Enabling Technologies for Carbon Capture with 2-EEMPA

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Background

- PNNL's single component, water lean solvent, 2-EEMPA, continues to climb TRL scale (6→7) as preparations are underway for pilot scale testing at the National Carbon Capture Center (NC[3]).

- To ensure success, 2-EEMPA requires enabling technologies to prepare for unforeseen behavior and mitigate risks for industry adoption.

- To this end, *FWP-82917* awarded for 04/2024 – 03/2025. This project will focus on enabling technologies for 2-EEMPA including a) **process analytics** and b) **heat stable salt management**.

National Carbon Capture Center

Motivation

A. Flexibility on high VRE grid demands more dynamic controls, requiring online solvent CO_2 loading analysis. Currently, little to no real-time solvent analytics for monitoring solvent composition in process. Conventional analysis requires offline, indirect, multiple platforms (titration, GC, LC etc.), and complex calibrations. Can we have a low-cost, online, and single platform providing all needed solvent analytics?

B. Heat stable salt (HSS) accumulation for amine-based solvents is unavoidable. Solvent reclamation processes required to avoid degradation of solvent performance. Existing technologies require costly and complex unit operations with additives or high energy input.
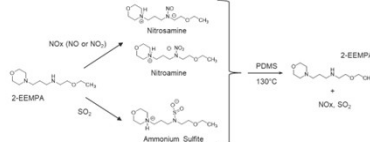
However, polarity swing based assisted thermal regeneration (PSAR) at temperatures similar to CO_2 regeneration is promising alternative. Can we demonstrate an integrated HSS regeneration methodology with continuous capture that is supported by technoeconomic assessment analysis (TEA) to be favorable to conventional makeup techniques?

Process Analytics

- Goal: Develop and validate Raman spectroscopy-based analytical method for CO_2, H_2O, and trace contaminant composition (SOx, NOx) in 2-EEMPA.
- Raman advantages: nondestructive, little sample prep, real-time inline signals, not sensitive to water interference, low-cost units commercially available.
- Recent work (Lines et al. Anal. Chem., 2023, 95, 42, 15566) established proof-of-concept via 3-component solvent system: CO_2, H_2O and 2-EEMPA. This work will revise existing model with new training set data.
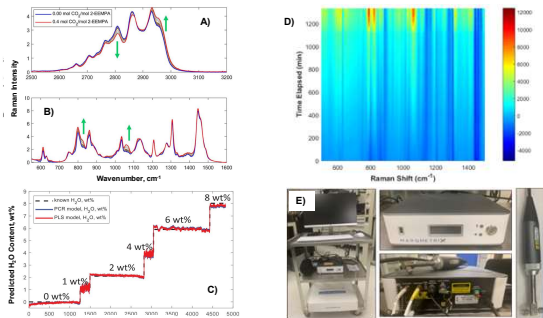

Figure 1. (A, B) Raw Raman spectra on original 3-component training set. (C) H_2O model (version 1) prediction compared to measured data. (D) Plot of time-dependent Raman data as more CO_2 is loaded on 2-EEMPA showing the growth (and/or disappearance) of major peaks. (E) Photograph of the Raman probe flow-cell assembly and the compact spectrometer.
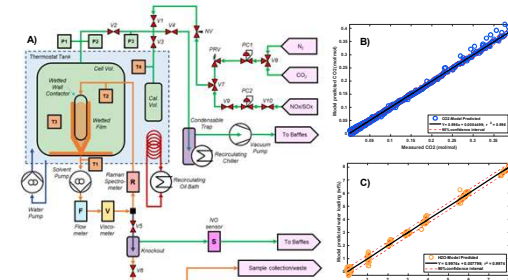

Figure 2. A) Custom vapor-liquid equilibrium infrastructure retrofitted to collect in-situ Raman spectroscopy data. Revised 3-component chemometrics model for B) CO_2 and C) H_2O showing comparison between measured and predicted values.
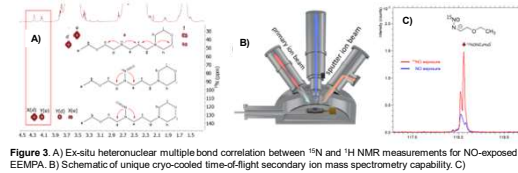

Figure 3. A) Ex-situ heteronuclear multiple bond correlation between ^{15}N and ^1H NMR measurements for NO-exposed 2-EEMPA. B) Schematic of unique cryo-cooled time-of-flight secondary ion mass spectrometry capability. C)

Both in situ (**Fig. 2**) and ex situ (**Fig. 3**) gas absorption capabilities have been utilized to generate samples with quantifiable gas loading compositions to match corresponding Raman spectra.

Heat Stable Salt Management

- Goal: Validate solid-PSAR concept for thermal regeneration of EEMPA containing SOx/NOx HSS via fundamental property testing as well as proof-of-concept prototype design and evaluation.
- 2-EEMPA has high boiling point (>300°C). Conventional thermal reclaiming requires higher energy use, equipment costs, and higher solvent loss.
- However, recent work (Zheng et al. Energy Fuels., 2016, 30, 1192) has demonstrated this PSAR approach extensively with 2-EEMPA and CO_2. Preliminary data with HSS-containing 2-EEMPA suggests a similar approach with solid substrate is also possible.
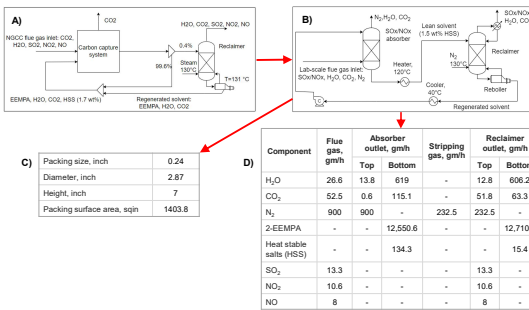

Figure 4. Prototype design approach starting from industrial scale HSS reclamation process model. (A) Reclaimer process simulation flowsheet for NGCC capture system using 2-EEMPA. (B) Reclaimer process simulation flowsheet for laboratory-scale capture system using 2-EEMPA. (C) Estimated laboratory-scale reclaimer sizing parameters used for prototype fabrication. (D) Stream table for PNNL laboratory-scale reclaiming process system.
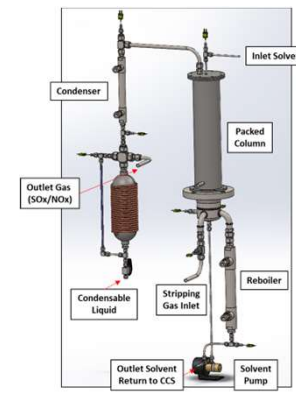
Component	Flue gas, g/m	Absorber outlet, g/m		Stripping gas, g/m	Reclaimer outlet, g/m	
		Top	Bottom		Top	Bottom
H_2O	26.6	13.8	619	-	12.8	606.2
CO_2	52.5	0.6	115.1	-	51.8	63.3
N_2	900	900	-	232.5	232.5	-
2-EEMPA	-	-	12,550.6	-	-	12,710.5
Heat stable salts (HSS)	-	-	134.3	-	-	15.4
SO_2	13.3	-	-	-	13.3	-
NO_2	10.6	-	-	-	10.6	-
NO	8	-	-	-	8	-

Packing size, inch	0.24
Diameter, inch	2.87
Height, inch	7
Packing surface area, sqin	1403.8

To develop lab-scale equipment that will collect translatable experimental data, a unique approach starting from the industrial scale process model was utilized (**Fig. 4**).

Based on sizing and flowsheet generated from process model, a prototype, packed column, solid-PSAR-based thermal reclaimer unit was designed and prepared for fabrication (**Fig. 5**).

The prototype will be packed with high surface area ProPak random packing that is coated with a nonpolar substrate to demonstrate solid-PSAR thermal reclamation (**Fig. 6**).
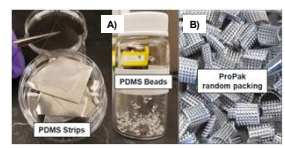

Figure 5. SolidWorks design of the envisioned lab-scale solvent reclaimer prototype to be used with existing PNNL capture system for integrated capture and regeneration.

Figure 6. (A) Nonpolar PDMS substrate samples prepared for vapor-liquid equilibrium measurements with 2-EEMPA. (B) High surface area 0.24" ProPak random packing to be coated with PDMS for solid-PSAR experiments.

Planned Work

- Continue to collect vapor-liquid equilibria (VLE) and absorption kinetics experimental data for SOx/NOx on 2-EEMPA. Measurements at 40°C with corresponding Raman spectra are required for chemometrics model revision. Measurements at higher temperatures (100-120°C) with and without the presence of nonpolar substrate are required for prototype design updates. All experimental data → process simulation model. Representative test data is shown in **Fig. 7**.
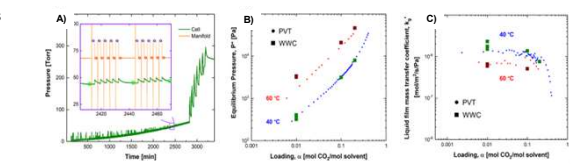

Figure 7. (A) Representative raw data generated from PNNL's 'PVT-cell' apparatus after gas absorption on 2-EEMPA. (B) VLE data reduced from PVT-cell experiment showing equilibrium partial pressure of target gas as a function of solubilized gas in 2-EEMPA. (C) Absorption kinetics data reduced from PVT-cell experiment showing liquid-phase mass transfer coefficient as function of solubilized gas in 2-EEMPA.

- Fabricate laboratory-scale reclaimer prototype unit based on current design and begin testing with integrated capture system. Quantify output stream composition to validate process model that will translate this data to industrial scale.

- Begin preliminary TEA on process flowsheet with and without this integrated reclaimer operation to quantify cost and estimate impacts on solvent durability/longevity.

Potential Impacts

Live process analytics on solvent composition.

Lower total cost of capture.

Extended solvent longevity.

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