# 16th International Conference on Greenhouse Gas Control Technologies **GHGT-16**

## 23-27th October 2022, Lyon, France

## Advancing the large-scale development of PCC processes by providing essential VLE data for aqueous solutions of amines

Charithea Charalambous[a,*], Ardi Hartono[b], Hanna Knuutila[b], Susana Garcia[a]

*[a]Research Centre for Carbon Solutions, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom*
*[b]Department of Chemical Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*

**Abstract**

Aqueous solutions of alkanolamines are commonly used solvents to remove $CO_2$ from flue gases in amine-based post-combustion carbon capture (PCC) systems. The amines chemically bind $CO_2$ in the absorber where the solvent is directly contacted with the flue gas. The reactions are reversed at high temperatures in a regeneration column and a pure $CO_2$ stream is produced. After regeneration the solvent can be reused to absorb $CO_2$. Solvent volatility and degradation due to unwanted side reactions are known drawbacks of using the technology, as they lead to increased solvent replacement, liquid waste treatment and the adoption of costly gas treatment strategies to avoid the emissions. Solvent volatility increases the amount of solvent leaving the absorber as vapor and separate water wash sections are used to minimize or even eliminate amine emissions to the atmosphere.[1,2] The amine degradation, due to presence of oxygen and other impurities, like nitrogen oxides, as well as elevated temperatures during solvent regeneration, can result in other gaseous emissions of degradation compounds, like ammonia.[3] The direct contact of solvent and flue gas provides a pathway for the carry-over of amine and degradation products into the exhaust gas as vapor or suspended liquid.

To make the PCC process economically viable, the energy requirement and environmental impact of the process must be reduced, while maintaining optimal $CO_2$ recovery. The most well-known and broadly used amine in carbon capture systems is monoethanolamine (MEA) due to its low chemical cost, fast reaction rate and high capacity to capture $CO_2$ even at $CO_2$ low partial pressures. However, this solvent is moderately volatile and a significant amount of energy is required to regenerate the $CO_2$ rich solvent in the stripper column. Therefore, interest has recently grown in mixing alkanolamines to reduce energy, solvent losses and solvent degradation.[4,5]

2-Amino-2-Methyl-1-Propanol (AMP) and Piperazine (Pz) mixtures merge useful properties from both amines. AMP has a higher $CO_2$ loading capacity and can be regenerated at lower temperatures than MEA. However, AMP has lower $CO_2$-absorption rates than MEA. Pz, a diamine, effectively promotes rapid formation of carbamates and can theoretically absorb two moles of $CO_2$ per mole of amine. Adding Pz to AMP is reported to be an energy and material saving alternative to conventional MEA-based solvents for the PCC process.[6] The AMP/Pz mixture has been considered as the new benchmark for liquid-based capture systems (e.g. European ERA-ACT project ALIGN-CCUS (www.alignccus.eu) and the EU project in the 7th framework program CAESAR).

The integration of advanced washing systems, like water wash systems, in amine-based PCC processes can provide a significant reduction in, or even elimination of, amine emissions to the atmosphere. As a consequence, washing systems can reduce the environmental impact and energy requirement of the carbon capture process, making PCC systems economically viable.[2] It has been recorded that these systems can reduce solvent emissions up to two orders of magnitude in comparison to amine systems

---

\* Corresponding author. Tel.: +44-131-451-8121, *E-mail address:* c.charalambous@hw.ac.uk

without washing systems. As these systems control the solvent emissions to atmosphere, it is essential to accurately model, simulate and design these systems.

Vapor-liquid equilibria are fundamental properties for the accurate design and simulation of any separation processes. The data is required for process modelling and simulations of nonideal liquid systems, like aqueous amines. However, there is a lack of experimental vapor-liquid equilibrium (VLE) data at low amine concentrations recorded in the washing sections of the PCC systems. Regardless, existing models are used which do not make use of this critical data, leading to inaccurate predictions in the solvent losses to atmosphere, the extent of amine degradation, and consequently the inaccurate performance of the capture plant.

Our study aims to improve the economics and to de-risk large-scale development of PCC processes by providing essential VLE data, which is currently lacking, for aqueous solutions of amines (i.e., MEA solution, AMP and Pz solution). This data is key to developing a rigorous design of water wash systems in amine-based carbon capture technologies. The VLE data can be used to build reliable simulations and models of the capture process and, subsequently, to reduce the inconsistency between real plant data and results obtained from process modelling.

The experiments were performed using a modified Swietoslawski ebulliometer to measure the volatility of aqueous amines at low concentrations when $CO_2$ is not present.[7-9] The obtained experimental data describes how the pressure, temperature, and liquid phase composition (30 vol.% MEA and 2:1, 4:1 and 6:1 AMP:Pz solutions) influences the vapor pressure (volatility) of the tested amines. For the combined aqueous AMP + Pz systems advanced analytical methods were performed (LC-MS). Analytical methods used vary from simple titration to LC-MS methods to quantify the amines in the liquid and in the gas phase (volatility). The data will be used to fit and verify a VLE simulation model possibly developed in ASPEN Plus.

*Keywords:* carbon capture; advanced aqueous systems; vapor liquid equilibria; water wash; absorption

---

**References**

1. Moser et al. (2014). Demonstrating Emission Reduction – Results from the Post-combustion Capture Pilot Plant at Niederaussem. *Energy Procedia*, 63, pp. 902-910.
2. Rieder et al. (2017). Understanding solvent degradation: A study from three different pilot plants within the OCTAVIUS project. *Energy Procedia*, 114, pp. 1195-1209.
3. Spietz et al. (2018). Ammonia emission from $CO_2$ capture pilot plant using aminoethylethanolamine. *Int. J. Environ. Sci. Technol.*, 15(5), pp. 1085-1092.
4. Artanto et al. (2014). Pilot-scale evaluation of AMP/PZ to capture $CO_2$ from flue gas of an Australian brown coal-fired power station. *Int. J. Greenh. Gas Con.*, 20, pp. 189-195.
5. Li et al. (2013). Characterization of Piperazine/2-Aminomethylpropanol for Carbon Dioxide Capture. *Energy Procedia*, 37, pp. 340-352.
6. Nwaoha et al. (2017). Advancement and new perspectives of using formulated reactive amine blends for post-combustion carbon dioxide (CO2) capture technologies. *Petroleum*, 3(1), pp. 10-36.
7. Wanderley et al. (2020). Investigating opportunities for water-lean solvents in $CO_2$ capture: VLE and heat of absorption in water-lean solvents containing MEA. *Purification Technology*, 231, 11583.
8. Bernhardsen et al. (2019). Vapour-liquid equilibrium study of tertiary amines, single and in blend with 3-(methylamino)propylamine, for post-combustion $CO_2$ capture, *J. Chem. Thermodyn.*, 138, pp. 211-228.
9. Hartono A. et al. (2017). Characterization of 2-Piperidineethanol and 1-(2-Hydroxyethyl)piperidine as strong bicarbonate forming solvents for $CO_2$ Capture. *Int. J. Greenh. Gas Con.*, 63, pp. 260–271.