Characterization of Loading Rate of CO_2 with Mono Ethanol Amine Continuous Reactor Experimentation & Titrimetric CO_2 Loading Evaluation

N. Sriniwasa Prabhu[1,*], S. Govindaradjane[1], Raman Saravanane[1]
[1]Puducherry Technological University, Puducherry, India
*Corresponding author email: sriniwasaprabhu@ptuniv.edu.in

Abstract. This study delves into leveraging a continuous reactor experiment setup for CO_2 Capture using Mono Ethanol Amine (MEA). A series of experiments were conducted utilizing various concentrations of MEA from 10% to 30% wt/wt under controlled conditions to determine their CO_2 loading rates. The continuous reactor system offered insights into the kinetics and equilibrium behaviours of the MEA-CO_2 interaction. The CO_2 loading with MEA solvents is estimated using a titrimetric method, the UOP 829-82[1] which consumes less resources for research in a laboratory setup. This enabled repetitive and reciprocal loading rate assessments of CO_2 loading rate analysis with MEA solvents. The CO_2 content in the experimented amine samples ranged from 0.13 to 0.45 mol CO_2 / mol MEA while varying the CO_2 concentration between 10% to 20% and MEA Concentration from 10% to 30% for a range of absorption time periods. The CO_2 loading performance showed only a marginal performance improvement was found between 20% and 30% MEA concentration. The results of this study can help pave pathways for more efficient MEA based CO_2 Capture Technologies.
Keywords: CCS, CO_2 Capture, MEA, CO_2 Continuous Reactor, Titrimetric CO_2 Loading Estimation

1. Introduction

The dire need to combat climate change has necessitated cutting edge solutions, with Carbon Capture and Storage (CCS) emerging as the critical technology against rising greenhouse gas emissions. Among various CCS methodologies, Post-Combustion Capture (PCC) holds an unavoidable stature, given its capability to retrofit into industrial infrastructures, providing an effective and practical means to mitigate carbon dioxide (CO_2) emissions.

Industries like Coal, Cement and Steel are some of the prime contributors to anthropogenic CO_2 emissions, contributing substantially to the global carbon footprint [1]. Addressing this challenge demands the integration of PCC within industrial processes, an approach that involves capturing CO_2 emissions post-combustion, thereby preventing their release into the atmosphere, and subsequently creating pathways for utilization and/or sequestering them in secure geological formations.

Nations worldwide, including India, have pledged to curb their emissions and transition towards sustainable practices. The Intergovernmental Panel on Climate Change (IPCC) emphasizes the urgency of such actions to limit global warming and mitigate the associated adverse impacts. For India, a country experiencing rapid industrial growth, the adoption of PCC aligns seamlessly with its commitment to the global climate agenda [2]. By integrating PCC into its industrial landscape, India not only contributes substantively to the global effort but also upholds the integrity of its INDC commitments. This integration is pivotal, ensuring a resilient and sustainable trajectory for the nation's industrial development while fostering global climate resilience.

Currently, industries have started adopting the first go-to decarbonization measures like energy efficiency and renewable energy adoption. Whereas, IPCC and International Energy Agency (IEA) has substantiated in their reports that without Direct CO_2 Capture Technology it will be near impossible to reach Net-Zero State in the realm of CO_2 Emission Mitigation [3].

Mono Ethanol Amine (MEA), a primary amine, exhibits high affinity for CO_2, making it an excellent candidate for PCC applications. MEA's significance lies in its widespread application as a solvent in CO_2 capture processes [4,5]. In PCC, MEA-based solutions act as absorbents, selectively capturing CO_2 from industrial flue gases. The subsequent regeneration of MEA, often through thermal means, enables the release of captured CO_2 for sequestration or utilization [6,7].

[1] This method can be found through ASTM International and is a titrimetric method to determine CO_2 in ethanolamine solutions.

MEA's utility becomes furthermore significant because of its cost-effectiveness, wide market availability and less logistic constraints [7,8,9]. As a primary amine, MEA is produced on a large scale, contributing to its affordability. The widespread industrial use of MEA in sectors such as the production of detergents and textiles ensures its consistent availability [10], reducing logistical challenges associated with procurement.

Unlike batch reactors, continuous systems provide real-time data, allowing precise control and enhanced scalability [11,12]. Continuous reactor estimations offer insights into MEA's dynamic behaviour, improving process efficiency and facilitating industrial implementation.

2. Experimental Setup

2.1 Equipment and Reagents

Commercial-grade CO_2 with a purity of 99 % was purchased from a local vendor in Puducherry. MEA with a purity of 99 % was from Pon Pure Chemicals Co., based in India. All materials were used as received without further purification. The chemicals were diluted to desired molarity levels using double distilled water. Dilution of CO_2 was done using air obtained from a small lab vacuum pump of 50 lpm capacity. The gas flow levels were maintained using rotameters from S.Y Industries, Thane, India. Janatics Pressure Gauges of 10 bar capacity with a resolution of 0.5 bar and Temperature Gauges of 150 °C capacity with a resolution of 2.5 °C were used. Methanol (99% purity), Sulfuric Acid solution, Sodium Hydroxide Solution, Thymolphthalein indicator were the main chemical reagents used.

2.2 Experimental Apparatus

The schematic of the continuous absorption reactor used in the study is given in Figure 1. The continuous reactor consists of a gas dilution setup, absorption column, spray system, solvent circulation pumps, reservoirs, sample collection points, solvent thermal regenerator, and PLC thermostat control for the heating. The entire experimental setup is hoisted on a skid made up of Mild Steel.

The dilution of CO_2 gas to varying concentrations from 8% to 20% using ambient air obtained from a lab vacuum pump is performed using two rotameters. The CO_2 rotameter is of 10 lpm capacity and 0.5 lpm resolution. The Air rotameter is of 50 lpm capacity and 1 lpm resolution. The experiments were repeated several times to average out any errors due to flow fluctuations in the rotameter.

The absorber and stripper reactors in the setup are cylindrical vessels constructed from Stainless Steel (SS) 304 grade, ensuring durability and resistance to corrosion. All solvent connections within the system are also fabricated from SS 304, maintaining consistency in material choice for reliability and chemical resistance. The lines carrying the Air/CO2 mixture are made of pneumatic tubing crafted from Teflon material, chosen for its excellent chemical inertness and pressure carrying capacity.

The Monoethanolamine (MEA) chemical is stored in a Polypropylene tank, which offers a cost-effective and chemically resistant solution for containing the solvent. From this tank, the MEA is pumped into the system as needed. To regulate the flow of substances at various points within the setup, SS 304 type Gate Valves are employed, as depicted in Figure 1. These valves provide precise control and are noted for their robustness and longevity.

Additionally, all thermocouple contactors are made from SS 304, ensuring accurate temperature readings and compatibility with the other components. Both the absorber and stripper vessels are equipped with advanced temperature and pressure sensors, enabling precise monitoring and control of the process conditions within these critical reactors. This comprehensive and carefully selected material setup ensures the system's efficiency, reliability, and longevity.

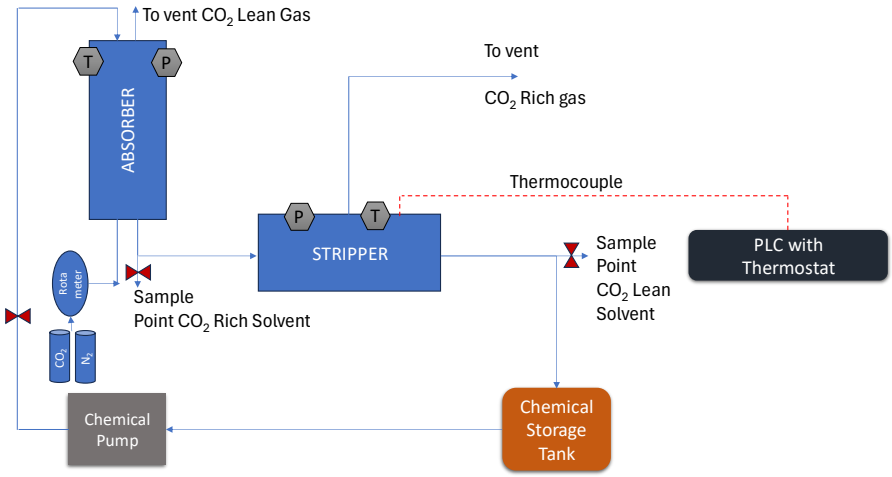

Figure 1. Lab Scale Continuous CO_2 Absorption Reactor - Process Schematic

The absorber operates in a counter-current flow condition between the diluted CO_2 stream and the MEA solvent. The MEA solvent is sprayed with a single-spray nozzle and the CO_2 stream enters from the bottom of the absorber column. The air entry portion is provided with an umbrella setup to avoid solvent entering the air inlet. This umbrella setup will also be resourceful in increasing the residence time of the solvent spray and provides improved surface contact area between the CO_2 stream and the MEA stream. The absorption column is held in place inside the skid.

Solvent recirculation is achieved through use of a chemical pump. The pump is made up of Polypropylene to avoid any corrosion from the solvent used. The maximum flow of the pump is 30 lpm and can provide a water head of 0.5 bar. The recirculation system consists entirely of SS 304 lines of ½" diameters throughout the system.

The MEA solvent is stored in polypropylene containers within the skid. These chemical tanks are connected to the solvent recirculation system. These tanks are also provided with sampling ports to take solvents before, during and after the experiments.

The reactor also contains a thermal stripper to regenerate loaded CO_2 using Ceramic Band Heaters. The temperature of the heaters was controlled using temperature controller with a PLC[2] system (Program Logic Controller). This PLC system offers automatic power cut off to the heaters as soon as the temperature of the stripper exceeds the desired temperature. The band heaters are insulated with rock wool padding for safety. The reactor system was installed with both a pressure and temperature sensor in both the absorber and the stripper.

2.3 Procedure

The MEA solvent was prepared to necessary concentrations as laid out in Table 1. The solvent concentration was varied to 10%, 20% and 30% wt/wt using double distilled water. This MEA solvent was loaded on to the chemical tanks in the reactors. The CO_2 dilution was varied from 10% to 20% as mentioned in Table 1.

In the system, the solvent recirculation system was first initiated to operate the system in a continuous mode. The solvent spray was started, and level was maintained in both the absorber and stripper vessels to reach steady state. Only after this step, the CO_2 flow was initiated from the CO_2 cylinders controlled by the rotameter. The pressure in the absorber vessel was checked to ensure it is well below 0.5 bar. Higher pressure in the absorber vessel will result in reduced absorption of CO_2 with MEA solvent.

The experiment was conducted for various time intervals to also ensure that complete absorption of CO_2 with MEA is achieved to saturation. The recirculation cycles were also monitored for varied counts as mentioned in Table 1.

[2] PLC Thermostat is Programmable Logic Controller for temperature control

Table 1. Operation Parameter of the Continuous CO_2 Absorption Column

Parameter	Variation Range
Solvent Concentration	10%, 20% and 30% wt/wt
CO_2 Concentration	10%, 15%, 20% vol/vol
Recirculation Time	10, 20, 30 minutes

The continuous reactor was operated for each set of condition and samples were collected from the sampling ports provided in the chemical tanks. The stripper was used to regenerate the MEA after each experiment run and the CO_2 loading was estimated to ensure release of absorbed CO_2 which was found to be on average 90%. The regeneration temperature was maintained at 110 °C to ensure complete regeneration possible.

3. Data Observation

3.1 CO_2 Loading Measurements

The UOP Method 829-82 [13] facilitated systematic calculation of loading rates of CO_2 with MEA solvent. It is a method used for titrimetric determination of CO_2 in ethanolamine solutions. The CO_2 loaded samples were dissolved in anhydrous methanol to estimate the loading rates. This solution will be titrated against a standard methanolic sodium hydroxide (MeONa) solution to calculate the CO_2 content. Hence, this method is also referred to as the MeONa method.

Methanol solution of 100ml is taken in a 500ml Erlenmeyer flask and thymolphthalein indicator. 0.5 M Methanolic Sodium Hydroxide solution is prepared and titrated against this Methanol solution to a light blue colour while constantly stirring the solution in the flask. This titrant value is recorded as B. This represents the Methanol Blank value.

Now, 10ml of the CO_2 loaded sample is taken in a pipette and added to the Erlenmeyer flask. The light blue colour disappears. This sample and methanol solution is now titrated against 0.5 M MeONa solution till light blue colour appears. This titrant value is recorded as A. The CO_2 content of the sample can now be calculated using the formula given below [13],

$$\text{Cu.ft of } CO_2 \text{ / gallon of sample} = \frac{3.2\,(A-B)M}{V} \quad (1)$$

Where,
A – Total volume of Standard MeONa added in ml
B – Volume of Standard MeONa added for methanol blank in ml
M – Molarity of MeONa
V – Sample Volume in ml

4. Results and Analysis

4.1 CO_2 Loading Rates

The estimated CO_2 loading rates are summarized in Table 2.

Table 2. Summary of Experiment Results

	10% MEA		20% MEA		30% MEA	
10% CO_2	10 mins	-*	10 mins	0.18	10 mins	0.20
	20 mins	0.13	20 mins	0.26	20 mins	0.28
	30 mins	0.15	30 mins	0.28	30 mins	0.31

15% CO_2	10 mins	-*	10 mins	0.25	10 mins	0.35
	20 mins	0.19	20 mins	0.32	20 mins	0.36
	30 mins	0.21	30 mins	0.36	30 mins	0.39
20% CO_2	10 mins	-*	10 mins	0.35	10 mins	0.40
	20 mins	0.32	20 mins	0.40	20 mins	0.43
	30 mins	0.35	30 mins	0.42	30 mins	0.45

- *All loading rates are expressed in mol CO_2 / mol of amine.*
- *For 10% MEA and <10 mins of recirculation, values are low for titrimetric measurements**

5. Conclusion

The continuous reactor was used to estimate the CO_2 loading with MEA solvent under various operating conditions of solvent concentration, CO_2 dilution and recirculation periods. The titrimetric procedure to estimate the CO_2 content in the amine samples were useful to estimate the absorption load with minimal resources at the lab scale. The CO_2 load values fall well within the previously reported range of 0.2 to 0.5 mol CO_2 per mol of MEA [8]. The continuous reactor has been monument in practically ensuring the absorption capacity of MEA solvents at various concentrations.

The CO_2 levels in the tested amine samples varied between 0.13 to 0.45 mol CO_2 / mol MEA. This variability was achieved by adjusting the CO_2 concentration within the range of 10% to 20%, and the MEA concentration from 10% to 30% over different absorption time periods. It was observed that the CO_2 loading performance demonstrated a direct correlation with the CO_2 concentration in the inlet stream. Nevertheless, there was only a slight improvement in performance noted when the MEA concentration increased from 20% to 30%.

Albeit being a titrimetric method, the UOP 829-82 can be used confidently in this experiment because there are no alkaline carbonates or acidic compounds resulting from amine decomposition [14]. The continuous reactor ensured complete saturation and quicker process flow to avoid amine decomposition. There are also no presence of Sulfur dioxide or Hydrogen Sulphide in this experiment which could affect the titration process in this experiment setup. In addition, to ensure amine decomposition is not present, the CO_2 loaded samples were regenerated in the stripper section in the continuous reactor and then the samples were again tested for presence of any CO_2 content.

The insights gained from this experiment have significant implications for direct CO_2 capture high climate polluting industrial sectors like Coal, Cement, Steel, Ore processing and Chemical manufacturing. Especially through optimized CO_2 capture processes using MEA solvents. The challenges include dynamic heterogeneous emission stream with varying CO_2 concentrations and contaminants. Both these can be overcome by using a continuous reactor and a versatile chemical absorbent like MEA even at low concentrations.

To further improve the CO_2 capture process, several strategies can be considered:

Enhanced MEA Solvents: Use of additives and catalysts that can help reduce the volatility and energy requirement to desorb CO_2 from MEA can be revolutionary in the Carbon Capture domain.

Innovative Reactor Designs: Designing advanced reactors with improved heat and mass transfer characteristics can facilitate quicker and more complete CO_2 absorption and desorption cycles.

Operational Optimization: Using the most advanced control systems to accurately control temperature, pressure, and flow rates to maximize CO_2 capture efficiency while minimizing energy consumption.

Utilization of Renewable Energy: The cost of capture can be brought down drastically by utilizing abundant renewable energy sources to power the CO_2 capture and release processes. This can provide an added benefit of further reducing the carbon footprint of the carbon capture process.

By carefully studying the experimental behaviour of MEA-CO_2 in such continuous reactor setup can fast track the process of designing the optimum CO_2 Capture systems for industries at commercial and large scale adoptions in the quickest time possible.

Acknowledgments

The authors acknowledge that no funding support was received for conducting this experiment.

References

1. IPCC. (2018). "Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change."
2. Government of India. (2015). "Submission on the Road to COP21 Paris: Intended Nationally Determined Contributions (INDCs)." Ministry of Environment, Forest and Climate Change, Government of India.
3. IEA (2021), Coal 2021, IEA, Paris https://www.iea.org/reports/coal-2021
4. Rochelle, G. T. (2009). Amine scrubbing for CO_2 capture. Science, 325(5948), 1652–1654.
5. Danckwerts, P. V. (1979). The absorption of carbon dioxide into aqueous solutions of alkali. Chemical Engineering Science, 34(3), 443–446.
6. Iliuta, M. C., Larachi, F., & Păvăloiu, R. D. (2007). Carbon dioxide capture by reactive absorption with chemical solvents: A review. Industrial & Engineering Chemistry Research, 46(20), 6413–6437.
7. Rubin, E. S., & Chen, C. (2019). Technological learning in CCS: Lessons from historical development trajectories. International Journal of Greenhouse Gas Control, 88, 246–261.
8. Sunkyung Kim, Hu Shi, Jin Yong Lee, CO_2 absorption mechanism in amine solvents and enhancement of CO_2 capture capability in blended amine solvent, International Journal of Greenhouse Gas Control, Volume 45, 2016, Pages 181-188, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2015.12.024.
9. Reynolds A. Frimpong, Don Johnson, Lisa Richburg, Brian Hogston, Joseph E. Remias, James K. Neathery, Kunlei Liu, Comparison of solvent performance for CO_2 capture from coal-derived flue gas: A pilot scale study, Chemical Engineering Research and Design, Volume 91, Issue 6, 2013, Pages 963-969, ISSN 0263-8762, https://doi.org/10.1016/j.cherd.2012.10.006.
10. Omoregbe, O., Mustapha, A.N., Steinberger-Wilckens, R., El-Kharouf, A., Onyeaka, H., 2020. Carbon capture technologies for climate change mitigation: A bibliometric analysis of the scientific discourse during 1998–2018. Energy Reports 6, 1200–1212. https://doi.org/10.1016/j.egyr.2020.05.003
11. Eliane Blomen, Chris Hendriks, Filip Neele, Capture technologies: Improvements and promising developments, Energy Procedia, Volume 1, Issue 1, 2009, Pages 1505-1512, ISSN 1876-6102, https://doi.org/10.1016/j.egypro.2009.01.197.
12. Ashkanani HE, Wang R, Shi W, Siefert NS, Thompson RL, Smith K, Steckel JA, Gamwo IK, Hopkinson D, Resnik K, Morsi BI (2020) Levelized cost of CO_2 captured using fve physical solvents in pre-combustion applications. Int J Greenh Gas Control 101:103135. ISSN 1750-5836. https://doi.org/10.1016/j.ijggc .2020.103135
13. UOP Method 829-82. (1982) Titrimetric determination of CO_2 in ethanolamines. ASTM Intl. Publ.
14. Arnold JL and Pearce RL (1960) Analysis of glycol and amine solutions and the interpretation thereof. Gas conditioning Inst., Liberal, Kansas.