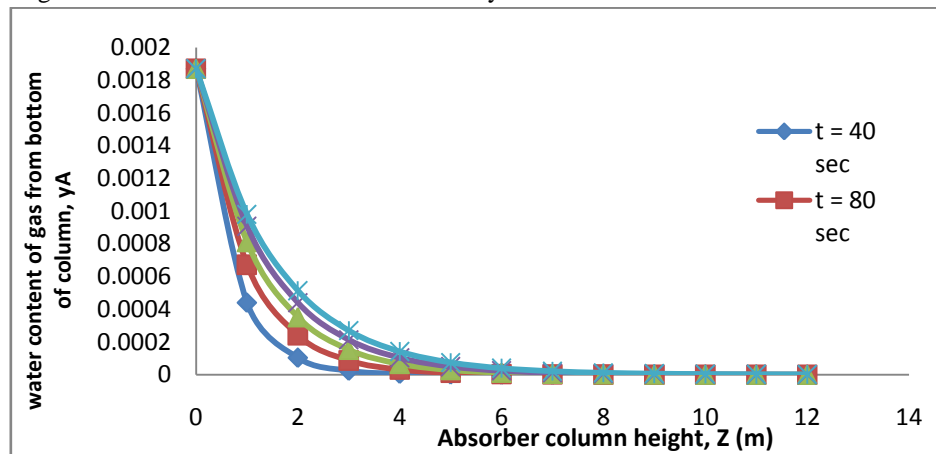


Figure 5: Variation of gas water content (mole fraction) from bottom of column

In addition, the solutions to the model will be represented as a three dimensional surface plot where the dependent variable, gas water content, is found on the z-axis and the independent variables, dehydrator column height and time, are on the x-axis and y-axis respectively. The purpose of the surface plots is to visualize the propagation of the gas water content in time and space and to make conclusions based on the subsequent trends. The surface plots are not intended to give the exact numerical values, but for visualization.

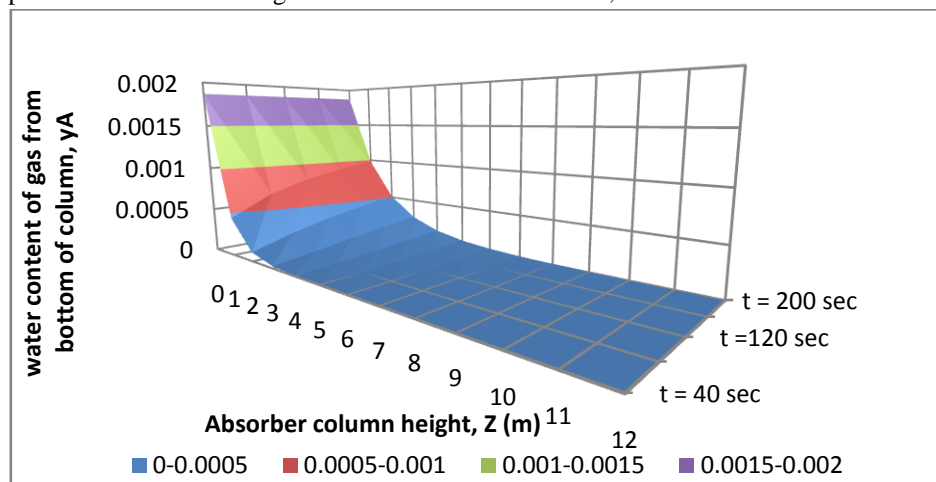


Figure 6: Surface plot showing gas water content propagation along the column



The natural gas propagates from the base of the dehydrator and initially holds a water concentration of 0.187 mol%. The low resistance in the gas bulk will cause the gas and liquid bulk phases to reach chemical equilibrium virtually instantaneous. The steep transient observed at the lower part of the column confirms the trend illustrated by Fig. 6; it is also in agreement with plant data. Also, as operation proceeds half way up the column, the absorption of water from natural gas becomes numerically insignificant and remains constant.

### 3.2. Variation of water content of gas across column height at different mass diffusivities

The quantity of material that exists in the system (mass) gives an idea of the rate or how fast at which a given component is transferred across a concentration gradient. This property is a vital parameter in this work. From Fig. 7, it is evident that given a fixed time of 40 seconds, at higher mass diffusivities, the rate of transfer of water vapour in gas to the liquid stream decreases slightly as we move up the column. As the mass diffusivity reduce the rate of transfer of water vapour in gas to the di-ethylene glycol stream increases sharply. This implies that the mass diffusion coefficient of the gas through the DEG should be as low as  $\leq 3.65 \times 10^{-10} \text{ m}^2/\text{s}$  for optimal absorption.

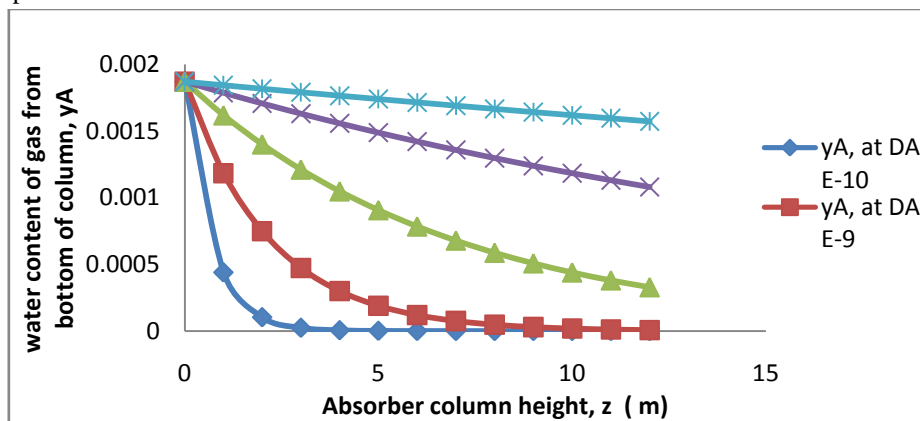


Figure 7: Variation of water content of gas at different mass diffusivities at  $t=40$  seconds

The surface plot in Fig. 8 shows that the gas water content variation widely spreads across the column's height at different mass diffusivities. In the same manner final gas water content values are obtained at mass diffusivities of  $3.65 \times 10^{-9} \text{ m}^2/\text{s}$  and  $3.65 \times 10^{-10} \text{ m}^2/\text{s}$

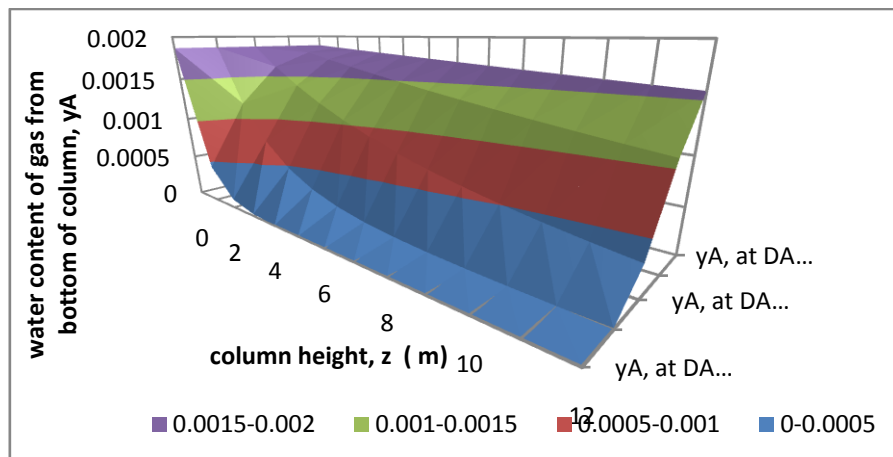


Figure 8: Surface plot showing gas water content variation at different mass diffusivities when time = 40 seconds

## 4. Conclusion

Mathematical model,  $\frac{\partial y_A}{\partial t} = D_{AB} C_{AO} \frac{\partial^2 y_A}{\partial z^2}$  of the dehydrator of a glycol dehydration facility was developed using the principles of conservation of mass. A model that could predict the variation of the water content of gas in





mole fraction across the column was developed. The models developed contain contributions from bulk and diffusion flows. The effect of diffusion on the process occurring in the dehydrator was studied in this work. The models were validated using the initial conditions in the plant data from an SPDC DEG unit in Soku Gas Plant to ascertain if the outlet conditions predicted by the models meet the plant data outlet requirements. The results obtained showed that the effect of diffusion was noticed between  $z=0$  and  $z=0.004\text{m}$ . A deviation from plant data of 0% was observed for the gas water content at a residence time of 20 seconds, at  $z=0.004\text{m}$  which makes this a best fit. A reasonable conclusion to draw from this study is that the effect of diffusion on absorption of a flow process (like the one studied in this work) is negligible compared to the effect of bulk flow.

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