

HEAT OF ABSORPTION OF CO₂ IN NOVEL ENERGY REDUCING SOLVENTS FOR BIOGAS UPGRADING

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Abstract

Biogas upgrading is done for the removal of CO₂ to produce clean bio-methane. CO₂ capture is a method that can accomplish this task. This project focuses on the chemical absorption process using amine as a baseline. The energy required for CO₂ capture can be optimized by the use of new additives termed vapour reduction additives (VRAs). The heat of absorption of CO₂ in aqueous solutions of (30wt%) monoethanolamine (MEA) and (7.5wt% and 30wt%) VRAs have been measured at two temperatures (313K and 393K) at a pressure of 250 psi. The measurements were conducted by a SETARAM C80 calorimeter consisting of a flow-mixing cell. The enthalpies of mixing of CO₂ in the solvents have been obtained as a function of loading α (mol CO₂/mol MEA).

Keywords: *Biogas upgrading; Carbon Capture; Heat of absorption; Vapor reduction additives*

1. Introduction

The increasing levels of CO₂ in the atmosphere have proven to be a cause for serious concern. Energy productions of all forms contribute to 72% of greenhouse gas emissions [1]. Demand for energy across the globe is on the rise due to the rapid growth of economies. A majority of the world's energy needs are still met by fossil fuels. Renewable energy sources are expected to account for 34% of all energy sources by 2050. Even in this scenario, the CO₂ emissions are projected to be 22% higher than required, to limit the global temperature rise to 2°C [1]. Therefore, there is an increasing urgency in switching to CO₂-neutral sources while ensuring their cost-efficiency and economic viability.

One such potential alternative is Biogas. Biogas is produced by anaerobic digestion of organic waste from wastewater sludge, industrial wastes, and agricultural wastes. The composition of biogas depends on the raw organic material used. However, it generally comprises 60-70% Methane, 30-40% CO₂, and minor impurities of water vapour and H₂S [1]. Owing to the high CO₂ concentration, biogas has a low calorific value, making it a less appealing replacement to energy-dense fossil fuels. To increase its energy density, this CO₂ is removed. This process of biogas purification is called biogas upgrading and the technology used for achieving this goal is carb

on capture. Of the numerous CO₂ capture technologies available, chemical absorption by primary amines is state-of-the-art. Amines like Monoethanolamine (MEA), which are basic, react reversibly with acidic CO₂ gas. The process involves an absorber where CO₂ from the biogas dissolves in MEA, releasing pure bio-methane. The CO₂-rich solvent then enters a desorber where it is heated to regenerate MEA and a pure CO₂ stream. The regenerated MEA is recycled to the absorber and the pure CO₂ obtained is either sequestered or utilized as a raw

material. MEA has a high absorption capacity of CO₂ and a high reaction rate, which make it a suitable solvent.

Conventionally, the CO₂-rich solvent is heated to 105°C by lean-amine before being pumped to the top of the desorber, which is at 110°C. The reboiler at the bottom of the column is at 120°C. A high-energy requirement is the main limitation of this technology. The heat required for the solvent's regeneration is given as the sum of three terms [3]:

$$Q_{reb} = Q_{sens} + Q_{vap,H_2O} + Q_{abs,CO_2} \quad (1)$$

where, Q_{sens} is the sensible heat required to raise the temperature of the solvent to that of the reboiler's, Q_{vap,H_2O} is the heat of evaporation required to produce the stripping steam in the reboiler, and Q_{abs,CO_2} is the heat of absorption of CO₂ into the solvent. The equivalent amount of heat released by the exothermic absorption of CO₂ should be supplied to desorb it. The energy required for regeneration accounts for 70-80% of the whole process. Additionally, the high-temperature conditions result in degradation of the solvent leading to corrosion of the equipment. All of these result in significant operating costs. These disadvantages inhibit the wide-scale implementation of the process.

To optimize the regeneration of the solvent, new additives, known as vapour reduction additives are being investigated. Typically, a 30 wt% aqueous MEA solvent is used for the capture process. The high water content implies a high heat of vaporization, increasing the heat of regeneration and solvent losses. The vapour reduction additives (VRAs) are designed to replace water, thereby reducing the solvent's vapour pressure. This abates the amount of water evaporated along the column, thereby decreasing the energy requirements at the condenser situated at the top of the desorber. Further, the size requirements of the desorber are expected to decrease resulting in a decline in both capital and operating costs.

The heat required for regeneration of the solvent, as mention in equation (1), is dependent on the heat of absorption of CO₂ in the solvent. It is, therefore, important to determine the heat of absorption of CO₂ in the presence of the new additives and establish that they do not significantly increase the Q_{abs, CO_2} . Experimentally determining the heat of absorption for these solvents is also expected to aid in the development of accurate thermodynamic models like the Extended UNIQUAC model for representing the new solvent systems.

2. Experimental Setup

The heat of absorption of CO₂ in aqueous solutions of MEA and VRAs was measured using a flow mixing-cell adapted to a Setaram C-80 Calorimeter.

A schematic of the experimental setup is presented in Figure 1.

The system consists of three sub-units: the pre-heater, the mixing cell, and the calorimetric block. The pre-heater heats the fluids to the measurement temperature before they enter the mixing cell. The mixing cell consists of two parallel tubes for the flow of the solvent and CO₂. The tubes are coiled together at the lower end, where the mixing of the two fluids takes place. The outlet tube leaves the calorimeter and the pre-heater parallel to the inlet tubes. There are two mixing cells, one used for the mixing of the fluids, and the other as a reference cell.

The mixing cells are situated in a calorimetric block. The heat emitted by the absorption of CO₂ in the MEA solvent is transmitted to the calorimetric block through the wall of the vessel in an isothermal mode and is detected by thermopiles.

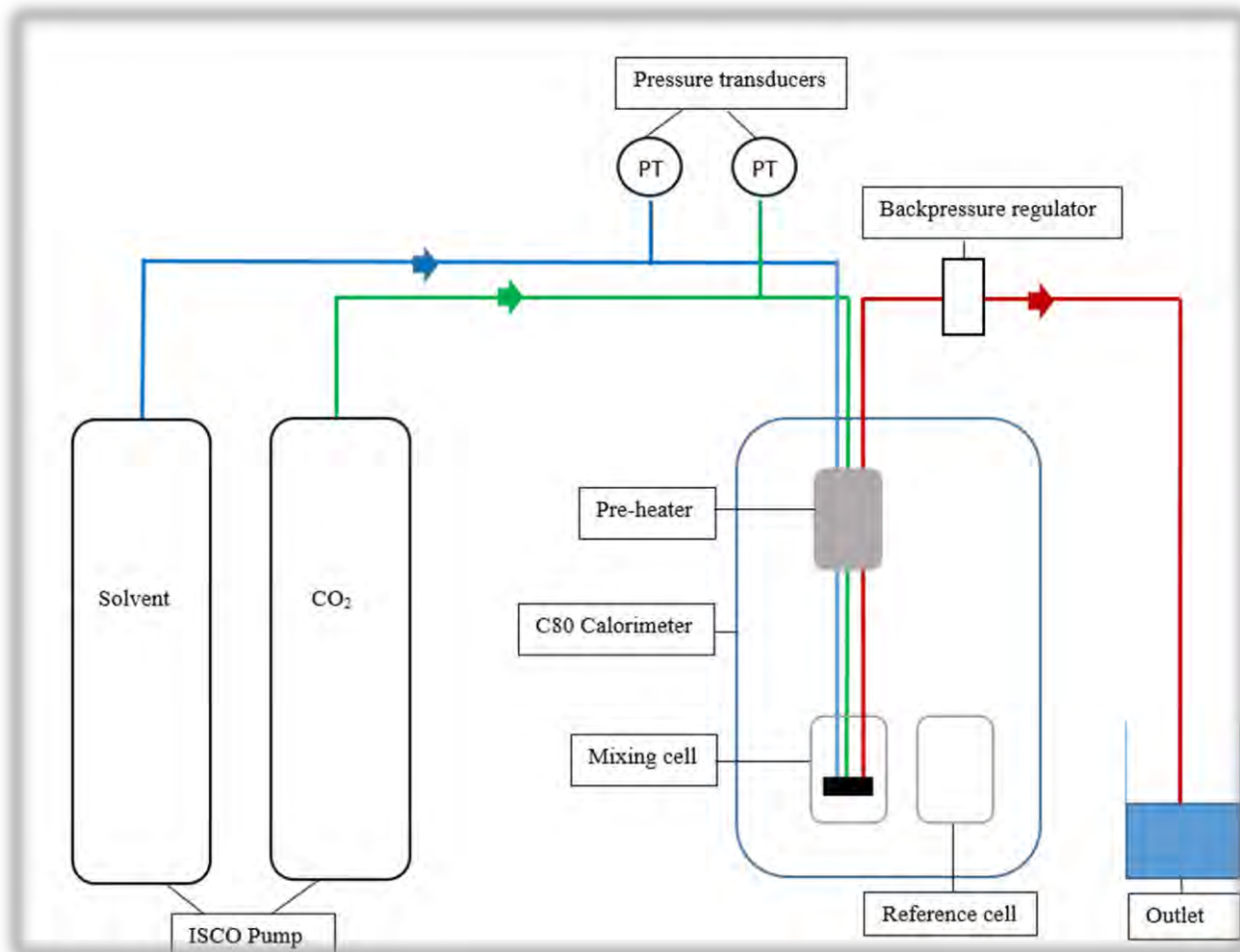


Figure 1: Schematic of the experimental setup

2.1 Operating conditions

The experiments were conducted at 40°C and 120°C, which is the temperature range of the CO₂ capture process. The pressure in the system was maintained at 250 psi by means of a backpressure regulator. The flow rate of the solvent was varied in the range of 0.02-0.3 ml/min while the flow of CO₂ was maintained constantly,

either at 0.4 or 0.6 g/h. The inlet pressure of CO₂ was maintained in the range of 32-35 bar. However, the inlet pressure of CO₂ does not have any impact on the measurements. Experiments were done for loadings in the range of 0.1-0.5 mol CO₂/mol MEA. The loading of the solvent was determined by the ratio of the molar flow rates of CO₂ and MEA, given as:

$$\alpha = \frac{n_{CO_2}}{n_{MEA}} \quad (2)$$

Both the fluids were pumped into the system by use of ISCO pumps. The molar flow rate of the solvent was determined from the volumetric flow rate, density, and concentration of the solvent. The density of the solvent was measured at 298K and atmospheric pressure. The flow of CO₂ was controlled by the use of a Coriolis mass flow controller. The molar flow rate of CO₂ was determined directly from this mass flow rate, eliminating the need for density estimation. Experiments were conducted for 30wt% MEA with and without the VRAs. The experiments are summarized as follows:

- Solvent: 30 wt% MEA
- Additives: 7.5 wt% and 30 wt% of VRA1 and VRA2
- CO₂ loading: 0.1-0.5 mol CO₂/mol MEA
- Temperature: 313 and 393K
- Pressure: 250 psi

2.2 Experimental Procedure

The solvent was first pumped through the system. A small baseline heat signal was observed. This was due to the difference in the temperature of the solvent and the temperature of the calorimetric block. The baseline signal could be reduced by adjusting the temperature of the pre-heater, but could not be eliminated. The solvent was allowed to flow through the system until a steady baseline signal was achieved. CO₂ was then pumped through the system at a pressure higher than the system pressure. This was done to ensure that the solvent does not enter the gas line. The solvent and the gas were allowed to flow through the calorimeter for an hour until a steady heat signal was observed. The loadings of CO₂ were changed in steps of 0.1. This was achieved by maintaining a constant flow rate of CO₂ and adjusting the solvent's flow rate.

The enthalpy of mixing is defined as the heat released per mole of fluid A or B. This enthalpy is obtained from the calorimetric signal S (μV). However, due to the temperature difference between the fluid entering from the pre-heater and the calorimetric block, a baseline signal occurs for the solvent. This signal is to be deducted from the heat signal resulting due to mixing and absorption. Therefore, the enthalpy of absorption is calculated as the ratio of the difference in calorimetric signal and the molar flow rate of CO₂.

$$\Delta H_{abs} = \frac{S_{abs} - S_{BL}}{Kn} \quad (3)$$

Where S_{abs} is the heat of absorption signal, S_{BL} is the baseline signal, K is the sensitivity ($\mu\text{V}/\text{Mw}$) which converts the calorimetric signal to heat power, and n is the molar flow rate of the fluid. In the current work, the standard sensitivity coefficient as a function of temperature, which was delivered with the C80 calorimeter was used.

3. Results and Discussion

3.1 Validation of the results

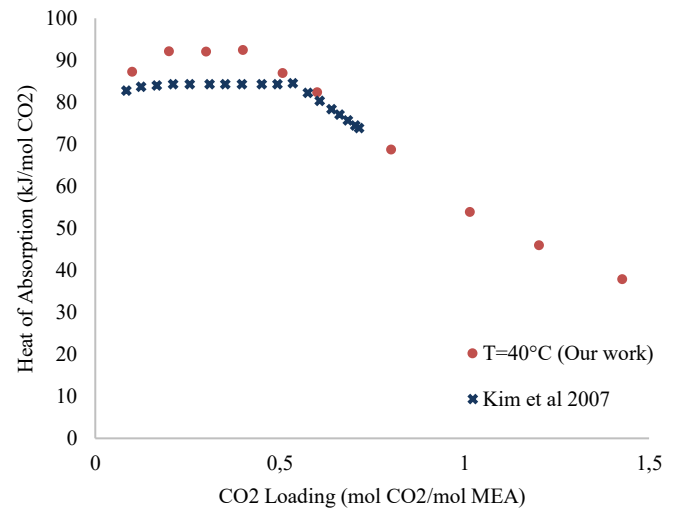


Figure 1: ΔH_{abs} of CO₂ in 30 wt% MEA at 40°C

The experimental results were validated by determining the heat of absorption of CO₂ in 30 wt% MEA at 40 and 120°C and comparing them to data found in the literature. The results for 40°C are presented in Figure 1. From Figure 1, it can be observed that the experimental data are fairly close to the data found in Kim et al [4]. However, a maximum in the heat of absorption is observed in our work. Theoretically, the heat of absorption is expected to be a constant value until saturation. This increasing trend can be considered as an experimental error as it lies within the uncertainty range of $\pm 3\%$. The difference between the experimental values and the data from literature was also observed to lie with a range of $\pm 5\%$. The validation of the method was also carried out for 30 wt% MEA at 120°C.

3.2 Results for 30 wt% MEA and VRA1

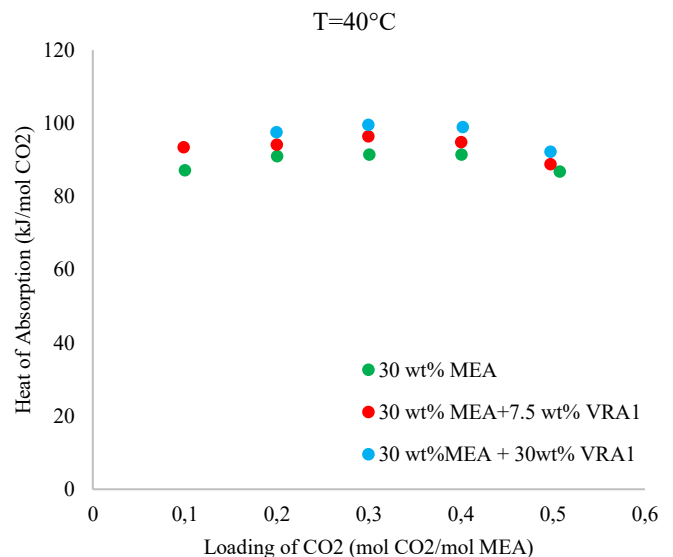


Figure 3: ΔH_{abs} of CO₂ in 30 wt% MEA + VRA1 at 40°C

Figure 3 represents the heat of absorption of CO₂ in 30wt% MEA and 7.5, 30 wt% VRA1 at 40°C. It can be observed that the heat of absorption in the presence of VRA1 is slightly higher than the base case scenario. The heat of absorption in the presence of 7.5 wt% VRA1 is higher by 4.4% than 30 wt% MEA and 30 wt% VRA1 is higher by 8.3%. Owing to the presence of uncertainty, these values are not significantly higher than 30 wt% to impact the $Q_{\text{abs,CO}_2}$ for the regeneration of the solvent. Experiments were also carried out for the remaining operating conditions.

4. Conclusion

Energy reduction of the solvent regeneration process plays a crucial role in the extensive establishment of biogas upgrading plants. The new solvent technology has the potential to meet these requirements. The vapour reduction additives are capable of reducing the energy requirements. Through this work, it has been established that the heat of absorption of CO₂ in MEA based solvents is not significantly higher in the presence of these additives. As a result, these additives can aid in reducing the energy consumed for solvent regeneration. Future work aims at estimating the heat of absorption of these solvents by use of thermodynamic models such as the Extended UNIQUAC model.

Acknowledgements

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