



Full Length Article

Optimization of natural gas treatment for the removal of CO₂ and H₂S in a novel alkaline-DEA hybrid scrubber[☆]

Samuel Eshorame Sanni^{a,*}, Oluranti Agboola^a, Omololu Fagbiele^a, Esther Ojima Yusuf^a, Moses Eterigho Emeterere^b

^a Department of Chemical Engineering, Covenant University, P.M.B 1023, Ota, Ogun State, Nigeria

^b Department of Physics, Covenant University, P.M.B 1023, Ota, Ogun State, Nigeria



ARTICLE INFO

Article history:

Received 21 February 2019

Revised 6 November 2019

Accepted 21 November 2019

Available online 12 December 2019

Keywords:

Absorption

Acid gas

Gas treatment

Process optimization

Process simulation

ABSTRACT

Contaminated natural gas when carelessly handled, often poses human and equipment related problems ranging from lung and skin infections to corrosion, equipment fouling/failure and reduction in gas quality owing to the presence of acid gases. In this work, four natural gas (NG) samples were treated to remove CO₂ and H₂S using 10–50% Di-Ethanolamine (DEA) solutions mixed with 5% w/w 0.1 M calcium hydroxide. The treatment process gave increased acid gas removal at increased DEA concentrations. Based on the simulation results, cost effective treatment of the gas samples, require 0.1 M Ca(OH)₂ and DEA mixed solutions in the range of 27.4–30%. The optimum mixture concentration for the gas treatment was found to be 30% Ca(OH)₂-DEA hybrid solution with feed gas flow rate of 830 kscf/h. In terms of pressure energy consumption, pumping the hybrid mix at 830 kscf/h will save pressure energy as compared to pumping the feed gas at 1024.58 kscf/h since the lower and upper limit feed gas flow rates gave similar results. The optimum pressure for NG treatment was found to be in the range of 2–2.7 bar (2–2.7*10⁵ kgm⁻¹ s⁻²).

© 2019 Egyptian Petroleum Research Institute. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The risks posed by CO₂, H₂S and other impurities in Natural Gas (NG) are increasingly alarming owing to their negative consequences in humans, equipment and the environment. Natural gas may be classified as sweet or sour. It comprises of methane, ethane, propane, isobutene, n-butane, nitrogen, CO₂, O₂, isopentane, n-pentane, hexane and H₂ [1]. Other gases include helium, hydrogen sulphide and mercaptans which give the gas its characteristic odour. CO₂ and H₂S are the major pollutants in NG. For easy/safe transportation, <50 ppm CO₂ is desired [2]. CO₂ and H₂S can be trapped using amine solvents, absorption equipment and membranes [3]. Other contaminants, such as carbonyl sulphide, mercaptans, ethane, pentane etc., are usually removed via distillation and absorption. Gas purification depends on the target-solute solubility, partial vapour pressures of the constituents and the spent heat during solvent recovery [4,5]. Absorption of CO₂ from flue gas using several alcohol-amine solvents has been reported [6].

According to Fang and Zhu [7], the use of amines, carbonates, aqueous ammonia, polymer membranes, ionic liquids and enzymes are recent advances in gas treatment operations. Acid gas removal from contaminated gas depends on the desired application; in internal combustion engines, a CH₄ concentration >90% is friendly [8,9]. High CO₂ in NG reduces engine power [10,11], while ~3500 ppm H₂S in gaseous fuels may cause internal corrosion of engines [12]. High amount of CO₂ also reduces the burn-rate of natural gas [3]. Transportation of significant amounts of H₂S can cause pipeline corrosion [13], leakages, fire explosions and loss of aquatic and human lives [14] hence, the gas must be treated prior transportation [15]. In selecting a solvent for gas treatment, one must consider its solubility, viscosity, solvent corrosivity, density, thermal stability, % H₂S/CO₂ in feed gas, process economics and solvent recovery [16,17]. According to reports from National Energy Laboratory, the recommended residual sulphur threshold in NG is 0.1 ppm [18]. One popular amine for acid gas absorption is Di-ethanolamine (DEA) with formula HN(CH₂CH₂OH)₂ [19,20]. Natural gas contains significant quantities of H₂S and CO₂ [21] thus, controlling these contaminants is critical in quantifying the risks associated with equipment fouling. Natural gas liquefies at –161 °C and 1 atm which necessitates CO₂ removal [22,23].

Fig. 1 illustrates a traditional gas treatment process (i.e. the Rectisol process) where cold CH₃OH is used to absorb acid gases from

Peer review under responsibility of Egyptian Petroleum Research Institute.

* Corresponding author.

E-mail addresses: adexz3000@yahoo.com (S. Eshorame Sanni), oluranti.agboola@covenantuniversity.edu.ng (O. Agboola), omololu.oni@covenantuniversity.edu.ng (O. Fagbiele), esther.yusuf@covenantuniversity.edu.ng (E.O. Yusuf), moses.emeterere@covenantuniversity.edu.ng (M.E. Emeterere).

<https://doi.org/10.1016/j.ejpe.2019.11.003>

1110-0621/© 2019 Egyptian Petroleum Research Institute. Production and hosting by Elsevier B.V.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Nomenclature

Symbols Designations Units

Letters

F DEA flow rate kgmole/h
 G Gas flow rate kscf/h
 T Temperature °C
 P Pressure kPa, bar
 U Heat transfer coefficient kWK⁻¹
 A Heat transfer area m²
 ΔP Change in pressure kPa
 ΔT Change in temperature K

Subscripts

D_{EA} DEA concentration by volume %
 $M.f\ CO_2$ Mole fraction of CO₂ %
 $M.f\ H_2S\ Comp$ Mole fraction of H₂S ppm

Abbreviations

NG Natural gas
 DEA Di-ethanolamine
 MEA Methanolamine
 DGA Di-glycolamine

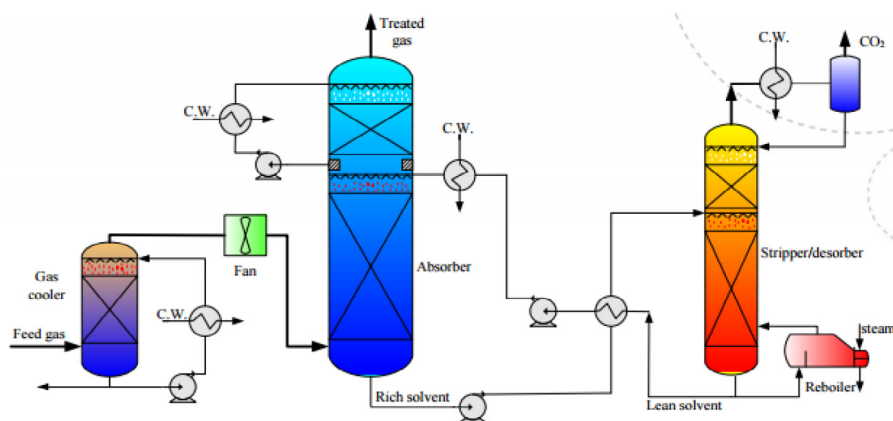


Fig. 1. A typical absorption process at atmospheric pressure.

contaminated gas [4,24–26]. Another approach is the Fluor process which takes advantage of CO₂ partial pressure and propylene carbonate (C₄H₆O₃) as solvent for removing CO₂. The Selexol process uses dimethyl ethers of polyethylene glycol to trap acid gases at 2.07–13.8 MPa. According to Tatin et al. 90% gas-purification is possible [27]. Other modelling and simulation works recorded higher but <98% gas purity [28–35]. In this study, a novel hybrid DEA and Ca(OH)₂ mixture, not previously investigated, was tested for its ability to remove acid gases in order to meet lower pumping costs and product specification of <1% vol/vol of H₂S and CO₂. An amine package (AMSIM) with adaptable features to the Kent-Eisenberg model [36–38] was adopted for the simulation.

2. Materials and methods

Equipment and Reagent: Conval Clampseal throttling valve (USA), PIBV2 post indicator and butterfly target valve supervisory switch (Ohio, USA), AYZAZ AFBT flash tank (Istanbul UAE), multi-stream heat exchanger (Linde Engineering, Germany), Gas absorber/Stripper (Rufouz Hitek Engineers Pvt. Ltd., Mumbai, India) separator (UOP7MKII, Armfield), 20-tray regenerator (Haldor Topsoes, Denmark), DEA- Ca(OH)₂ mixer (Transtech Fabrication, Texas USA), centrifugal pump (EDUR GmbH, Germany), cooler and reboiler (Industrial Heat Transfer Inc.). 10 mg of 26.6 mL of 99% DEA solution (Ludwigshafen, Germany) and 0.1 M, 5 w/w% Ca(OH)₂ of 96% purity (Muby Chemicals, India).

2.1. Process configuration

Four gas samples from fields W, X, Y and Z as given in Tables 1a and 1b were separately released from cylinders under pressure and

sent to the absorber; the method adopted here uses an alkaline-amine hybrid mixture with possibility of attaining gas purity >99%, <0.1% CH₄ loss and high solvent recovery [17]. Lean amine in parts of 10–50% DEA + 0.1 M Ca(OH)₂ mix were prepared separately in the mixer. Afterwards, each stream was pumped to the regenerator and allowed to flow through the heat exchanger (HE1) and cooler respectively. The mixture from the cooler was then allowed to flow counter-currently with samples W-Z in the absorber (Fig. 2). However, prior to conducting the experiment for the hybrid mix, it is necessary to carry out the following control experiments in order to embrace the necessity of combining both solvents (DEA and Ca(OH)₂) as hybrid mix. For the control experiments, the procedure described above was carried out for gas sample 4 (i.e. sample D) using DEA only as well as (Ca(OH)₂) only as separate solvents pumped from the mixer to the regenerator and then to the absorber. Gas sample 4 was chosen because all gas samples have near-similar/similar compositions.

After each run, on hourly basis, sweet gas was recovered from the top of the absorber while rich amine-alkaline mix from the absorber bottom was allowed to flow through a throttle valve into a separator where CH₄, H₂ and trace amounts of CO₂ were recovered. The liquid at the bottom of the separator was then contacted with the incoming regenerator hybrid-mix in HE1. From HE1, the mix was sent to the regenerator for solvent recovery. Acid gases were stripped off the rich amine-alkaline mix by raising the regenerator temperature from 93.33 to 131.56 °C. The recovered alkaline-amine was sent back as recycle-stream to the absorber in order to save energy while ensuring a continuous operation. Each amine + Ca(OH)₂ mix was taken per operation from the sample point at the regenerator for analysis. Table 1a gives the gas assays for samples 1–4 (S1-4) from fields W, X, Y and Z

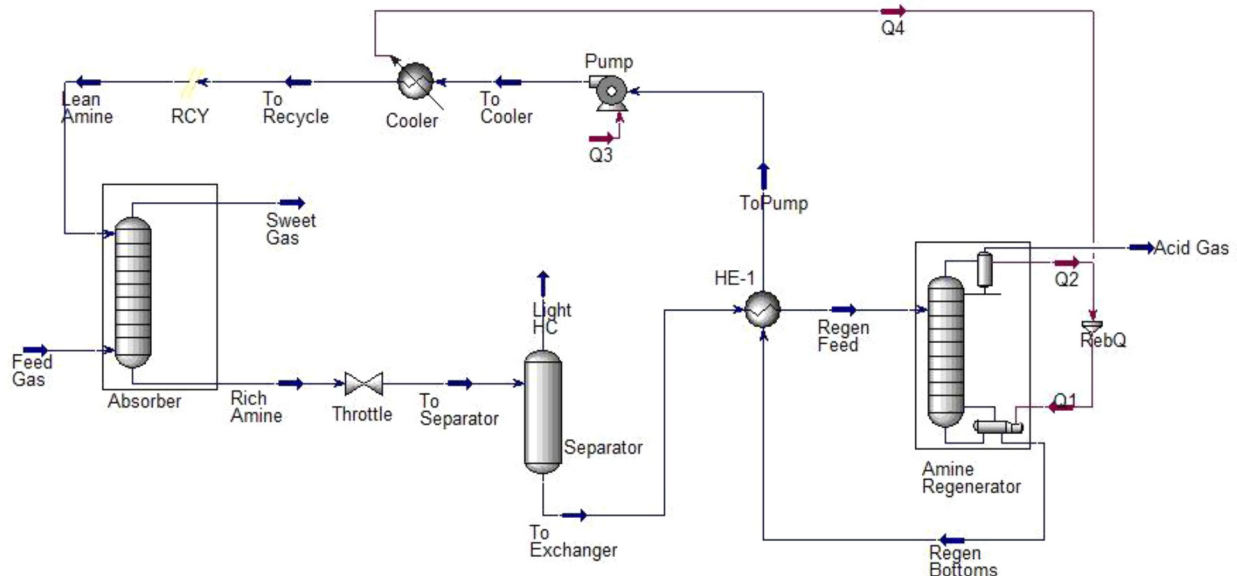


Fig. 2. Flow diagram of the absorption process.

Table 1a

Composition of Natural Gas (Feed Gas) from Fields W, X, Y and Z.

Components	Mole fraction (–)			
	Gas Sample 1	Gas Sample 2	Gas Sample 3	Gas Sample 4
Hydrogen Sulphide	0.13	0.100	0.11	0.13
Carbon dioxide	0.18	0.240	0.22	0.18
Methane	0.69	0.660	0.67	0.69
Ethane	0.000	0.000	0.000	0.000
Propane	0.000	0.000	0.000	0.000
i-Butane	0.000	0.000	0.000	0.000
n-Butane	0.000	0.000	0.000	0.000
i-Pentane	0.000	0.000	0.000	0.000
n-Pentane	0.000	0.000	0.000	0.000

respectively. The %H₂S in the samples range from 10 to 13 %; those of CO₂ and CH₄ are 18–24% and 66–69% respectively.

2.2. Process simulation

Feed gas compositions as given in Table 1b, were added to the simulation environment per simulation run. Table 2a gives the conditions in the absorber (plant data) before and after treatment. A separator with inlet temperature and pressure of 35 °C and 1650 kPa was added with estimated flow rates (Table 3). Standard

ideal liquid volume flow = 43 m³/h, % DEA-hybrid mass fractions were specified as 10–50% whilst taking into cognisance, prototype solvent specifications [39]. Number of absorber stages = 20, top pressure = 3617 kPa, bottom pressure = 3548 kPa with 40 and 70 °C as their corresponding temperatures. Tray weir height, length and diameter are 0.082, 3.3 and 4 ft respectively. %H₂S and CO₂ in the treated gas were estimated (Table 2a). Rich DEA-hybrid leaves the absorber at 482.63 kPa. Regenerator feed temperature = 93.3 °C. ΔP = 70 kPa across HE1. The regenerator consists of 20 stages. A damping factor of 0.4 was selected to control the step size and allow

Table 1b

NG/Feed Gas-Composition from Fields W, X, Y and Z Adopted for HYSYS Simulation.

Components	Mole fraction (–)			
	Gas Sample 1	Gas Sample 2	Gas Sample 3	Gas Sample 4
Hydrogen Sulphide	0.129	0.095	0.11	0.127
Carbon dioxide	0.178	0.238	0.22	0.175
Methane	0.686	0.660	0.667	0.689
Ethane	0.0031	0.0030	0.0033	0.0030
Propane	0.0022	0.0020	0.002	0.0021
i-Butane	0.00022	0.0002	0.00021	0.0002
n-Butane	0.00019	0.0002	0.00015	0.00022
i-Pentane	0.00004	0.000044	0.00042	0.00041
n-Pentane	0.00004	0.00037	0.00004	0.000039
C7+	0.00003	0.00004	0.00003	0.00003
Hydrogen	Trace	Trace	Trace	Trace
Nitrogen	0.002	0.004	0.004	0.003
Oxygen	Trace	Trace	0.0001	0.0001

Table 2a
Process Stream Conditions for Plant DEA-hybrid Treatment of NG.

Parameter	Gas Sample A Before treatment	Gas Sample B Before treatment	Gas Sample C Before treatment	Gas Sample D Before treatment	Gas sample A After treatment 10%	Gas Sample B After treatment 20%	Gas sample C After treatment 30%	Gas sample D After treatment 35%
M.Flow (kscf/h)	1024.58	2207.13	829.4	1027.3	1024.58	2203.1	830	1027.8
T (°C)	81.5	81.5	81.5	81.5	52.8	52.8	52.8	52.8
P (kPa)	6390	5270	7230	6390	5310	5270	5250	6040
Valve Opening	3/5	4/5	2/5	3/5	3/5	4/5	2/5	2/5
CO ₂ (mole frac) (-)	0.18	0.24	0.22	0.18	0.07	0.11	0.05	0.05
H ₂ S (ppm)	58.2	58.8	58.5	58.8	1.08	1.21	1.09	0.86
NO _x (-)	Trace	Trace	Trace	Trace	-	-	-	-
CN (-)	-	-	-	-	-	-	-	-

Table 2b
Process Plant Pre- and Post-natural Gas Treatment with 30% DEA + Ca(OH)₂ (Experimental Data).

Plant section 1					
Equipment	Pressure (kPa)	Temperature (°C)	No. of Trays		
Absorber (Top tray)	3535	43.3	20		
Absorber (Bottom tray)	3549	37.8			
Separator	482.6	66.2			
Amine Regenerator (Top Tray)	241.3	43.3			
Amine Regenerator (Bottom Tray)	262	131.6			
Plant section 2					
	ΔT (°C)	ΔP (kPa)	Heat Duty (kW)	Adiabatic Eff (%)	UA (kWK ⁻¹)
Pump	41.2	3390	69.7	75	-
Cooler	-63.96	0	228.5	-	-
Heat exchanger	0.42 °C	34.47	93.19	-	2.37

Table 3
Equipment Operating Conditions for DEA Hybrid Treatment of Natural gas (Simulation Results).

Stream	Temperature (°C)	Pressure (kPa)	Molar Flow (kgmole/h)
CH ₄ from absorber	37.78	3617.65	249.04
CO ₂ from regenerator	43.41	3534.92	173.77
Rich Amine mix	65.73	3548.70	2348.87
H ₂ from separator	66.21	482.63	1.16
H ₂ S from regenerator	43.33	241.32	77.64
Regen Bottoms	131.56	262.00	2270.07
Inlet to Exchanger	66.21	482.63	2347.71
Inlet to Cooler HE-1	107.30	3617.68	2270.07
Lean Amine mix	43.33	3617.68	2273.60
Regen Feed	93.33	448.16	2347.71
Inlet to Separator	66.21	482.63	2348.87
Inlet to Pump	106.78	227.53	2270.07
Recycle	43.33	3617.68	2270.07

for a faster/stable convergence. Condenser type = total condenser. The solver method = Modified HYSIM inside-out. Condenser pressure = 3617.68 kPa with ΔP of 15 kPa, reboiler pressure = 482.63 kPa, tray 1 temperature = 100 °C, reboiler temperature = 131.56 °C. Reflux ratio = 1.5. Condenser exit temperature = 43.3 °C with heat duty = 1.3×10^7 kJ/h. A mixer was used to combine the lean amine-hybrid from the regenerator and make-up amine-hybrid mix. Mixer temperature and hybrid-mix mole number = 25 °C and 1 respectively. Volume flow of cooled DEA-hybrid mix = 43 m³/h. ΔP in the condenser = 35 kPa. A pump was used to transport/recycle the cooled DEA. To ensure steady state, the multiplier was set to 1 and the offset was set at -43.3 kPa. Number of parameters = "10" while the transfer direction was chosen as "forwards" for all. The calculated and assumed stream values were compared within the specified tolerance until they converged.

3. Theory: Material balance around the absorber and estimation of absorption efficiency of the hybrid mix

Considering the liquid–gas extraction system given in Fig. 3: Y₁, Y₂ = Mole fractions of CO₂ and H₂S in the feed gas respectively, Y₁,

Y₂ = Mole fractions of CO₂ and H₂S in the exit/treated gas respectively, X₁, X₂ = Mole fractions of CO₂ and H₂S in the lean hybrid mix respectively, X₁', X₂' = Mole fractions of CO₂ and H₂S in the rich hybrid mix respectively. According to Seader and Henley [40], across a stage/plate in the absorber (Fig. 3), the total material balance is given by (1):

$$G_1 + L_1 = G_2 + L_2 \quad (1)$$

$$\text{Or } G_1 - G_2 = L_2 - L_1 \quad (2)$$

where G₁, G₂ = Feed and treated gas flow rates, L₁ and L₂ = Lean and Rich hybrid flow rates respectively. Then, for the contaminated gas entering and leaving a stage,

$$G_1(Y_1 + Y_2) = G_2(Y_1' + Y_2') \quad (3)$$

$$\frac{G_1}{G_2} = \frac{(Y_1' + Y_2')}{(Y_1 + Y_2)} \quad (4)$$

For the components in the liquid entering and leaving a stage,

$$0 = L_2X_1' + L_2X_2' \quad (5)$$

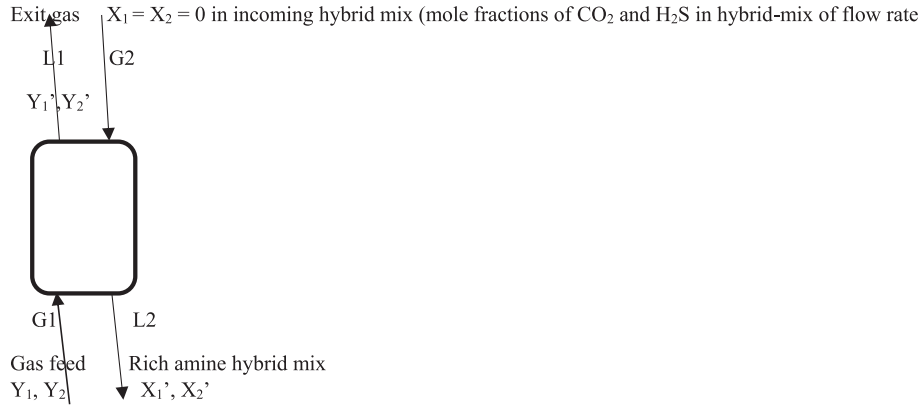


Fig. 3. Typical Absorber operation with in and outgoing streams.

From (3) and (5),

$$G_1 Y_1 + G_1 Y_2 - G_2 Y_1' - G_2 Y_2' = L_2 X_1' + L_2 X_2' \quad (6)$$

But from (2),

$$G_1 = G_2 + L_2 - L_1 \quad (7)$$

Substituting (6) in (7) gives:

$$G_2 Y_1 + L_2 Y_1 - L_1 Y_1 + G_2 Y_2 + L_2 Y_2 - L_1 Y_2 - G_2 Y_1' - G_2 Y_2' = L_2 X_1' + L_2 X_2' \quad (8)$$

$$G_2 (Y_1 - Y_1') + (L_2 - L_1) Y_1 + G_2 (Y_2 - Y_2') = L_2 (X_1' + X_2') \quad (9)$$

$$\frac{(Y_1 - Y_1')}{(X_1' + X_2')} + \frac{Y_1(L_2 - L_1)}{G_2(X_1' + X_2')} + \frac{(Y_2 - Y_2')}{(X_1' + X_2')} = \frac{L_2}{G_2} \quad (10)$$

From (2), $G_1 - G_2 = L_2 - L_1$, then

$$\frac{(Y_1 - Y_1')}{(X_1' + X_2')} + \frac{Y_1(G_1 - G_2)}{G_2(X_1' + X_2')} + \frac{(Y_2 - Y_2')}{(X_1' + X_2')} = \frac{L_2}{G_2} \quad (11)$$

Which gives:

$$\frac{1}{(X_1' + X_2')} \left[(Y_1 - Y_1') + Y_1 \left(\frac{G_1}{G_2} - 1 \right) + (Y_2 - Y_2') \right] = \frac{L_2}{G_2} \quad (12)$$

$$Y_1' = \left[Y_1 + Y_1 \left(\frac{G_1}{G_2} - 1 \right) + (Y_2 - Y_2') \right] - \frac{L_2}{G_2} (X_1' + X_2') \quad (13)$$

The absorption efficiency of the hybrid mix is then given by (14)

$$\left(\frac{\text{Initial amount of acid gas in feed} - \text{residual acid gas after absorption}}{\text{Initial amount of acid gas in feed}} \right) \times 100\% \quad (14)$$

Energy balance:

The energy of the system is estimated in terms of enthalpy changes which is a function of temperature and pressure of the absorber.

$$H = U + PV \quad (15)$$

$$\partial H = \partial U + P \partial V + V \partial P \quad (16)$$

H = Enthalpy, U = internal energy of the gas and PV = pressure * volume which is a measure of the work done by the absorber and can be expressed as:

$$H = f(T, P) \text{ at constant volume} \quad (17)$$

∂U , ∂V and V are the change internal energy, change in volume and volume of the gas respectively.

$$\partial H = C_p \partial T + \left(\frac{\partial H}{\partial P} \right)_T \partial P \quad (18)$$

∂H , ∂T , $\left(\frac{\partial H}{\partial P} \right)_T$, ∂P , C_p are changes in enthalpy, temperature, enthalpy with pressure at constant temperature, and the specific heat capacity at constant pressure. By interpolation, Eq. (18) was used to estimate the heat duties in the pump, cooler and heat exchanger.

4. Results and discussion

The results for the natural gas characterization are as given in Table 1a. The data in Table 1b is an excerpt of Table 1a that was used in carrying out the simulation. Since the entire simulation work was targeted at three major components, Table 1b was obtained with its approximated data showing the actual concentrations of methane, CO_2 and H_2S inputted to the Graphical User Interface/simulation environment of HYSYS during simulation while other components were assumed to have zero concentrations owing to their insignificant concentrations.

Tables 2a and b are plant data (Production and Exploration Company, Nigeria) obtained from the gas treatment process for 4 samples. From Table 1, gas samples 1–4 are similar in components but differ slightly in composition hence, the samples can be seen as same gas/one NG specie (NG with different compositions) since gas samples from separate fields within a province have similar history; 10 kg each of the gas samples 1, 2, 3 and 4 were retagged A, B, C and D and treated with 10, 20, 30 and 35% DEA hybrid solutions respectively. The gases were delivered at different pressures as given in Table 2a. The molar flow rates of the absorbed acid gases (i.e. CO_2 and H_2S) are not the same (Table 2b) due to their dissimilar molar masses.

For samples 1–4 (i.e. A–D), under the flow conditions established in Table 2b (plant data), the amount of H_2S in the feed gas was in the range of 52.8–58.8 ppm (Table 2a). After treatment with DEA-hybrid mix, H_2S concentration dropped to 1.08, 1.21, 1.09 and 0.86 ppm in the treated samples respectively. For CO_2 , the initial mole fraction in the feed gases A, B, C and D, were 0.18, 0.24, 0.22 and 0.18 respectively, but after scrubbing, the CO_2 mole fraction reduced to 0.07, 0.11, 0.05 and 0.05, respectively. At increased pressures, the removal of CO_2 and H_2S improved significantly. Based on the results in Table 2a, gas samples C and D gave low and medium pumping requirements of 830 and 1027.8 kscf/h respectively; the least residual CO_2 concentration of 0.05 mol fraction was obtained for gas samples (C and D) with corresponding H_2S concentrations of 1.09 and 0.86 ppm respectively. The absor-

ber pressure was in the range of 3549–3535 kPa. The separator temperature and pressure were estimated to be 66.2 °C and 482.6 kPa. The amine-hybrid regenerator temperature and pressure were in the range of 93.3 – 131.6 °C and 262–448.16 kPa, respectively. H₂S and CO₂ have dissimilar molar masses of 34 and 44 kgmole⁻¹ respectively, hence their gas velocities are not the same. The gas flow rate for NG was in the range of 830 – 2203.1 kscf/h and the DEA-hybrid molar flow rate and temperature were 251.8 kgmole/h and 52.8 °C respectively. Considering Table 3, the results from pre-gas-treatment and post-gas-treatment operations for the 4 gas samples (Table 2b) are given for 10–35% DEA-alkaline mix and the residual CO₂ and H₂S in the treated samples 1–4 are in the range of 0.05–0.11 and 0.86–1.21 ppm after pre-treatment based on plant data which give accuracies of 61, 54, 77, 72% for CO₂ removal and 98, 98, 98, 99% for H₂S removal, respectively. For higher %DEA in the hybrid mix, absorption of CO₂ and H₂S increased owing to the additional properties infused in the hybrid DEA mixtures for CO₂ and H₂S dissolution. Comparing plant with simulation results for sample 4 (i.e. pre- and post-treatment plant data in Table 2b with simulation data in Table 4a), the results from plant operations and simulation are in close agreement but, the simulation results for CO₂ gave higher accuracies/removal rates which may have resulted from changes in pressure, flow rate, temperature and concentration of absorbent [39]; gas sample 4 was chosen because, the best acid gas removal was obtained for the sample. Table 3 gives the pressure loss of the

incoming stream at the pump inlet/suction and exchanger as 3390 kPa and 34.47 kPa respectively. The stream temperature was cooled to –63.96 °C in the cooler after going through the exchanger. The power consumptions in the three equipment imply that the cooler performed more work than the heat exchanger and pump which further implies that a substantial amount of heat was dissipated in the cooler. The adiabatic efficiency of the pump is 75% which may have resulted from pressure or temperature drop at pump casing thus reducing the flow rate of the pumped liquid [39]. The molar flow rates of the stripped CO₂ and H₂S are given in Table 3. Furthermore, only 6% of the reboiler heat was lost in the absorber which makes energy conservation in this unit about 94% efficient.

Concentrations of acid gas components in the Ca(OH)₂-amine stream were expressed in terms of loadings i.e. ratio of moles of acid gas to moles of the Ca(OH)₂-amine mixture. The spreadsheet in Aspen HYSYS was used to estimate the loadings directly which were then incorporated in the simulation to serve as control for optimizing the gas treatment process and the results are as given in Fig. 4. Conditions in the absorber, separator and regenerator are as given in Table 3. In order to pass a good judgement for the treated gas samples, gas sample 4 which contained the highest amount of CO₂ and H₂S, was used to determine the best treatment conditions for the gas samples (see Tables 4 a and b).

The results obtained from the control experiments discussed in section 2.1 are contained in Table 4b; efforts were made to main-

Table 4a
Summary of Simulation Results for Treated Gas Sample 4 (Sample D).

Parameter	Simulation Data for Treatment of Sample 4				Data for Repeated Simulation for gas sample 4					
	Case1 (10% DEA _{hyb})	Case2 (20% DEA _{hyb})	Case3 (30% DEA _{hyb})	Case4 (35% DEA _{hyb})	Case5 (25.3% DEA _{hyb})	Case6 (27.4% DEA _{hyb})	Case3' (30% DEA _{hyb})	Case4' (35% DEA _{hyb})	Case 7 (40% DEA _{hyb})	Case 8 (50% DEA _{hyb})
Gas Flow (kscf/h)	1024.58	2203.1	1024.58	1027.8	2203.1	830	1024.58	1027.8	2203.1	2203.1
Ca(OH) ₂ -DEA Flow (kgmole/h)	251.8	251.8	251.8	251.8	251.8	251.8	251.8	251.8	251.8	251.8
T (°C)	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8
P (kPa)	5000	5000	5310	6040	5270	5250	5310	6040	5000	5000
Valve Opening	-	-	-	-	-	-	-	-	-	-
Mole frac CO ₂ (-)	0.16	0.024	0.00	0.001	0.004	0.00	0.00	0.00072	0.00	0.00
ppm H ₂ S (ppm)	12.19	6.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mole frac NO _x (-)	-	-	-	-	-	-	-	-	-	-
Mole frac CN (-)	-	-	-	-	-	-	-	-	-	-

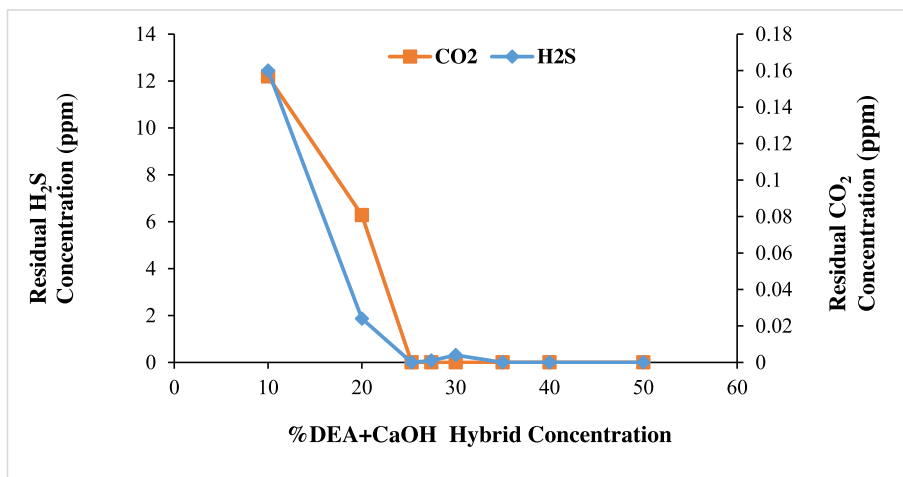


Fig. 4. Simulation results of CO₂ and H₂S absorption from NG using 0.1 M, 5 w/w% Ca(OH)₂ and 10–50% DEA.

tain the same process conditions for each solvent (i.e. DEA only or Ca(OH)₂ only) used in the gas cleaning process as contained in Table 4a for 10, 20, 30 and 35% concentrations of the hybrid mix. Here, the DEA solution was able to trap CO₂ and reduce the CO₂ gas concentration to 0.03 at increased concentrations of DEA from 10 to 30%, however, at 35% DEA concentration, the amount of trapped CO₂ increased for 10–30% DEA but increased slightly by about 27% for 35% DEA over the value obtained for 30% DEA solution; this may have been caused by the resistance posed by the presence of some H₂S in the DEA after some time. This can be justified by the results in Table 4b where more H₂S was absorbed by the DEA at increased concentration, thus, this also suggests an optimum around DEA concentration of 30%. In addition, the Ca(OH)₂ solution reduced the H₂S and CO₂ concentrations of the gas significantly (i.e. from 58.8 to 0.003 for H₂S and from 0.18 to 0.042 mol fraction for CO₂) however, in lieu of the DEA solution being able to reduce the CO₂ and H₂S significantly, there was continuous reduction in CO₂ concentration in the gas whereas, for H₂S, the best results were obtained with 10% Ca(OH)₂ which also defines an optimum concentration around the 10% for Ca(OH)₂. This may have been caused by steric effect of the overlapping ions from the solution which form a repulsive cloud that tends to prevent further absorption or interaction of electron species between the H₂S gas and the Ca(OH)₂ solution at 20–30% concentration (i.e. see Table 4b; 11.6 ppm is the concentration of H₂S in the gas after treating with 20 and 30% Ca(OH)₂ solution). However, increasing the solution concentration of Ca(OH)₂ to 35% breaks this electron cloud and thus allows for further transfer/dissolution of the H₂S molecules into the Ca(OH)₂, thus giving H₂S residual gas concentration of 8.4 ppm. Overall, the CO₂ concentration in the gas decreased for the 10–30% DEA wt/wt solution but increased for the 35% DEA solution; this then suggests that, the 35% DEA solution must have been too saturated with water which mixes with the DEA and would not allow further comingling of the DEA and water

molecules. Beyond 20% DEA conc i.e. at 30% DEA wt/wt%, the conc of CO₂ in the gas increased to 0.06 from 0.033. Also, for the DEA solution, H₂S concentration only dropped to zero for the 30–35% DEA solution which suggests that the optimum DEA concentration for H₂S removal can be as high as 35% or more when used alone for natural gas treatment, hence, the need to consider optimizing the gas treatment process in order to obtain better results. Comparing the results obtained in Table 4a with that of Table 4b, it is clear that better removal rates were obtained.

The results for the quantities of CO₂ and H₂S removed from sample 4 (sample D) as well as the estimated efficiencies have been summarized in Tables 4a and b, and 5 respectively. Based on the results, if scrubbing efficiencies >90% are desired, DEA-hybrid solutions of 10–20% concentrations should not be used for scrubbing NG contaminated with similar compositions of H₂S and CO₂ (Table 1b) since both solutions gave the lowest scrubbing efficiencies from experiment and simulation studies (Table 5).

Considering the highest and minimum pumping rates/gas flow rates of the gas, the flow rates of the simulated gas treatment operation was adjusted (Table 4a) to fall within the flow rates adopted for 10–35% DEA-hybrid solution as given in Table 2a. In Table 4, the results for CO₂ and H₂S removal imply that, gas treatment with concentrations in the range of 27.4–30% DEA hybrid solution gave the best result. Also, the results suggest that treating the gas with 10% DEA hybrid mix is not favourable considering the estimated percent efficiencies i.e. < 40%. Maximum amine-hybrid loading for removal of CO₂ and H₂S as specified by Peng and Robinson are 0.45 and 0.35 respectively [41], whereas, this work gives better Ca(OH)₂-DEA and lower mixture concentrations of 0.27–0.3 for the removal of both gases from natural gas (Table 4a, Fig. 4).

For gas sample 4, between 2 and 2.7 bar, the CO₂ and H₂S gas concentrations in the treated gas were negligible. Gas treatment at such pressures leaves the stream almost entirely free of acid gases whereas, for pressures within 3–4 bar, CO₂ removal seems

Table 4b
Summary of Simulation Results for Treated Gas Sample 4 (Sample D).

Parameter	Experimental Data for Sample 4-DEA only				Experimental Data for Sample 4-Ca(OH) ₂ only			
	Case1 10%	Case2 20%	Case3 30%	Case4 35%	Case1 10%	Case2 20%	Case3 30%	Case4 35%
Gas Flow (kscf/h)	2203.1	2203.1	1024.58	1027.8	2203.1	2203.1	1024.58	1027.8
LiqFlow (kgmole/h)	251.8	251.8	251.8	251.8	251.8	251.8	251.8	251.8
T (°C)	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8
P (kPa)	5000	5000	5310	6040	5000	5000	5310	6040
Valve Opening	4/5	4/5	3/5	3/5	4/5	4/5	3/5	3/5
Mole frac CO ₂ (-)	0.17	0.06	0.033	0.042	0.087	0.064	0.048	0.03
ppm H ₂ S (ppm)	20.2	15.5	5.88	0.003	7.6	11.6	11.6	8.4
Mole frac NO _x (-)	-	-	-	-	-	-	-	-
Mole frac CN (-)	-	-	-	-	-	-	-	-

Table 5
Scrubbing Efficiencies for the Alkaline-DEA Hybrid Solutions.

	Samples 1–4				Sample 4				
	H ₂ S Cnc	CO ₂ Cnc	CO ₂ removal eff	H ₂ S removal eff	H ₂ S Cnc	CO ₂ Cnc	%DEA HYBRID	CO ₂ eff	H ₂ S eff
S1	58.2	0.18	61	98	58.8	0.24	10	33	79
S2	58.8	0.24	54	98			20	90	89
			-	-			25.3	100	100
			-	-			27.4	99.6	100
S3	58.5	0.22	77	98			30	98.3	100
S4	58.8	0.18	72	99			35	100	100
							40	100	100
							50	100	100

Hint:

Cnc = Concentration, eff = efficiency, S1-4 = Samples 1–4.

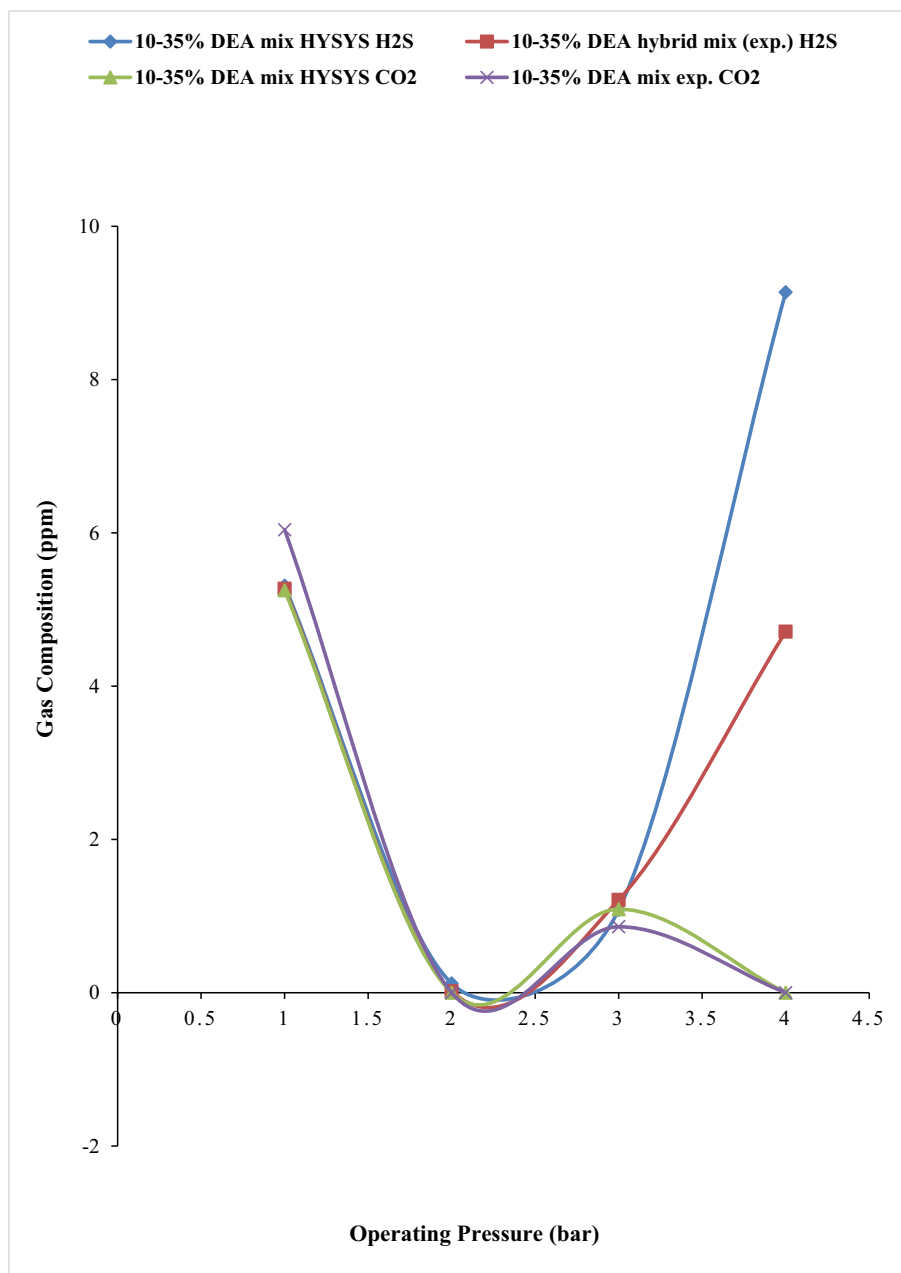


Fig. 5. Mole fraction of CO₂ and H₂S in the treated gas sample 4 at different pressures.

to be higher compared to H₂S (Fig. 5) hence, there is a close agreement between plant data and simulation results.

Another reason for the higher accuracy of CO₂ removal relative to H₂S is the increase in pressure [42] above the critical value, say in the region of 5310 kPa with corresponding flow rate of 1024.58 kscf/h where acid gas removal is highest (see left side of Table 4a); the reverse is the case at higher or lower pressures and concentrations, which then suggests the need to establish an optimum point as given on the right side of Table 4a. Considering [39], for non-hybrid DEA, the required concentration of amine/absorbent lies between 0.35 and 0.65 mol amine per mol acid gas absorbed. However, results from simulation were best for DEA-hybrid mix with concentration range of 27.4–30% mol amine/%mol gas which reduces the cost of the amine used; this also validates the findings of Erfani et al. [6] and Van-Daal and Bouallou [43].

Furthermore, the 27.3% DEA-hybrid mix gave the best results due to changes in pressure, flow rate [42,44] and the concentration of the absorbent used [39].

Considering the results of other modelling and simulation works [28–31,35], where scrubbing efficiencies <98% were obtained, and the findings of this study, 100% acid-gas removal efficiency can be guaranteed (Table 5).

4.1. Effect of pressure and temperature on the absorption/process economics

While should be noted that feed conditions remain unchanged in an absorption process, interstage variation in process conditions, such as flow rate, pressure and temperature occur because of the counter-current flow of the feed gas (natural gas) and the hybrid absorbent. Hence, it becomes necessary to account for these

changes. Across the absorber, inter stage variation in pressure, temperature and flow rate are caused by the interactions between absorbent and the absorbate which bring about pressure drop in the gas stream caused by heat exchange/mass transfer of molecules between the absorbent and the natural gas. In the acid gas removal process described by Al-Marzouqi et al. [45], for different absorbent-concentrations at increased pressures, the solubility of the acid gases (H_2S and CO_2) increased when the $\%H_2S$ removed increased with pressure for 1 wt% DEA+(10–30)wt% K_2CO_3 solutions. However, at 50 bar, the highest $\%H_2S$ removed was 99% for the DEA + 20–30 wt% K_2CO_3 solution, whereas, it was 99.3% for the 10 wt% K_2CO_3 + 1 wt% DEA, hence, the solution with 10 wt% base gave the best H_2S removal with a slight difference of 0.3%. However, the CO_2 removal rates were 97, 85.7 and 73.8% for the 1 wt% DEA + 30, 20 and 10 wt% K_2CO_3 solutions respectively. This confirms the trend obtained in the current study despite the difference in types of solvent mixed with DEA (i.e. K_2CO_3 – a base and $Ca(OH)_2$ – an alkali) in their work relative to the current study. Based on the trend observed, they suggested the need to determine the optimum pressure for highest/maximum gas removal so as to limit or reduce pumping costs which will save some amount of energy, as well as the amount of time spent on recycling the treated gas when it falls below the required specification at conditions below the optimum pressure. Also, the integrity of the equipment is preserved since equipment hammering/bombardment could ensue if the optimum pressure is exceeded; excessive pressures can result in hazards or explosions, loss of absorbent and low CO_2/H_2S removal efficiencies, which may be quite expensive to manage considering the cost that may accrue from repairs, replacement, lost production/processing time and recycling to meet specification. They also recounted that, the effect of altering the feed gas pressure is not pronounced hence, regulating the feed gas flow rate/pressure may not be necessary in an absorption process. In lieu of this, regulation of the process or inter-stage pressures during absorption is very important. Also, in their work, even when the flow rate of absorbent was constant, the effect of temperature was seen for water absorption of H_2S and CO_2 at 65 and 100 °C with the gas temperature fixed at 50 °C. It should be noted here that the gas temperature is fixed but the liquid/water temperature was varied. For both acid gases i.e. H_2S and CO_2 , absorption in water was lower at higher temperatures and vice-versa. This is because, at 100 °C which is the boiling point of water, the gas molecules are activated and their average kinetic energy is increased which makes the absorbate-molecules travel faster through the absorbent thus reducing the contact time. The longer the contact time between the absorbate and absorbent, the better the absorption and vice-versa for both physical absorption and chemical absorption. Again, at an optimum pressure of 50 bar, the best acid gas removal was achieved. Based on their results, inter-stage temperature effect is significant when the absorbent is either water or base i.e. K_2CO_3 /alkali. However, if DEA solution is used alone, the effect of temperature on the absorption process is less significant and this may be due to the slow response of the viscosity of DEA to temperature changes, hence, it is advisable to use DEA of low/measurable concentrations alongside other solvents for effective natural gas purification. Other drawbacks on the use of DEA solution as the only absorbent for acid gases include equipment corrosion, solvent degradation, foam formation and high energy requirements (due to its viscosity) hence, the need to consider combining DEA with other suitable solvents such that both adsorbents offer their individual characteristics/synergistic effects in the combined adsorbent. This also would help reduce the cost of DEA solution needed for use with cheaper solvents that have good absorption potentials for acid gases. In addition, in the same study, the absorption rate increased with increase in temperature for the absorbent (DEA + K_2CO_3). This is because, K_2CO_3 is

lighter than DEA and can easily get heated and transported with the gas at higher temperatures.

The work of Pouladi et al. [46] also considered the effect of temperature and pressure on the absorption of CO_2 from ethane gas using DEA only, or pure DEA as absorbent. The design efficiency of the plant was estimated to be a CO_2 capture of 85% which is equivalent to 19 ppm in the absorber outlet. The data generated was simulated using ASPEN HYSYS. They employed a static approach in determining the optimum conditions and found that pressure variation in the system did not have any significant effect on the absorption process. This may have been caused by the use of DEA only, its viscosity as well as the low pressure variation/difference i.e. 24–26 bar adopted in their study. However, it was observed that, the absorption efficiency of the amine improved with increase in amine-volumetric flow rate and the absorption tower inlet temperature. The effect of temperature was highly significant as obtained from simulation studies. The optimum conditions for the CO_2 absorption from ethane as feed gas were found to be 2118 kg mol h^{-1} , 75 $m^3 h^{-1}$, 53 °C and 24 bar, which are indicative of the molar flow rate of amine, the volumetric flow rate of the amine as well as the system's temperature and pressure, respectively. Again, because DEA is highly viscous, the pressure required when used alone is usually high if high acid gas removal efficiencies are desired. They obtained an optimum pressure of 50 bar which is way higher than the pressure obtained in the current study. The increase in absorption efficiency was observed from 30 to 53 °C but beyond and below 53–70 °C, CO_2 absorption declined. From all observations, these then suggests that, the behaviour exhibited by each system is a function of the absorbent, the absorbate/target component and the gas to be treated. It was also observed that the amine flow rate dropped from 120 $m^3 h^{-1}$ to 75 $m^3 h^{-1}$ at optimum conditions which then informs a low circulation/pumping cost of the amine; in essence, the results corroborate the findings in the current study. Although, pressure variation may not be somewhat significant for lone amine (i.e. when only amine is used as absorbent), however, changes may then set in if the system is hybridized (i.e. one involving combined absorbents) such that, the drawbacks of the amine (i.e. high viscosity, degradation, corrosion etc.) are complemented by the additional solvent. Furthermore, there exists a mutual relationship between the pressure and temperature exerted by a gas having a close behaviour to that of an ideal gas i.e. its pressure decreases with temperature when the gas' behaviour is near/approximately that of an ideal gas. This implies that, DEA absorbent, when used alone, renders the ideal-effect of such gases negligible.

4.2. Effect of temperature on the raw gas and the lean Amine-Hybrid Mix: The rule of thumb

Several rules are employed in the design and operation of gas sweetening units. These rules were enacted several years back. The question often arises as to how absolute or flexible these rules are. Several of these rules have been suggested for absorber conditions. The rules specified include a minimum absorber temperature of 5 °C (i.e. the temperature differential between the incoming acid gas and the lean amine-hybrid feed) in the absorber, 0.12 kg/L specification for reboiler steam, 99 °C lean/rich exchanger outlet temperature, as well as the regenerator pressure/reboiler temperature. Although these conditions or “rules of thumb” are excellent starting points, however, none of them actually depicts the optimum conditions for all cases and, considering the peculiarity of the situation, violating these rules could in turn offer considerable advantages/disadvantages to process efficiency [47], especially when the circulating fluid/coolant is a refrigerant. Gas compositions differ, and several situations may require a thorough investigation as to the validity of these set points and whether they are

beneficial to the entire process as well as offset any additional risks. Maintaining the minimum temperature of 5 °C in the absorber helps to prevent condensation of any natural gas liquid in the hydrocarbon, which will in turn lower the performance of the absorber due to foaming, loss of product and blocking of carbon filters or pipelines [25,48,49]. However, cases of natural gas liquid (i.e. components $\geq C_2$) condensation have been recorded at temperatures <28 °C for the Khazak type of natural gas [47]. Also, it has been established that, decreasing the temperature of the absorber improves its performance, which in turn enhances the absorption of H_2S while CO_2 absorption is more favoured at higher temperatures (i.e. 30–50 °C) and vice-versa [47], thus, in the current study, the amine-hybrid alkaline mix helps to alleviate this problem as the $Ca(OH)_2$ helps to complement the mix by modifying the amine component of the hybrid absorbent such that, its affinity for CO_2 is enhanced despite the temperature reduction effect which may seem to favour more H_2S absorption relative to CO_2 . Furthermore, studies have shown that, at temperatures in the range of 5–28 °C, CO_2 absorption is low while that of H_2S is higher and vice versa. In addition, it was observed that high tray temperatures at the bottom of the absorber minimized any reduction in the kinetic rate of CO_2 absorption. According to them, it is advisable to keep the bottom tray temperature of the absorber at 30–40 °C above the feed gas temperature, as this helps to create near equilibrium conditions. This further suggests that, practical limitations of the scrubber/absorber should not be ignored. For example, temperatures <25 °C have been reported to cause a drastic increase in DEA viscosity thus making the operation of the contactor/absorber/scrubber exceedingly difficult. Also, high temperatures can also speed up amine degradation. In this study, the inlet stream to the exchanger is at 66.21 °C and reaches the pump at 106.78 °C before entering the cooler at 107.30 °C (see Table 3); the inlet stream temperature to the cooler is quite excessive and will therefore lead to undesirable consequences in the absorber [47] hence, the need to cool the stream before it enters the absorber. In the current study, operating at an absorber temperature of 37.8 (methane exit temperature at the top of the absorber) to 65.73 °C (rich amine-hybrid mix temperature at the absorber bottom) also helps limit the tendencies for the recovery of inherent natural gas liquids (NGLs or condensates) [47–49]. Again, looking at Table 3 of the current study, the lean amine mix to the absorber enters at 43.3 °C which is within the recommended temperature spec of 45 °C [47].

For clarification, a closer look at Fig. 2 shows the heated lean amine-hybrid mix which leaves the regenerator and transits via a pump through HE-1. At the start of the operation, fresh amine-hybrid mix is taken at the suction of the pump linked to line Q3. At this point in time, before entering the absorber, the lean DEA + $Ca(OH)_2$ stream then goes to the cooler (second heat exchanger) which uses cooling water to help moderate the temperature of the regenerated amine-hybrid mix before it is sent to the absorber or storage unit after the entire process. In order to avoid thermal shock, once the incoming lean amine-hybrid mix is certified free of acid gases at the sample point on the line, its temperature is moderated before it enters the absorber, but if otherwise, the lean amine-hybrid mix is sent back/recycled to the regenerator for regeneration/stripping of the acid gases, and then the cycle goes on. At this time if the lean amine mix is certified okay, it is then allowed to flow to the absorber through the heat exchanger which serves to cool the lean amine entering the absorber; the process is largely a physical process and, heat sensitive, especially at the amine-hybrid mix regeneration stage (desorption stage). The reason for cooling this lean amine stream is to help regulate the temperature of the absorbent-mix prior its entry to the absorber so as to avoid the tendency for thermal shock i.e. if this stream is not cooled, there may be a sharp or sudden rise in temperature of

the NG or sudden drop in the amine-hybrid mix temperature which may cause the escape of some of the acid gases or loss of solvent due to the less contact time available for the lean amine-hybrid mix and the NG as they flow counter-currently in the absorber; also, there may be some evidential equipment hammering. Thus, moderating the temperature of the amine-hybrid mix via cooling is necessary in order to maximize or attain high efficiency in the absorption process which in turn affects the gas-amine hybrid interaction during acid gas stripping from the NG. Another function of the cooler is that it would help cool the regenerated DEA-alkaline hybrid mix upon complete removal of the acid gases before the mix is sent to the storage unit for future use. Also, since the amine-hybrid mix is less viscous than the ordinary amine, it is necessary to transport the mix at moderate temperatures in order to abate the tendencies for thermal degradation of the DEA-hybrid mix. For practical purposes, according to Addington and Ness [50], it is somewhat easy to control the absorber temperature while bearing in mind the feed gas temperature because, there are evidences of hydrocarbon dew point variations with respect to natural gas compositions. However, a blanket rule that bothers on the feed temperature set point may cause the operator to lose out on some benefits that may accrue from lowering the cooler temperature. Furthermore, despite the potential for saving operating costs, a decrease/increase in absorber performance may result in benefits/loses when the feed gas temperature decreases/increases due to capacity limitations imposed by operational constraints on the absorber. However, since absorptions of this type are quite peculiar, an investigation into optimizing the system's performance is necessary in order to maximize the benefits and risks of varying/-controlling the lean amine temperature [50].

4.3. Economic effect of optimizing pressure and temperature in a gas cleaning process

To process larger quantities of gas, more stringent specifications ought to be achieved by operating profitably at optimal conditions. This then gave rise to the need for searching other viable alternatives. From the study of Lunsford and McIntyre [51], for chemical systems involving ethanol amines, potassium carbonate or an alkali, an increase in H_2S absorption or decrease in CO_2 absorption may ensue based on the sorption kinetics. This may also slightly enhance the absorption of alkanes greater than C_1 such as C_2 – C_7 while ensuring efficient dehydration of the treated gas. According to them, for physical and chemical solvents that may approach their equilibrium concentrations, operating the absorber at lower temperatures may promote the uptake of light contaminants. However, considering the case of chemical solvents, whose reactions may have some rate/kinetically limiting steps, colder/lower temperatures may subsequently result in lowering the absorbed quantity of a particular contaminant. They also asserted that, an attempt to efficiently and economically eliminate H_2O , H_2S and CO_2 helps to reduce the tendencies for hydrate formation, environmental pollution etc. They added that, solvent type, concentration, pressure, and solvent circulation can be manipulated to produce high quality hydrocarbon product specs. Generally, based on the vapour-liquid equilibrium of absorption systems, lower temperatures tend to improve absorption of light molecular weight components. Also, it has been stated that physical solvents obey this principle, whereas, for an absorption process that involves some measure of reaction/reactive interactions, this may not be true for systems that may approach equilibrium, hence, lower temperatures may not favour the absorption of low molecular weight components. But, in the event that the absorption is kinetically limited i.e. the case with CO_2 in contact with certain amines, temperature effect on the absorption process will require certain additional information for the effect to be explicit. This anomaly/

ambiguity comes from the permissible competing phenomena/opposite effect temperature has on reaction rates and solubility. Evidence also has it that, for H₂S and CO₂ absorption in alkanolamines or mixtures of amines and other solvents, H₂S absorption reaches equilibrium while CO₂ absorption is kinetically limited in some instances. However, they concluded that, the performance of various amines and physical solvents may be compared based on criteria such as solvent and feed gas temperatures. Furthermore, a clear insight on the conflicting phenomena of absorption-equilibrium and kinetics may breed situations where optimum gas cleaning conditions may be exploited for profitable operations [51].

Basiri [52] stated that chemical absorption processes are generally categorized as systems highly dependent on heat of absorption which also require a high heat of regeneration of the spent absorbents. Consequently, the quantity of steam supplied to a reboiler increases as the heat of regeneration increases which also imposes a resultant increase in production cost. The operation of a stripper column in series with an absorber in an absorption process as done in the current study, helps to reduce the heat spent in regenerating the spent solvent which subsequently lowers the heat requirement of the process thus enhancing the continuous removal of CO₂ from natural gas. Process parameters including concentration, pressure and temperature were altered in order to determine the optimum process conditions required for minimum heat supply in the regenerator. Based on the results obtained in [52], the optimum conditions for optimal CO₂ removal from natural gas are DEA concentration, reboiler temperature and stripper pressure of 25–35 wt%, 118–121 °C, and 1.5–1.75 bar respectively. Despite showing a variation in pressure, the pressure values obtained in the study are not too far from the lower limit pressure obtained in this study i.e. 2–2.7 bar; this may have been caused by variation in other process parameters such as flow rate, type of absorbent, operating temperature and regenerator conditions.

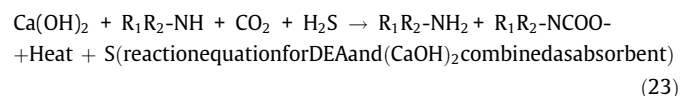
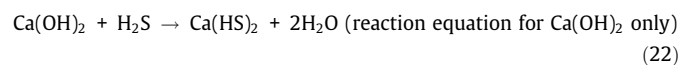
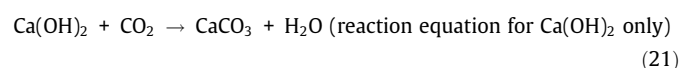
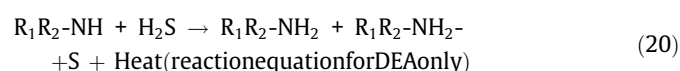
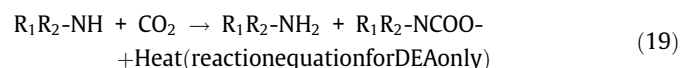
The study carried out by Aliabad et al. [53], for CO₂ and H₂S removal using MDEA and DEA in an absorber with 20 stages, gave amine outlet mass flow rates of 12938.94 and 19276.6 kg mol/h which are both 51.4 and 76.55 times the mass flow rate (i.e. 251.8 kgmole/h; see Table 4) obtained in this study. Considering the difference in the estimated flow rates for both studies, it then suggests that the current study lowers the pumping cost significantly, with high levels of accuracy in the range of 99–100% for H₂S and CO₂ removal from natural gas.

4.4. Reasons for avoiding the use of Ca(OH)₂ or DEA only for the absorption of CO₂ and H₂S and its effect on the process economics

For ethanol amine, literature has it that, the heat of regeneration is 20 Giga Joule per tonne-carbon (GJ/t-C) while for an alkali such as NaOH/(CaOH)₂ it is about 15 GJ/t-C. It is no arguable fact that the recovery of a fluid in an absorption process is usually at higher temperatures (high temperature swings)/lower pressures (low pressure swings) than those required during absorption. However, unlike NaOH, the recovery of Ca(OH)₂ can be achieved without the need for calcination at about 900 °C [54]. Although the use of DEA for gas absorption is a well proven technology with extensive commercial application as well as capital costs, however, the solvent has low tolerance for SO₂, NO_x and O₂ which are often present in natural gas. Also, since DEA is usually administered in low concentrations in order to abate issues such as equipment corrosion, this also limits its loading capacity for CO₂. In addition, DEA can undergo degradation when contaminated. Compared to Ca(OH)₂, DEA attracts higher energy requirements during regeneration of the spent solvent in an absorption process [54]. There is also the issue of solvent loss due to mist-formation for absorption systems using DEA only. An evaluation of new amine-based solvents

such as those with: low heats of absorption, high CO₂ loading (i.e. strong bicarbonate formers such as calcium hydroxide), reduced degradation/desorption and addition of additives/Ca(OH)₂ to improve absorptive performance bring about an increase in reaction rate, CO₂ loading and process improvements as well as to lower energy requirements, improve heat integration, increase solvent/DEA absorptive capacity, reduce in solvent loss (which improves mass transfer for contact between the absorbate and absorbent) as well as the ability to inhibit solvent/DEA degradation which is one of the useful properties infused by Ca(OH)₂ in the hybrid amine mix.

Based on ref. [54], the following mechanisms were proposed for the reactions between the acid gases and the DEA-Ca(OH)₂ mix for the current study:



In equations 1a and b and, 2a and b, although each solvent (i.e. DEA or Ca(OH)₂) has high affinity for H₂S and CO₂, however, the CO₂ and H₂S in the NG will compete for the DEA or Ca(OH)₂ solution thus making each solution give more preference to one type of acid gas relative to the other when used separately; the absorption preference of the acid gases with respect to DEA is more to H₂S than CO₂ while, for the Ca(OH)₂, the preference is more to CO₂ than H₂S because, CO₂ is polar with respect to the aqueous/water-containing Ca(OH)₂. The beauty of the combined mixture of DEA-Ca(OH)₂ system is that, unlike other systems where pH regulation can only be done by the addition of acid such as HCl, the hybrid-system described is self-regulating in terms of pH (i.e. from about 10.41) which favours the formation of CaCO₃ to a pH of 8–10 (i.e. 8 < pH < 10) which favours the formation of Ca(HCO₃)₂ [55]; this pH regulation helps to convert the insoluble CaCO₃ formed to CaHCO₃ by an extra step that is brought about by the continuous absorption of CO₂ by the caustic alkali. Borrowing a leaf from the explanation offered by Rackley [54] on the use of NaOH as absorbent for CO₂ capture, the use of Ca(OH)₂ as absorbent in the current study is of great advantage because, for the case of NaOH, which is a group 1 alkali, the NaOH regeneration is quite expensive because, it cannot be achieved under mild conditions such as low temperature and pressure swings, hence it will require an extra chemical reaction step such as the addition of Ca(OH)₂ to the carbonate (Na₂CO₃) formed from the trapped CO₂ + NaOH reaction. The addition of CaCO₃ to Na₂CO₃ then forms CaCO₃ and NaOH. The CaCO₃ in this case is not in continuous contact with CO₂ and hence the slurry would have attained equilibrium and would need to be heated at about 900 °C to drive off water and calcine the CaCO₃ for CO₂ regeneration; this actually makes the process more expensive and a bit more complicated. Thus, considering the last statement, for the case of the hybrid solvent comprising of Ca(OH)₂ and DEA, the produced water combines with some of the available CO₂ to form H₂CO₃ which helps to solubilize/dissolve the cloudy

CaCO₃ obtained from the reaction between the Ca(OH)₂ and CO₂ leading to the formation of soluble calcium hydrogen carbonate CaH(CO₃)₂ which is a clear solution. This continues up to/through the quasi-equilibrium state and finally ceases when equilibrium absorption of CO₂ is attained. The formation of soluble CaH(CO₃)₂ makes the regeneration of the CO₂ easy without any need for it to be calcined at an extreme temperature of say 900 °C as highlighted for NaOH + DEA absorbent and, according to Chandel and Williams [56], high cost involvement of CO₂ capture during natural gas synthesis corresponds to increased cost of natural gas obtained from the process.

5. Conclusion

NG purification was achieved using DEA solutions of 27.4–30% v/v with 0.1 M Ca(OH)₂ flowing at 258.1 kg-mole/h and at 52.8 °C. The results imply that, the quantity of acid gas removed is a measure of the quantity of Ca(OH)₂-DEA mixture used in treating the NG. The simulation results were seen to conform with standard pipeline specifications of ≤2.0 vol% CO₂ and 4 ppm (volume H₂S) which are indicative of zero tolerance for waste and environmental pollution. From the results, the optimum pressure for treating the natural gas lies within from 2 to 2.7 bar. Therefore, an optimization of the process parameters and absorbents will not only provide a clean gas, but also provide pure NG for use. Higher removal efficiencies were obtained for H₂S than for CO₂. 10–20% amine-alkaline mix gave poor results because, they are lower than the optimum concentration required for the operation with pressure above the critical value of 5250 kPa.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors wish to appreciate Exploration and Production Nigeria Limited for their assistance during the field/bench work of this research.

References

- [1] A. Demirbas, Natural Gas: Methane Gas Hydrate. Springer, Ch. 2, pp. 57–76, 2010. SBN: 978-1-84882-871-1. <http://www.springer.com>
- [2] International Energy Agency, World Energy Outlook, International Energy Agency, 2010. <http://www.worldenergyoutlook.org>.
- [3] D. Huo, The Global Sour Gas Problem, *Energy Resource Engineering*, Stanford University, 2012.
- [4] O. Bolland, CO₂ Capture in Power Plants, Norwegian University of Science and Technology, 2013. http://www.ivt.ntnu.no/ept/fag/fordypn/tep03/innhold/EP03_Part4_Absorption.pdf.
- [5] C. Carpenter, J. Petrol. Technol. 67 (2015) 1–11.
- [6] A. Erfani, S. Boroojerdi, A. Dehghani, *Petrol. Coal* 57 (1) (2015) 85–92.
- [7] M. Fang, D. Zhu, Chemical Absorption. In: Handbook of Climate Change Mitigation, Springer, New York Dordrecht Heidelberg London, 2012. ISBN 978-1-4419-7990-2.
- [8] M. Harasimowicz, P. Orluk, G. Zakrzewska-Trznadel, A. Chmielewski, *J. Hazardous Mater.* 144 (3) (2007) 698–702.
- [9] U. Marchaim, Biogas processes for sustainable development, FAO, Rome, Italy, 1992.
- [10] L. Hien, International Conference on Effects of Gas Composition – Aug 02, 2002, CFS International Pty Ltd.
- [11] V.K. Vijay, R. Chandra, P.M.V. Subbarao, S. Kapid, 2nd Joint International Conference on Sustainable Energy and Environment (SEE), 2006, Bangkok, Thailand.
- [12] D.P. Gosh, The Tri-Service Corrosion Conference, December 3–7, 2007, Denver, Colorado, USA.
- [13] China National Corporation, Sour Natural Gas Corrosion Protection and Purification, Dongzhimen North Street, Beijing, China, 2012.
- [14] L.T. Popoola, S.A. Grema, G.K. Latinwo, B. Gutti, A.S. Int. J. Ind. Chem., 4, 2013, 1–15.
- [15] J. Lee, Soft Systems. Retrieved March 24, 2017 from Oil and Gas Blog, 2015. <https://croftsystms.net/oil-gas-blog/what-is-acid-gas-sour-gas>.
- [16] R.E. Treybal, Operaciones de Transferencia de Masa, 2nd ed., Mc Graw Hill, Mexico, 1996.
- [17] J.I. Huertas, N. Giraldo, S. Izquierdo, Removal of H₂S and CO₂ from biogas by amine absorption, Intech. Open, China (2011).
- [18] National Energy Laboratory, Syngas Contaminant Removal and Conditioning, Retrieved March 27, 2017. <https://www.netldoe.gov/research/coal/energy-systems/gasification/gasifipedia/agr>.
- [19] A. Nobel, Functional Chemicals. Alliance Chemicals, USA, 2017. <https://alliancechemicals.com/wpcontent/uploads/2011/09/DEASpecification.pdf>.
- [20] C. Perry, Activated Carbon Filtration of Amine and Glycol Solutions. Gas Conditioning Conference, University of Oklahoma Extension Division, Oklahoma, USA, 1994.
- [21] Petropedia Inc., Acid Gas. Petropedia, USA, 2017. <http://www.petropedia.com/definition/88/acid-gas>.
- [22] R. Rivera-Tinoco, C. Bouallou, *J. Clean. Product.* 18 (2010) 875–880.
- [23] N. Rodriguez, S. Mustati, N. Scenna, *Chem. Eng. Res. Des.* 89 (2011) (2011) 1763–1773.
- [24] A.E. Salako, Removal of Carbon Dioxide from Natural Gas for LNG Production, Trondheim, Norwegian University of Science and Technology, Institute of Petroleum Technology, Norway, 2005. <https://pdfs.semanticscholar.org/37ea/1e656cc310e4797ded37b8781dd06d97694c.pdf>.
- [25] A. Kohl, R. Nielsen, Gas Purification, 5th., Gulf Publishing Company, Houston Texas, 1997.
- [26] P.H. Santana, S.V. Bajay, *Chem. Eng. Res. Des.* 2 (2016) 22–26.
- [27] R. Tatin, L. Moura, N. Dietrich, S. Baig, *G. Hebrard* 104 (2015) 409–415.
- [28] M.S. Horikawa, M.L. Rossi, M.L. Gimenes, C.M.M. Costa, M.G.C. da Silva, *Braz. J. Chem. Eng.* 21 (3) (2004) 415–422.
- [29] T. Zucca, L.A. Pellegrini, C. Nava, R. Bellasio, R. Bianconi, *Chem. Eng. Trans.* 6 (2005) 629–634.
- [30] L.A. Pellegrini, S. Gamba, S. Moiola, *Ind. Eng. Chem. Res.* 49 (2010) 4923–4932.
- [31] L.A. Pellegrini, S. Moiola, S. Gamba, *Chem. Eng. Res. Design.* (2010b).
- [32] M.B. Hagg, *Chem. Eng. J.* 172 (2011) 952–960.
- [33] C.A. Scholes, G.W. Stevens, S.E. Kentish, *Fuel* 96 (2012) 15–28.
- [34] J.F. Palomeque-santiago, J. Guzman, A.J. Zuniga-mendiola, *Revista Mexicana De Ingenieria Química* 15 (2) (2016) 611–624.
- [35] B. Belaissaoui, E. Favre, *Separat. Purificat. Technol.* 193 (2018) 112–126.
- [36] Aspen Tech, Modelling and Simulation using HYSYS: Training Manual, Aspen Tech, Australia, 2006.
- [37] AspenTech, Physical Property System: Physical Property Models, Version 7, Aspen Tech. Inc., 2010.
- [38] R.L. Kent, B. Eisenberg, *Hydro. Proc.* 55 (2) (1976) 87–90.
- [39] R. Tennyson, R. Schaff, *Oil Gas J.* (1997) 78–85.
- [40] J.D. Seader, E.J. Henley, Separation Process Principles, 2nd Edition., John Wiley and Sons, USA, 2006.
- [41] D. Peng, D.B. Robinson, *Ind. Eng. Chem. Fund.* 15 (1976) 59–63.
- [42] J. Hao, P.A. Rice, S.A. Stern, *J. Membrane Sci.* 320 (2008) 108–122.
- [43] E.S. Van-Dal, C. Bouallou, *J. Cleaner Production* 57 (2013) 38–45.
- [44] H. Lababidi, G.A. Al-Enezi, H.M. Ettouney, *J. Membrane Sci.* 112 (1996) 185–197.
- [45] M. Al-Marzouqi, S. Marzouk, N. Abdullatif, Removal of Acid Gases from Natural Gas using Gas-Liquid Contactors, Microsoft Power point -1-2 GCC-JCCP-Al-Mazouqi, UAE University, 2014.
- [46] B. Pouladi, M.N. Hassankiadeh, F. Behroozshada, *Energy Reports* 2 (2016) 54–61.
- [47] Lunsford, K.; Bullin, J.A. Optimization of Amine Sweetening Units, Proceedings of the AIChE Spring National Meeting, New York, USA, 1996.
- [48] Coathien, S., Hasemit, R.; Pauley, C.R. Analysis of Foaming Mechanisms in Amine Plants, Proceedings of the AIChE Summer Meeting, Denver, Colorado, Canada, 1988.
- [49] Bourke, M.J.; Mazzoni, A.F. "The Roles of Activated Carbon in Gas Conditioning", Proceedings of the Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, 1989.
- [50] Addington, L.; Ness, C. An Evaluation of General "Rules of Thumb" in Amine Sweetening Unit Design and Operation. Bryan Research and Engineering, Inc. Bryan, Texas, USA, 2010.
- [51] K. Lunsford, G. McIntyre, Decreasing Contactor Temperature Could Increase Performance, Bryan Research and Engineering, Inc. – Technical Papers, Bryan Texas, USA, 2006.
- [52] F.B.A. Basri, Bachelor of Chemical Engineering Thesis, Faculty of Chemical & Natural Resources Engineering Universiti Malaysia Pahang, Malaysia, 2014.
- [53] Z.H. Aliabad, S. Mirzaei, *Int. J. Chem. Molecular Eng.* 3 (1) (2009) 50–59.
- [54] S.A. Rackley, Carbon Capture and Storage. Elsevier Inc., 2017. <https://doi.org/10.1016/C2015-0-01587-8>. ISBN: 9780128120415.
- [55] S.-J. Han, M. Yoo, D.-W. Kim, J.-H. Wee, *Energy Fuels* 25 (2011) 3825–3834.
- [56] M. Chandel, E. Williams, Synthetic Natural Gas (SNG): Technology, Environmental Implications, and Economics, Duke University, Climate Change Policy Partnership, 2009.