# Experimental Investigation of Natural Gas Sweetening Process Using Piperazine-Activated Methyldiethanolamine Solution

**Uche Noel P. Ajie[1] Emeka J. Okafor[1] and Dulu Appah[1]**
[1]Petroleum and Gas Engineering Department, University of Port-Harcourt, Choba, Nigeria.
*Corresponding Author Email Address: uche.ajie@eni.com

DOI: 10.56201/ijemt.v10.no3.2024.pg94.111

***Abstract***
*The paper presents an experimental design and data collection method for investigating the relationship between electrical conductivity and concentration with operational variables such as temperature, pressure, amine circulation rate, pH, and $CO_2$ content, being analyzed. This is viewed in the context of existing, high pressure and parallel operating $CO_2$ Absorption Columns and critical as well as accurate data sets and insights into the role of electrical conductivity in natural gas sweetening using Piperazine-Activated Methyldiethanolamine (PZ+MDEA). Pre-optimization findings reveal an average $CO_2$ content of 19,593.64 ppm in a rich inlet natural gas stream and a lower PZ-activated MDEA inlet stream average concentration of 36.47 g/100ml, leading to the production of sweet natural gas that is off-specification by an average $CO_2$ level of 1,368.74 ppm above the desired 250.0 ppm contractual limit over four days, and which showed a strong negative correlation between PZ+MDEA conductivity and concentration. We also observed a slight temperature increase in the amine outlet solution which resulted in suboptimal absorption performance of 93.06%.*

***Keywords:***
*Piperazine-Activated Methyldiethanolamine; $CO_2$ Absorption Columns; Gas sweetening process.*

## 1.0 Introduction

Conventional natural gas, composed of alkanes and 80% methane, is safer than heating oil due to its lower carbon dioxide emissions (Saunois *et al.*, 2020). It accounts for one-third of energy demand and electricity generation, emits less pollution, and requires acid gas treatment (Sumida *et al.*, 2012; Kemfert *et al.*, 2022).

In respect of natural gas sweetening, we consider facility laboratory reports which indicate elevated carbon dioxide levels in the produced lean gas with an average $CO_2$ concentration of 1,368.74 parts per million (ppm), exceeding the allowable 250 ppm limit which is due to an unstable PZ+MDEA delivery concentration, monitoring, analysis, and manual intervention protocols.

This paper presents the characterization and quantification of the physical properties of Piperazine-Activated Methyldiethanolamine (PZ+MDEA) solution to bridge knowledge gaps on concentration versus electrical conductivity correlations, and to optimize acid gas sweetening process performance, making valuable contributions to gas sweetening and carbon capture technologies. The impact of different concentrations and electrical properties of Piperazine-Activated Methyldiethanolamine (MDEA) solutions on $CO_2$ absorption performance is analyzed, aiming to develop a kinetic model for predicting parallel operating absorption columns.

## 2.0 Materials and Method

The research was conducted in an existing 80-barg and parallel operating $CO_2$ Absorption Column-A/B (unit-C on stand-by) in a gas gathering and processing plant (Figure 1) to characterize, quantify, analyze, monitor, and use the piperazine-activated methyldiethanolamine electrical conductivity properties for future prediction, control, and optimization of the PZ+MDEA concentration and subsequent improvement of the gas sweetening/$CO_2$ removal performance based on the fundamental cause and effect philosophy.

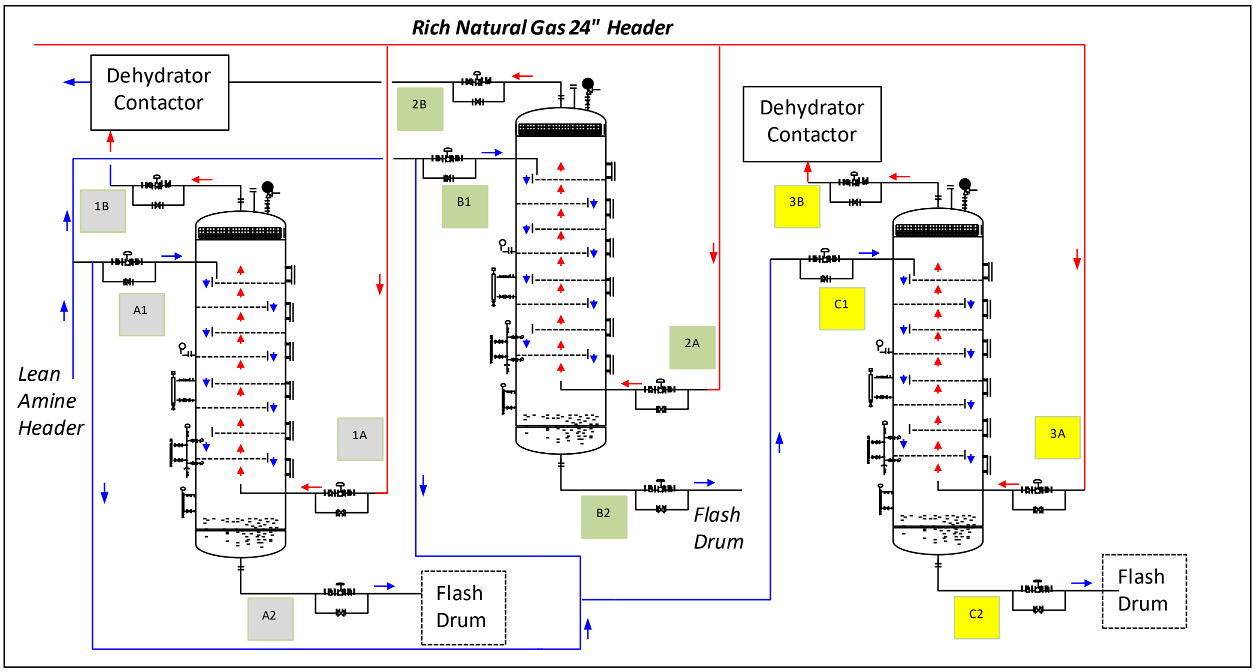


*Figure 1: CO2 Absorption Column Layout, Basic Schematic, and Sampling Plan*

## 2.1 Research Design and Data Collection

The planning of $CO_2$ Absorption Column-A/B characterization of electrical conductivity and concentration properties research, experimental design, and data analysis designates the electrical conductivity on the x-axis, as the predictor independent variable and the concentration on the y-axis, as the dependent variable. This work attempts to advance academic understanding of piperazine-activated methyldiethanolamine-based gas sweetening units through experimental and empirical studies and its industrial application. The effective and efficient use of the two well-proven primary and secondary data collection methods are considered with the objective to gain a broader and deeper understanding of the investigated problem, and thereafter validate the results coming out of it.

### 2.2 Experimental Setup and Instrumentation

For collecting natural gas stream samples, stainless steel cylinders are use and the preference this types of cylinder is because of their durability and non-reactivity, which helps preserve the sample's composition (Choopani, *et al.,* 2016). A gas chromatograph machine was used for the gas stream compositions (Xu *et al.,* 2023). Temperature control is another essential aspect, managed through the use of refrigerated storage units for PZ+MDEA solutions, thereby maintaining their efficacy for extended periods. Advanced syringe pumps were used to inject precise volumes of the PZ+MDEA solution into experimental setups, which ensures consistency and reproducibility of the work and results (Batista *et al.,* 2020).

Analytical balances are indispensable in accurately weighing chemical compounds, ensuring precise solution concentration determinations (Andersen, 2018). Conductivity and TDS meters were utilized in measuring the electrical conductivity and total dissolved solids of the solutions, thereby providing insights into the ionic content and solubility. The pH was measured using pH meters, and hydrometers or digital density meters were employed to gauge the relative density. The boiling point - initial, range, and at 95% recovery - was determined through a distillation apparatus, water solubility tests were carried out in temperature-controlled environments to ensure reproducibility, using constant temperature baths and magnetic stirrers to maintain the homogeneity of the solution (Qing *et al.,* 2022). The assessment of the solution's color and odor is more subjective, often relying on visual inspection and olfactometry, respectively. Working pressures, temperatures, and flow rates are strictly measured using pressure gauges, digital thermometers, chart recorders, transmitters, and DCS/SCADA display units to ensure the safety and integrity of the experimental setup (Sabzevari and Rad, 2019). Let us now review some of the experiments.

#### 2.2.1 Experiment-1: Piperazine-Activated Methyldiethanolamine Concentration

The acid-base titration method was used to determine the PZ-activated MDEA basic solution (11.74 initial average pH) concentration:

1. About 200 – 500.0 ml of representative samples were collected from the Absorption Column-A/B amine inlet and outlet stream to the laboratory.
2. All relatively hot or warm samples collected were adjusted through a cooling water medium to standard room temperature of 22-23$^{o}$C before analysis.
3. Collected 2.0 mls known volume of Piperazine-Activated Methyldiethanolamine solution into a conical flask and added 98.0 mls of demineralized water to make the solution up to 100 mls.
4. Added 5 drops of Tashiro indicator and stirred very well.
5. 1.0 N standardized Hydrochloric acid solution was introduced into a 25.0 cm burette.

6. Commenced and concluded titration with Hydrochloric acid against the base Piperazine-Activated Methyldiethanolamine (PZ+MDEA) solution until the reaction reaches a colorless neutral solution endpoint (Khan, *et.al.*, 2017; Mishra, 2022).

The calculation was made to get the Piperazine-activated Methyl-di-ethanolamine (PZ+MDEA) solution concentration:

$$\text{Piperazine-activated Methyl-di-ethanolamine Concentration} = \frac{T*N*C*CF}{2} \quad (1.0)$$

$$\text{Piperazine-activated Methyl-di-ethanolamine Concentration wt. \%} = \frac{T*N*9.27*1.02}{2} \quad (2.0)$$

where:

$T$ = Titre value

$N$ = Normality of Acid

$C$ = Constant

$CF$ = Correction factor

2 = Volume of sample taken

**2.2.2 Experiment-2: Piperazine-Activated Methyldiethanolamine Conductivity**

The same original representative PZ-Activated MDEA sample collected is used for the conductivity analysis, considering the following steps:

1. The conductivity instrument was calibrated using a conductivity standard solution for calibration
2. Rinsed the electrode probe with distilled water properly before the analysis
3. About 30.0 mls of Piperazine-Activated Methyldiethanolamine solutions (PZ+MDEA) sample was taken into a beaker
4. The electrode probe was inserted into the sample
5. Reading was obtained from the conductivity meter

**2.2.3 Experiment-3: Absorption Column Compositional Analysis**

Using gas chromatography ISO standard method ISO 6974-6:1995 @ 288.15 $^{o}$C and 101.325 Kpa, the natural gas and $CO_2$ compositional analysis and energy content analytical were conducted.

**2.2.4. Experiment-4: Demineralised Water and Piperazine-Activated Methyldiethanolamine Ph**

ASTM D1293-18 standard test method was used to determine and monitor the pH of the de-mineralized water produced from the Resin-Bed unit-A or unit-B based on availability, before storage, distribution, and mixing-up or blending with the dry and 94% high purity Piperazine-activated Methyl-di-ethanolamine (MDEA).

### 2.2.5. Experiment-5: Piperazine-Activated Methyldiethanolamine Density and Relative Density

ASTM D4052 digital density meter standard test method was utilized for the Piperazine-Activated Methyldiethanolamine (MDEA) density and relative density experiments by dipping the graduated instrument into a representative cylinder sample size of the amine solution, thus analyzed against the medium operating temperature and atmospheric pressure.

### 2.2.6. Experiment-6: Piperazine-Activated Methyldiethanolamine Water Purity and Boiling Point

ASTM D4007 laboratory centrifuge procedure was applied in the determination of the Piperazine-Activated Methyldiethanolamine (MDEA) water content.

ASTM D5399-09(2017) test method was used for the supplied drums of dry and 94% high purity Piperazine-Activated Methyldiethanolamine 210 liters drum boiling point before the approval for industrial use.

## 3.0 Results

The findings of this work are limited to the $CO_2$ Absorption Column-A/B pre-optimization activities (planning, designing, all experimental and data collection methods) and discussed along the unit level, except the average PZ+MDEA correlation coefficient and statement of problem analysis.

### 1. Characterization and Quantification of PZ-activated MDEA Physicochemical Properties.

Absorption Column-A/B pre-optimization average (inlet) operating temperature and pressure remained relatively stable at 46.43 $^{o}$C and 79.0 barg respectively. The average amine circulation rate was 113.35 tons/hr, at lean PZ-Activated MDEA average inlet stream pH of 11.37.

### 2. $CO_2$ Absorption Column Unit-A/B/C Operating Set-Points Limiting Factor

The $CO_2$ Absorption Column unit-A/B/C operating set-points related to the amine and natural gas flow rates, liquid level, working pressure, temperature, the properties and production qualities of the demineralized water for PZ+MDEA blending are pre-set and not adjusted, nor altered during the study interval to minimize plant upset but monitored directly through the Plant indicators, transmitters, and DCS, which constitutes part of the limitations in identifying possible vital responses related to Piperazine-activated Methyl-di-ethanolamine concentration, conductivity and effect on $CO_2$ absorptions.

### 3. Manual PZ-Activated MDEA Stock Solution and Demineralized Water Make-up

The addition of an extra and external volume of high-purity Piperazine-Activated Methyldiethanolamine (MDEA) or demineralized water make-up into the processing circuit between the scrubbing and stripping unit, to compensate for the systemic circulation and concentration shortfalls is carried out through manual procedures due to design and sensitivity of the operations.

## 4. $CO_2$ Absorption Column-A/B PZ-Activated MDEA Concentration Synchronized Response

Absorption Column-A and B Piperazine-Activated Methyldiethanolamine (MDEA) solution concentration trends, through the inlets and outlet process sampling and over the 14 days acid-base titration intervals showed a synchronized symmetrical response varying between a maximum value of 42.41 g/100ml to a minimum strength of 28.12 g/100ml with a relatively constant PZ-MDEA circulation flow-rate of 135.0 tons/hr, average rich natural gas inlet flow-rate of 114,307.9 std $m^3$/hr, packed column operating average pressure of 79.0 barg (1,145.5 Psig), average inlet temperature of 46.4 $^oC$ and 1,069.1 micro S/cm average analyzed electrical conductivity.

## 5. PZ-activated MDEA Conductivity and Concentration Strong Negative Correlation

The study revealed an average - 0.9742759 negative correlation between the concentration of Piperazine-Activated Methyldiethanolamine and electrical conductivity, which was validated through additional 78-day sequence of sampling and laboratory investigations corresponding to: Unit-A PZ+MDEA Inlet Stream Validation (52 Observations: Correlation = - 0.78403), Unit-B PZ+MDEA Inlet Stream Validation (13 Observations: Correlation = - 0.84864), Unit-B PZ+MDEA Outlet Stream Validation (13 Observations: Correlation = - 0.79787) and Unit-B PZ+MDEA Outlet Stream Validation (27 Observations: Correlation = - 0.71176). An optimization summary is tabulated in table 1. Tabulation of some stream conditions for absorption columns A and B are shown in tables 2, 3, and 4. Figure 2 shows the graphical trends in the inlet and outlet stream indicating an increasing and decreasing profiles of analyzed concentration over fourteen days.

***Table. 1: Absorption Column-A/B Pre-optimization characterization average performance indicators***

| Absorption Column-A/B Pre Optimization Summary (Average Inlet Gas CO2 Threshold: 19,593.64 ppm) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Observations (Days) | Inlet PZ+MDEA Temperature (oC) | Outlet PZ+MDEA Temperature (oC) | PZ+MDEA Temperature (oC) Differential | Absorption Column Inlet PZ+MDEA pH (Analyzed) | Outlet PZ+MDEA pH (Analyzed) | PZ+MDEA pH Differential | PZ+MDEA Inlet Concentration Analyzed (g/100ml) | PZ+MDEA Inlet Analyzed Conductivity (micro S/cm) | Absorption Column -A/B Inlet Gas CO2 Content Analyzed (Mol.%) | Absorption Column-A/B Inlet Gas CO2 Concentrations (ppm) | Absorption Column -A/B Outlet Gas CO2 Content Analyzed (Mol.%) | Pre-Optimization Absorption Column Outlet Gas Residual CO2 Concentrations (ppm) | Pre-Optimization Absorption Column CO2 Removal Performance Average (%) |
| Day-1 | 48 | 51 | 3 | 11.23 | 9.42 | 1.81 | 40.54 | 812 | 2.5316 | 20,708.50 | 0.06065 | 496.1 | 97.6 |
| Day-2 | 48 | 51 | 3 | 11.11 | 9.38 | 1.73 | 40.3 | 922 | 2.5677 | 21,003.80 | 0.08079 | 660.9 | 96.85 |
| Day-3 | 48 | 52 | 4 | 11.24 | 9.47 | 1.77 | 39.58 | 924 | 2.16615 | 17,719.10 | 0.07505 | 613.9 | 96.54 |
| Day-4 | 44 | 46 | 2 | 11.33 | 9.13 | 2.2 | 39.34 | 961 | 2.22172 | 18,173.60 | 0.07904 | 646.6 | 96.44 |
| Day-5 | 45 | 56 | 11 | 11.19 | 9.24 | 1.95 | 35.85 | 994 | 2.50579 | 20,497.30 | 0.10609 | 867.8 | 95.77 |
| Day-6 | 44 | 52 | 8 | 11.23 | 9.06 | 2.17 | 35.38 | 1,048.00 | 2.52278 | 20,636.40 | 0.10985 | 898.5 | 95.65 |
| Day-7 | 45 | 56 | 11 | 11.44 | 9.5 | 1.94 | 34.96 | 1,135.00 | 2.05449 | 16,805.70 | 0.13704 | 1,121.00 | 93.33 |
| Day-8 | 45 | 52 | 7 | 11.54 | 9.77 | 1.77 | 34.21 | 1,289.00 | 1.98267 | 16,218.30 | 0.14275 | 1,167.70 | 92.8 |
| Day-9 | 45 | 53 | 8 | 11.71 | 9.99 | 1.72 | 33.04 | 1,320.00 | 2.39564 | 19,596.40 | 0.21942 | 1,794.80 | 90.84 |
| Day-10 | 46 | 53 | 7 | 11.42 | 9.92 | 1.5 | 31.86 | 1,351.00 | 2.5316 | 20,708.50 | 0.24263 | 1,984.70 | 90.42 |
| Day-11 | 48 | 57 | 9 | 11.22 | 9.5 | 1.72 | 30.69 | 1,383.00 | 2.5677 | 21,003.80 | 0.24911 | 2,037.70 | 90.3 |
| Day-12 | 48 | 55 | 7 | 11.29 | 9.63 | 1.66 | 30.23 | 1,414.00 | 2.3891 | 19,542.80 | 0.26042 | 2,130.20 | 89.1 |
| Day-13 | 48 | 55 | 7 | 11.4 | 9.74 | 1.66 | 29.52 | 1,425.00 | 2.6637 | 21,789.10 | 0.30063 | 2,459.20 | 88.71 |
| Day-14 | 48 | 53 | 5 | 11.25 | 9.75 | 1.5 | 28.82 | 1,460.00 | 2.4337 | 19,907.70 | 0.27911 | 2,283.10 | 88.53 |
| **AVERAGE** | **46.43** | **53** | **6.57** | **11.33** | **9.54** | **1.79** | **36.47** | **1,174.14** | **2.3953** | **19,593.64** | **0.16733** | **1,368.74** | **93.06** |

**Table 2.0: Absorption Column-A: Inlet Stream (Lean PZ-Activated Methyldiethanolamine) Initial**

| Absorption Column-A Piperazine-activated Methyl-di-ethanolamine Inlet Stream | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Observation (n) | Operating Temperature ($^oC$) | Operating Pressure (Barg) | Amine Circulation Rate (Tons/Hr) | Amine Inlet Concentration (g/100ml) | Amine pH | Amine Appearance (Colour) | Amine Conductivity Unit-A Inlet (micro S/cm) | Total Dissolved Solids (mg/l) |
| 1 | 48.0 | 77.0 | 135.0 | 34.21 | 11.23 | Yellow | 944.0 | 472.00 |
| 2 | 48.0 | 78.0 | 136.0 | 36.55 | 11.11 | Yellow | 1,289.0 | 644.50 |
| 3 | 48.0 | 78.0 | 135.0 | 35.38 | 11.24 | Yellow | 1,289.0 | 644.50 |
| 4 | 44.0 | 79.0 | 80.0 | 30.69 | 11.33 | Yellow | 1,414.0 | 707.00 |
| 5 | 45.0 | 79.0 | 75.0 | 28.82 | 11.19 | Yellow | 1,397.0 | 698.50 |
| 6 | 44.0 | 78.0 | 83.0 | 30.23 | 11.23 | Yellow | 1,048.0 | 524.00 |
| 7 | 45.0 | 78.0 | 80.0 | 35.85 | 11.44 | Yellow | 961.0 | 480.50 |
| 8 | 45.0 | 79.0 | 80.0 | 42.41 | 11.54 | Yellow | 812.0 | 406.00 |
| 9 | 45.0 | 79.0 | 80.0 | 40.54 | 11.71 | Yellow | 694.00 | 347.00 |
| 10 | 46.0 | 79.0 | 135.0 | 34.96 | 11.42 | Yellow | 1135.00 | 567.50 |
| 11 | 48.0 | 78.0 | 135.0 | 39.34 | 11.22 | Yellow | 994.00 | 497.00 |
| 12 | 48.0 | 79.0 | 135.0 | 40.30 | 11.29 | Yellow | 922.0 | 461.00 |
| 13 | 48.0 | 79.0 | 135.0 | 39.58 | 11.40 | Yellow | 924.0 | 462.00 |
| 14 | 48.0 | 79.0 | 135.0 | 41.73 | 11.25 | Yellow | 1,144.0 | 572.00 |

**Table 3.0: Absorption Column-A: Outlet Stream (Lean PZ-Activated Methyldiethanolamine) Initial**

| Absorption Column-1 Piperazine-activated Methyl-di-ethanolamine Outlet Stream | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Observation (n) | Operating Temperature (°C) | Operating Pressure (Barg) | Amine Circulation Rate (Tons/Hr) | Amine Outlet Concentration (g/100 ml) | Amine pH | Amine Appearance (Colour) | Amine Conductivity Unit-A Outlet (micro S/cm) | Total Dissolved Solids (mg/l) |
| 1 | 51.0 | 77.0 | 135.0 | 32.10 | 9.18 | Yellow | 11,090.0 | 5,545.0 |
| 2 | 51.0 | 78.0 | 136.0 | 34.91 | 9.23 | Yellow | 13,190.0 | 6,595.0 |
| 3 | 52.0 | 78.0 | 135.0 | 34.44 | 9.25 | Yellow | 13,190.0 | 6,595.0 |
| 4 | 46.0 | 79.0 | 80.0 | 29.29 | 8.79 | Yellow | 26,300.0 | 13,150.0 |
| 5 | 56.0 | 79.0 | 75.0 | 28.12 | 8.86 | Yellow | 16,560.0 | 8,280.0 |
| 6 | 52.0 | 78.0 | 83.0 | 29.29 | 8.84 | Yellow | 15,700.0 | 7,850.0 |
| 7 | 56.0 | 78.0 | 80.0 | 33.97 | 9.22 | Yellow | 13,060.0 | 6,530.0 |
| 8 | 52.0 | 79.0 | 80.0 | 41.23 | 9.44 | Yellow | 8,540.0 | 4,270.0 |
| 9 | 53.0 | 79.0 | 80.0 | 38.87 | 9.65 | Yellow | 7890.00 | 3,945.0 |
| 10 | 53.0 | 79.0 | 135.0 | 33.62 | 9.74 | Yellow | 7860.00 | 3,930.0 |
| 11 | 57.0 | 78.0 | 135.0 | 37.44 | 9.41 | Yellow | 8690.00 | 4,345.0 |
| 12 | 55.0 | 79.0 | 135.0 | 38.63 | 9.39 | Yellow | 7,280.0 | 3,640.0 |
| 13 | 55.0 | 79.0 | 135.0 | 38.39 | 9.64 | Yellow | 7,300.0 | 3,650.0 |
| 14 | 53.0 | 79.0 | 135.0 | 40.30 | 9.64 | Yellow | 8,240.0 | 4,120.0 |

**Table 4.0: Absorption Column-B: Inlet Stream (Lean PZ-Activated Methyl-di-ethanolamine) Initial**

| Absorption Column-2 Piperazine-activated Methyl-di-ethanolamine Inlet Stream | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Observation (n) | Operating Temperature (°C) | Operating Pressure (Barg) | Amine Circulation Rate (Tons/Hr) | Amine Intlet Concentration (g/100ml) | Amine pH | Amine Appearance (Colour) | Amine Conductivity Unit-B Inlet (micro S/cm) | Total Dissolved Solids (mg/l) |
| 1 | 51.0 | 77.0 | 145.0 | 34.91 | 11.21 | Yellow | 1,004.0 | 502.0 |
| 2 | 50.0 | 78.0 | 145.0 | 36.32 | 10.97 | Yellow | 1,336.0 | 668.0 |
| 3 | 50.0 | 78.0 | 146.0 | 36.08 | 11.14 | Yellow | 1,336.0 | 668.0 |
| 4 | 45.0 | 79.0 | 80.0 | 30.69 | 11.33 | Yellow | 1,414.0 | 707.0 |
| 5 | 45.0 | 79.0 | 78.0 | 28.82 | 11.19 | Yellow | 1,397.0 | 698.5 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 45.0 | 78.0 | 78.0 | 30.23 | 11.23 | Yellow | 1,048.0 | 524.0 |
| 7 | 45.0 | 78.0 | 80.0 | 35.85 | 11.44 | Yellow | 961.0 | 480.5 |
| 8 | 52.0 | 79.0 | 80.0 | 42.41 | 11.54 | Yellow | 812.0 | 406.0 |
| 9 | 54.0 | 79.0 | 80.0 | 40.54 | 11.71 | Yellow | 694.00 | 347.0 |
| 10 | 50.0 | 79.0 | 140.0 | 34.34 | 11.69 | Yellow | 856.0 | 428.0 |
| 11 | 55.0 | 78.0 | 140.0 | 38.63 | 11.23 | Yellow | 1027.00 | 513.5 |
| 12 | 54.0 | 79.0 | 140.0 | 39.34 | 11.26 | Yellow | 1,038.0 | 519.0 |
| 13 | 54.0 | 79.0 | 140.0 | 39.58 | 11.57 | Yellow | 648.0 | 324.0 |
| 14 | 53.0 | 78.0 | 140.0 | 41.49 | 11.57 | Yellow | 756.0 | 378.0 |

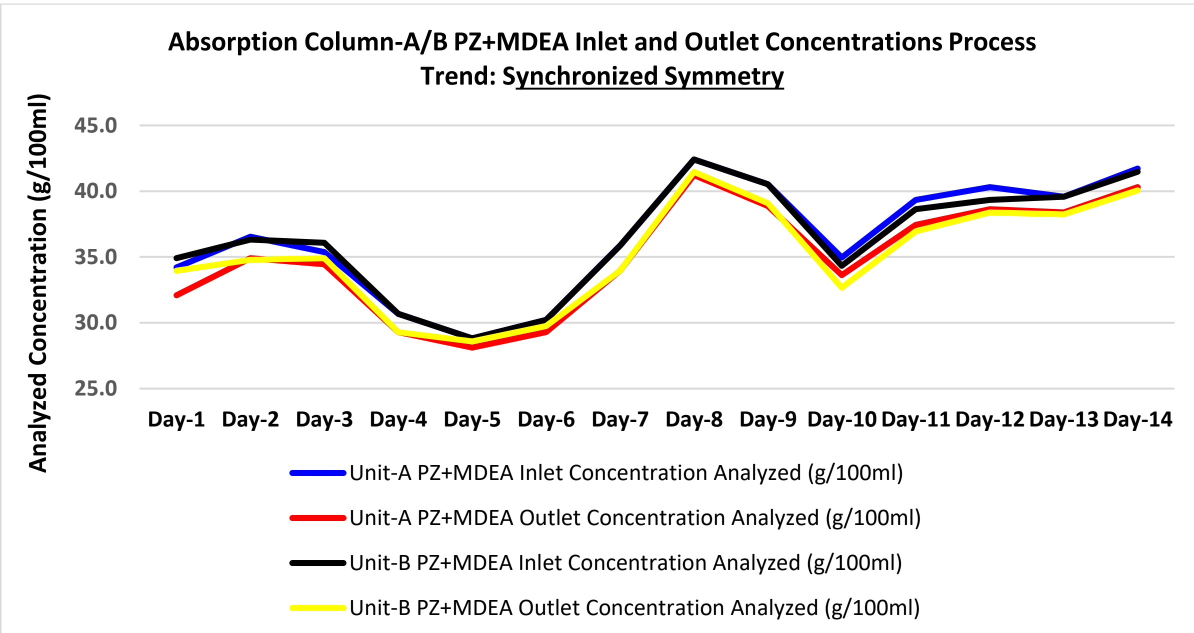


***Figure 2: Absorption Column-A/B PZ+MDEA onlet and outlet concentrations process trend: synchronized symmetry***

Figure 3 shows the pre-optimization sweet gas with elevated level of CO2 and Figure 4 shows a scatter plot of concentration against electrical conductivity that shows the dependence of the latter over the former. Figure 5 shows the profile in terms of pH, inlet and outlet temperatures.

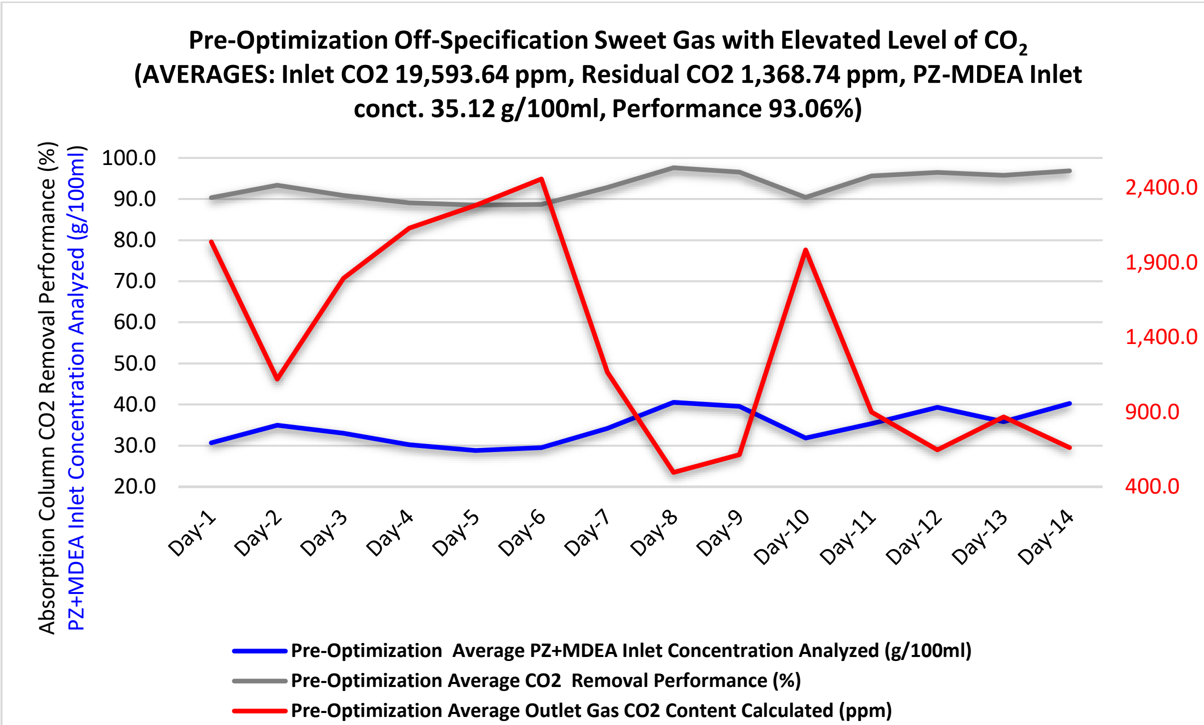


*Figure 3: Pre-optimization off-specification sweet gas with an elevated level of $CO_2$ failure mode*

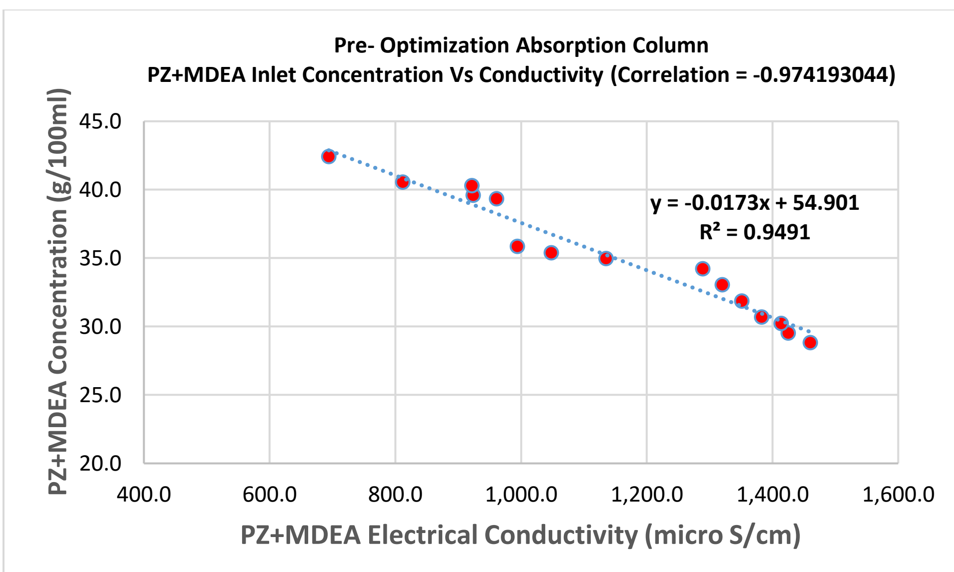


*Figure 4: Pre- Optimization Absorption Column-A/B PZ+MDEA Inlet Concentration Vs Conductivity Correlation = -0.974193044*

***$CO_2$ Absorption Column-A/B Stabilized PZ-Activated MDEA Circulation-Rate, Temperature and Pressure***

The characterization of PZ-Activated MDEA has emerged as a vital academic discussion among researchers (Khan *et al.*, 2018). The monitoring of pH levels of the amine solution facilitates the assessment of the unit's gas-sweetening capabilities – figure-5 (Alardhi *et al.*, 2023; Meng *et al.*, 2022; Ingo *et al.*, 2022; Barbez, 2023).

Absorption Column-A/B operating temperature, pressure, and PZ-Activated MDEA electrical conductivity and concentration were extensively monitored and stability was enhanced by the forced draft heat exchangers and pressure control valves for optimal performance of the unit as observed at the PZ+MDEA inlets stream: 48.32 ºC, 48.43ºC, and 78.54, 78.75 barg respectively (table- 1&2) before unit optimization. The amine circulation flow rate, oftentimes unstable and below optimum but did not directly relate with the PZ+MDEA analyzed concentration parameters due to manual dilutions and intervention with demineralized water of unspecified pH and quantity to address dwindling low-level condition at the Columns, (refer to Table-1-4).

The $CO_2$ Absorption Column-A/B PZ-activated MDEA $CO_2$ absorption process is an exothermic reaction, and the higher outlet temperature difference is an indication of the level of saturation and degradation of the inlet lean amine with $CO_2$ acid gas before exit (figure 5, table 1-4). The elevated electrical conductivity analyzed at 25ºC of 10,426.07 micro S/cm highlights a suboptimal PZ-activated MDEA concentration (Table 3).

***Absorption Column-A/B Operating Set-Points Outside Scope***

The study of $CO_2$ absorption columns often encounters various limiting factors that can affect the accuracy and generality of the outcomes (Tamidi *et al.*, 2023). During the investigation of $CO_2$ mass transfer, the demineralized water unit, amine and natural gas flow rates, liquid levels, working pressure, and temperature set-points were kept constant to avoid plant disruptions, table: 1-4, (Dager *et al.*, 2022; Ji *et al.*, 2022; Musaazi *et al.*, 2021; Huang *et al.*, 2017; Silva *et al.*, 2021; Pershin *et al.*, 2023; Men *et al.*, 2021). This operational constraint implies that potential dynamic responses of the system relative to the Piperazine-activated Methyl-di-ethanolamine absorption, could not be fully explored (Ghalib, 2016). The monitoring of these continuous variables was conducted via plant indicators, transmitters, and Distributed Control System (DCS), which may not provide as detailed data as laboratory analyses (Varlamov, 2022). Such limitations are significant when interpreting the results, as variations in concentration and conductivity which are crucial for understanding the solvent's efficiency and the overall mass transfer process, could not be extensively evaluated (Klopchevska *et al.*, 2022; Zhao *et al.*, 2014; Vuuren *et al.*, 2011).

***Manual Make-up of PZ+MDEA and Demineralized Water***

The investigations into the limitation of manual Piperazine-activated Methyl-di-ethanolamine (MDEA) and demineralized water make-up systems (table 1-4) revealed critical challenges in process optimization (Elhosane & Atway, 2016). The manual addition of high-purity lean PZ-activated MDEA and demineralized water blend into the closed circuit between the scrubbing and stripping units requires a precise control system to maintain the desired chemical balance, a feat that is demanding considering the sensitivity of the operations.

The reliance on manual protocols to compensate for circulation and concentration shortfalls introduces a significant margin for human error, potentially leading to inefficiencies or disruptions in the gas treatment process.

Studies highlight the need for automated, feedback-controlled systems to ensure consistent and accurate volumetric adjustments, thereby mitigating the risks associated with manual interventions. Despite the meticulous attention to detail by operators, the inherent limitations of manual make-up systems underline a vital area for further research technological advancement and process stability in gas treatment.

***Synchronized Symmetry of PZ-Activated MDEA Concentration***

The performance trends of absorption columns utilizing Piperazine-Activated Methyldiethanolamine solutions are of high academic and industrial interest (Burfeind *et al.*, 2015). The initial and final 14 days of acid-base titration intervals for packed Column-A/B amine inlet/outlets samples (figure-5) have indicated a synchronized symmetrical response in the PZ+MDEA concentration pattern, oscillating between 42.41 g/100ml and 28.12 g/100ml due to the single input Header and delivery system circulating flow and feeding both parallel columns simultaneously, except the unit is isolated on stand-by. This concentration variance occurred while maintaining an average stabilized PZ+MDEA circulation flow rate of 135.0 tons/hr implying a robust volumetric process control column operations. The rich natural gas inlet flow rate averaged 114,307.9 std $m^3$/hr, with the column operating under an average pressure of 79.0 barg (1,145.5 Psig) and an average temperature of 46.4°C, indicating a sustained operational condition for efficient $CO_2$ absorption process. Additionally, an average inlet electrical conductivity measurement of 1,069.1 micro S/cm (figure 2&4) further corroborates the synchronized PZ-Activated MDEA performance, providing critical data points for optimizing the $CO_2$ absorption process and implications on the overall system efficacy.

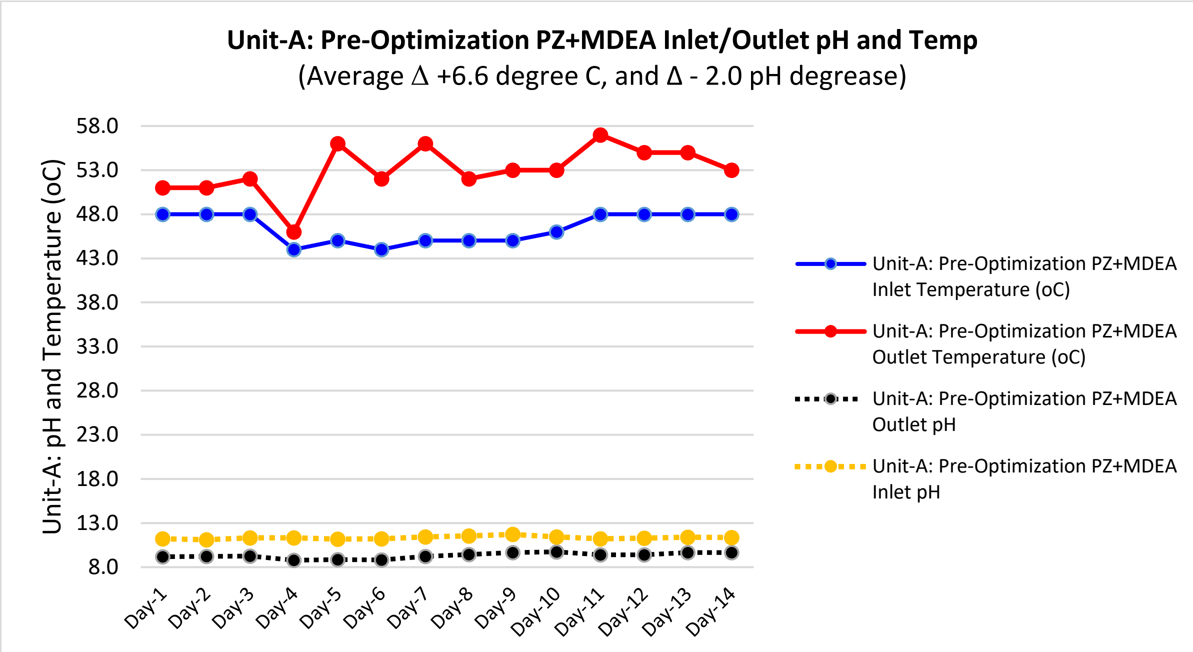


*Figure 5: Column-A: Pre-Optimization PZ+MDEA Inlet/Outlet pH and Temp*

***PZ-activated MDEA Outlet Temperature Increase and Decreased pH***

Before the unit optimization, the lean (inlet) Piperazine-Activated Methyldiethanolamine (MDEA) solvent concentration is critical in the gas sweetening process, for the efficient absorption of $CO_2$ from rich natural gas streams (Elhosane & Atway, 2016). Upon entering the parallel Absorption Column-A/B top-tray, the solvent, initially at an average temperature of 46.43°C, engages in acid gas mass transfer reaction, effectively absorbing $CO_2$ and increasing its temperature by an average of 6.57°C (see Figure 5). This results in the solvent exiting the column at an elevated temperature of approximately 53.0°C, indicative of the exothermic nature of the $CO_2$ absorption process.

Concurrently, the pH of the solvent inlet exhibits a notable decrease of 1.83 units' post-$CO_2$ absorption, a testament to the chemical shifts occurring during gas sweetening. This alteration in pH and thermal characteristics highlights the $CO_2$ removal performance efficiency (figure 6) before the solvent's regeneration phase, where the absorbed $CO_2$ is stripped, and the MDEA solvent is recovered for reuse.

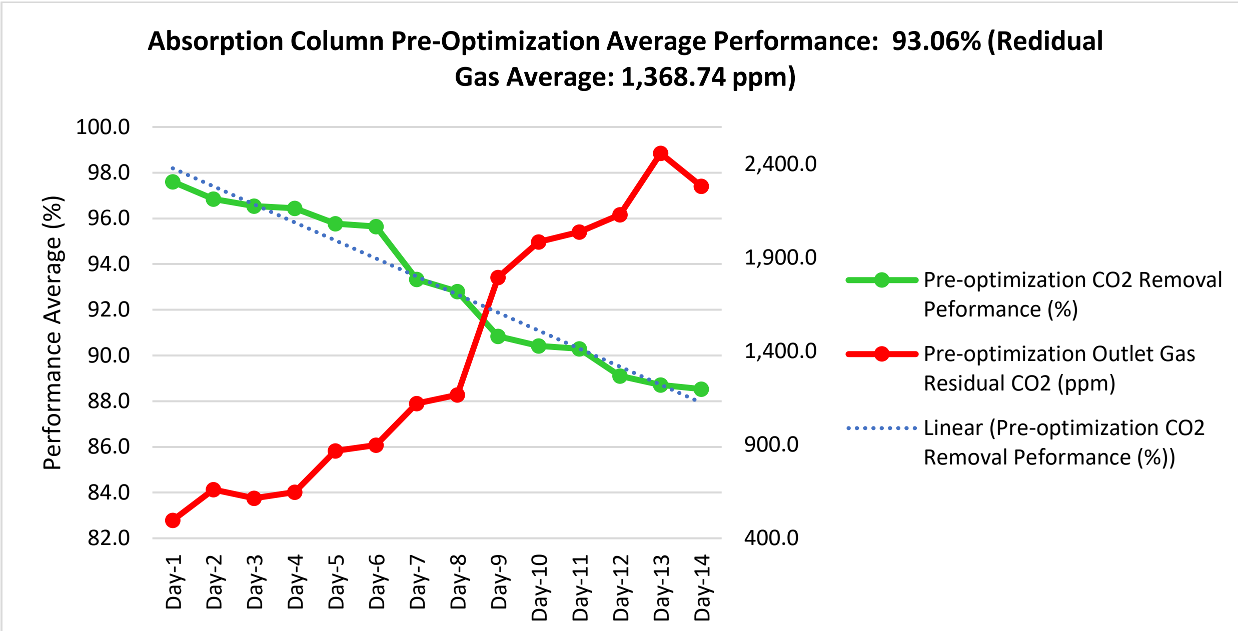


*Figure 6: Column-A/B: Pre-optimization average performance assessment*

**Validated Strong Negative Conductivity and Concentration Correlation**

The characterization and quantification of Piperazine-Activated Methyldiethanolamine electrical conductivity and concentration properties investigation yielded significant insights into PZ-Activated MDEA chemical behavior (Han & Wee, 2021), especially concerning the strong negative correlation coefficient of -0.9742759 between the concentration and electrical conductivity (Figure 4), implying that as the concentration of MDEA increases, the electrical conductivity decreases, and vice versa. This finding sheds light on the intricate dynamics of PZ+MDEA amine and its impact on electrical conductivity, providing valuable insights for further research, improvement, and application in relevant industries.

The findings was substantiated by an extra 78-day validation phase, which involved sampling and laboratory testing across various inlet and outlet streams. For instance, the Unit-A PZ+MDEA inlet stream validation with 52 observations revealed a correlation of -0.78403, while the Unit-B inlet and outlet stream validations produced correlations of -0.84864 and -0.79787, respectively, from 13 observations each. Moreover, the Unit-B PZ+MDEA outlet stream validation, consisting of 27 observations, further supported the initial results with a correlation value of -0.71176, (Abdelmouiz, 2022),

## 3.0 Conclusion

This study explored the planning, data collection, characterization, and quantification of the natural gas sweetening process by experimenting and examining how varying concentrations and electrical conductivity properties of Piperazine-Activated Methyldiethanolamine affect $CO_2$ absorption efficiency. Results leads to the following conclusion:

1. $CO_2$ Absorption Column-A/B before optimization studies showed stable operating temperatures and static pressure of 79.0 barg at an average amine circulation rate below 135.35 tons/hr, and PZ-activated MDEA average concentration of 36.42 g/100ml. However, lean PZ+MDEA electrical conductivity remained relatively high at 10,446.21 micro S/cm, while outlet solution temperature increased from 46.43°C to 53.01°C due to suboptimal concentration.
2. There is a strong negative correlation of -0.974, between the average concentration of Piperazine-Activated Methyl-di-ethanolamine and electrical conductivity analyzed. This finding was confirmed through an extended 78-day period of sampling and testing across the PZ+MDEA inlet and outlet streams and further demonstrated a consistent negative correlation ranging from -0.71176 to -0.84864.

3. During an initial 14-day study, PZ-Activated MDEA solution had an average concentration of 36.47g/100ml. This resulted in an average $CO_2$ concentration in the lean-treated gas of 1,368.74 ppm, achieving 93.06% $CO_2$ removal efficiency (refer to Figures 3& and 6). However, on average, the gas quality did not meet the customer's 250 ppm specification for $CO_2$ levels for about 4 days (Figure 3), which calls for further investigation.

4. Research equally indicates that increasing the concentration of PZ-Activated MDEA to the optimal range will improve $CO_2$ absorption efficiency in the gas sweetening Absorption Columns.

## References

Abdelmouiz, A. (2022). Comparative Kinetics Study of $CO_2$ Absorption into Aqueous MDEA/PZ, MDEA/Sulfolane, and PZ/Sulfolane Blended Systems Solution, Using Stopped-Flow Technique. SSRN Electronic Journal.

Alardhi, S., Al-Jadir, T. M., Hasan, A., Jaber, A., & Saedi, L. A. (2023). Design of Artificial Neural Network for Prediction of Hydrogen Sulfide and Carbon Dioxide Concentrations in a Natural Gas Sweetening Plant. Ecological Engineering & Environmental Technology.

Andersen, J. (2018). Understanding Uncertainty to Weighing by Electronic-Analytical Balances. Journal of AOAC International, 101(6), 1977-1984.

Barbez, E. (2023). Orchestrating pH levels in plants. eLife.

Batista, E., Mendes, R., Furtado, A., Ferreira, M. D. C., Godinho, I., Sousa, J., Alvares, M., & Martins, R. (2020). Calibration of Syringe Pumps Using Interferometry and Optical

Methods. World Academy of Science, Engineering, and Technology, International Journal of Biomedical and Biological Engineering, 14, 318-321.

Burfeind, B., Multhaupt, H., Brehm, A., Hofmann, J., & Mikow, U. (2015). Degradation rate and degradation kinetics of activated and non-activated aqueous N-Methyldiethanolamine (MDEA) absorption solutions.

Choopani, Y., Razfar, M., Saraeian, P., & Farahnakian, M. (2016). Experimental investigation of external surface finishing of AISI 440C stainless steel cylinders using the magnetic abrasive finishing process. The International Journal of Advanced Manufacturing Technology, 83, 1811-1821.

Dager, B., Kumar, A. M., & Sharma, R. S. (2022). Exploring the effects of pilot injection timing and natural gas flow rates on the performance of twin-cylinder compression ignition engine. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 44, 2730-2747.

Elhosane, Y., & Atway, A. (2016). Kinetic Study of Carbon Dioxide Absorption into Glycine Promoted Methyl di Ethanolamine (Mdea).

Ghalib, L. (2016). Modeling the Effect of Piperazine on Carbon Steel Corrosion Rate in Carbonated Activated MDEA Solutions. International Journal of Electrochemical Science, 11, 4560-4585.

Gilmartin, M., Graham, C., & Aljazzar, G. (2022). A Physical Solvent Approach to Blue Hydrogen. Day 2 Tue, February 22, 2022.

Han, S.-J., & Wee, J.-H. (2021). Comparison of $CO_2$ absorption performance between methyl-di-ethanolamine and tri-ethanolamine solution systems and its analysis in terms of amine molecules. Greenhouse Gases: Science and Technology.

Huhe, F., King, J., & Chuang, S. (2023). Amine-based sorbents for $CO_2$ capture from air and flue gas—a short review and perspective. Research on Chemical Intermediates, 49, 791-817.

Ingo, C., Tuuf, J., & Björklund-Sänkiaho, M. (2022). Impact of Hydrogen on Natural Gas Compositions to Meet Engine Gas Quality Requirements. Energies.

Ji, Y., Ran, J., Yang, Z., Li, H., & Hao, X. (2022). Optimization of energy recovery turbine in demineralized water treatment system of the power station by Box–Behnken Design method. Energy Reports.

Johnson, N., Fidelis, W. O., Julius, O. I., Chidubem, U. M., & Dozie, E. A. (2022). Development Design of Amine Sweetening Unit Plant of Natural Gas. International Journal for Research in Applied Science and Engineering Technology.

Kemfert, C., Präger, F., Braunger, I., Hoffart, F. M., & Brauers, H. (2022). The expansion of natural gas infrastructure puts energy transitions at risk. Nature Energy, 7(7), 582–587. https://doi.org/10.1038/s41560-022-01060-3

Khan, A. A., G. Halder, A. Saha (2017). Experimental investigation on efficient carbon dioxide capture using piperazine (PZ) activated aqueous methyl-di-ethanolamine (MDEA) solution in a packed column

Khan, S., Hailegiorgis, S. M., Man, Z., & Shariff, A. (2018). Solubility of $CO_2$ in piperazine (PZ) activated aqueous N-methyl diethanolamine (MDEA) solvent under high pressure.

Khan, S., Mekuria Hailegiorgis, S., Man, Z., & Shariff, A. (2018). Solubility of $CO_2$ in piperazine (PZ) activated aqueous N-methyldiethanolamine (MDEA) solvent under high pressure.

Klopchevska, J., Chadikovski, A., Kavrakovski, Z., Srbinoska, M., & Rafajlovska, V. (2022). Evaluation of solvent efficiency for extraction of bioactive curcuminoids from turmeric (Curcuma longa L.). Macedonian Pharmaceutical Bulletin.

Liu, X., Zhang, X., Li, J., Zhu, Q., Deen, N., & Tang, Y. (2023). Regeneration of iron fuel in fluidized beds, Part I: Defluidization experiments and theoretical prediction model. Powder Technology.

Meng, F., Meng, Y., Ju, T., Han, S., Lin, L., & Jiang, J. (2022). Research progress of aqueous amine solution for $CO_2$ capture: A review. Renewable and Sustainable Energy Reviews.

Mishra, S. (2022). Phenolphthalein Indicator in Titrimetric Estimation of Benzoic Acid Solubility and Distribution in Water and Benzene-Buffer Solutions. Asian Journal of Chemical Sciences.

Qing, R., Hao, S., Smorodina, E., Jin, D., Zalevsky, A., & Zhang, S. (2022). Protein Design: From the Aspect of Water Solubility and Stability. Chemical Reviews, 122, 14085-14179.

Sabzevari, M., & Rad, M. (2019). Resilience strategies against working pressures in midwives: A qualitative study. Journal of Education and Health Promotion, 8.

Saunois, M., Stavert, A. R., Poulter, B., Bousquet, P., Canadell, J. G., Jackson, R. B., Raymond, P. A., Dlugokencky, E. J., Houweling, S., Patra, P. K., Ciais, P., Arora, V. K., Bastviken, D., Bergamaschi, P., Blake, D. R., Brailsford, G., Bruhwiler, L., Carlson, K. M., Carrol, M., . . . Zhuang, Q. (2020). The Global Methane Budget 2000–2017. Earth System Science Data, 12(3), 1561–1623. https://doi.org/10.5194/essd-12-1561-2020

Shahraki, H., Sadeghi, J., Shahraki, F., & Mohebbi-Kalhori, D. (2020). Enhancement of CO2 mass transfer using SiO2 nanoparticles in an aqueous a-MDEA solution for CO2 absorption process. Volume 8, 117-125.

Sumida, K., Rogow, D. L., Mason, J. A., McDonald, T. M., Bloch, E. D., Herm, Z. R., Bae, T., & Long, J. R. (2011). Carbon dioxide capture in Metal–Organic frameworks. Chemical Reviews, 112(2), 724–781. https://doi.org/10.1021/cr2003272

Tamidi, A. M., Lau, K. K., Ng, L. H., Yusof, S. M. M., Azmi, N., Zakariya, S., ... Quek, V. C. (2023). Numerical Modeling and Economic Analysis of Ultrasonic-Assisted CO2 Absorption Process for Offshore Application. Processes.

Xu, Q., Qin, Y., & Gianchandani, Y. (2023). A Rule-Based Automated Chemical Recognition Algorithm for a Multi-Cell Multi-Detector Micro Gas Chromatograph. Separations.