Molecular Refinement of Transformational Solvents for CO_2 Separations
(FWP-72396)

[Discovery of Carbon Capture Substances and Systems (DOCCSS)]
[NETL/DOE Project Manager: Andy Aurelio]

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Capture
2020 Integrated Review Webinar
October-5-7 2020

Acknowledgment

"This material is based upon work supported by the U.S. Department of Energy under Field Work Proposal FWP-72396."

Project Objectives

Total Program Funding: $3,997,000 / 39 months

7/1/2017-12/31/2020

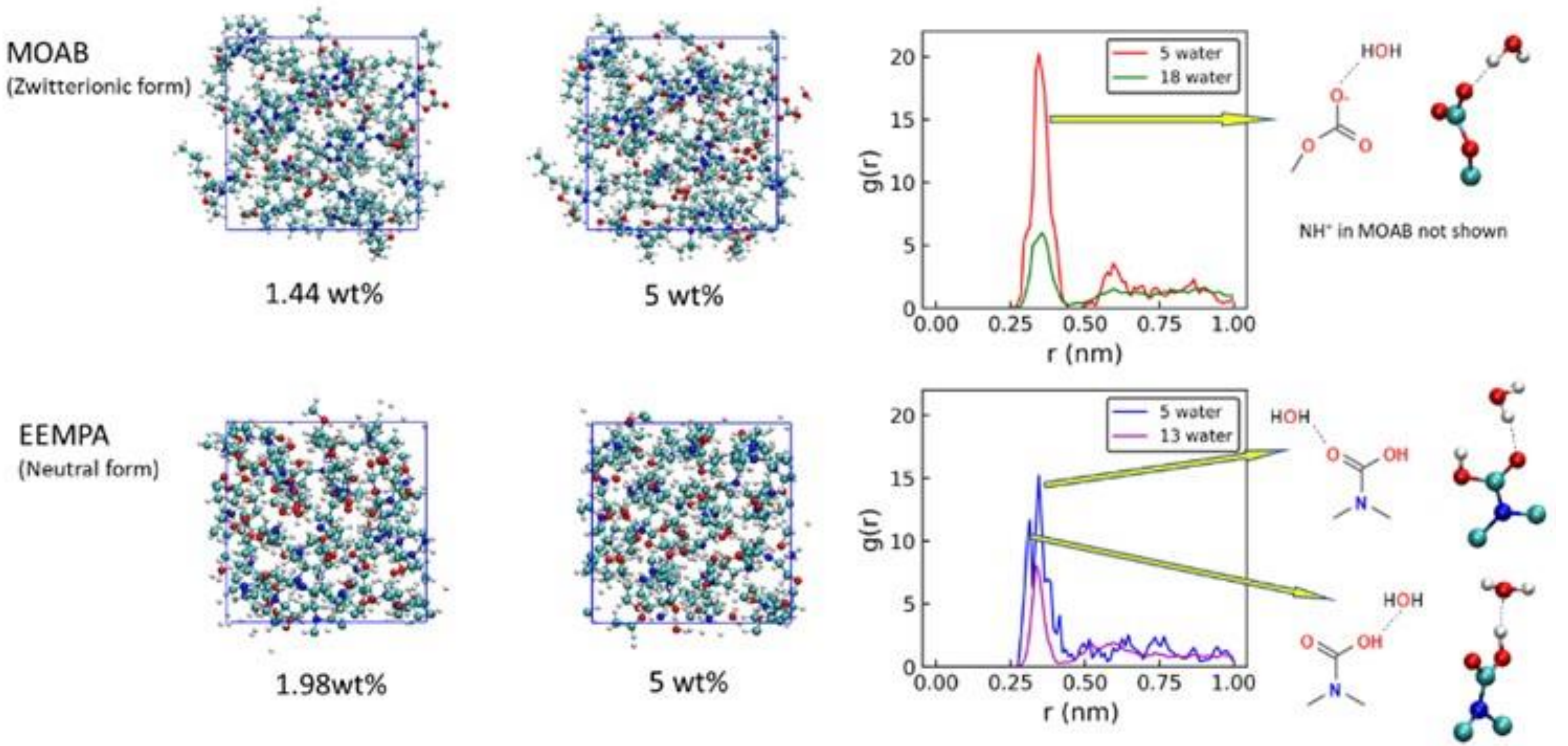
Key objective: continue the refinement of water-lean solvents to enhance physical and thermodynamic properties, final focus = chemical durability.

FY20 Work scope:

- Measure degradation reactions of carbamates and alkylcarbonates with O_2 and H_2O
  - *Controlled degradation reactions on reference solvents using advanced operando spectroscopy (NMR, IR)*
  - *Key reaction intermediates and rate constants in order to identify the reaction mechanisms*
  - *Quantify catalytic sources of degradation and assess impacts on reactivity*
- Model critical transition states to identify rate-limiting steps in the degradation reactions
  - *Construct reaction profiles and free-energy landscapes for un-catalyzed and catalyzed systems via metals*
- If needed: redesign solvents at molecular level to increase energy barriers as a means of mitigating degradation

Technical Approach – FY20

Approach: develop reactivity models to understand degradation pathways for derivatives of two solvent classes.



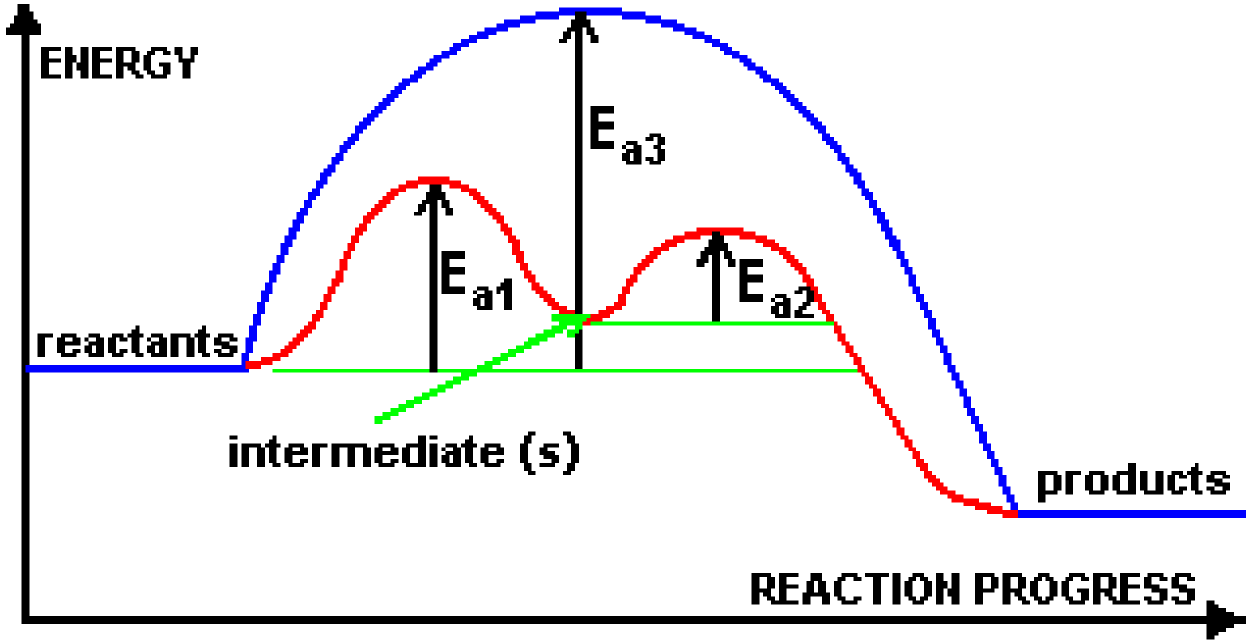
Technical Approach – FY20

Learn how water-lean solvents age and assess lifetime under absorber and stripper conditions.

How does this

Go to this?

Improve chemical durability for solvent-based processes via “anti catalysis”

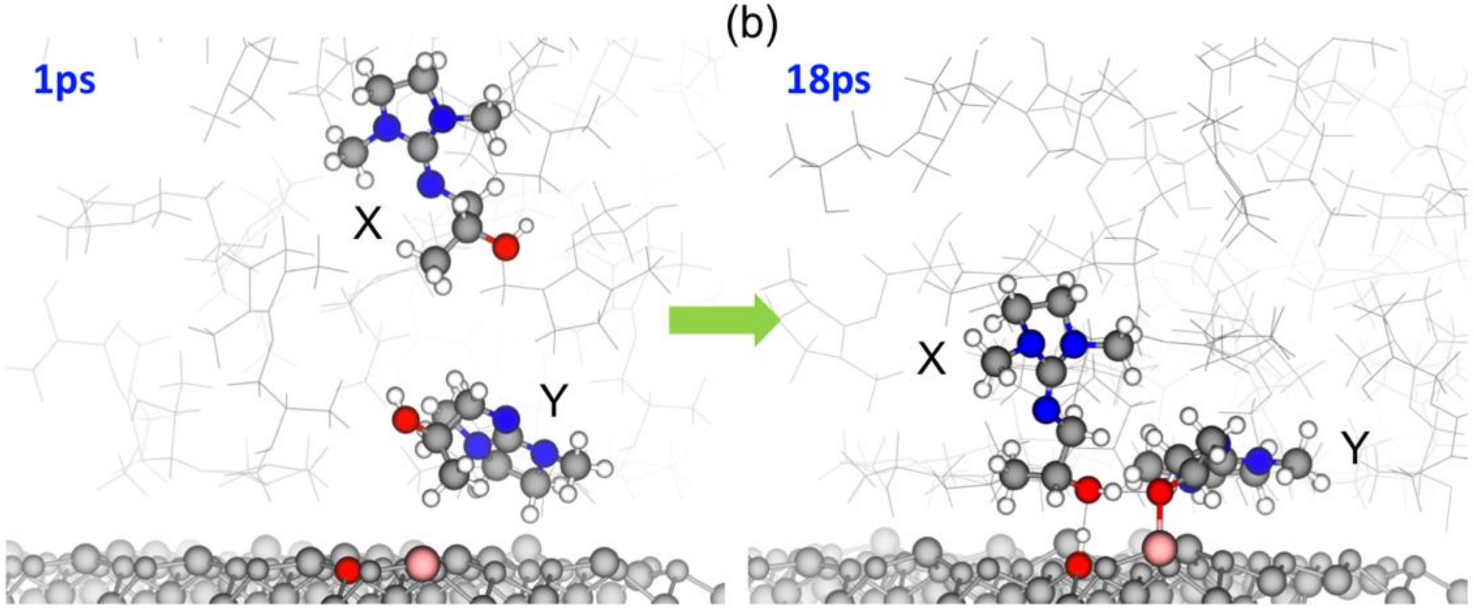


Remaining Milestones

		Original	Revised
8.1	MD-based assessment of oxidation mechanisms of up to 2 carbonates and 2 carbamates and prediction of the energy barriers of the rate-determining steps towards the goal of raising the oxidation barrier by 2-5 kcal/mol and subsequently reducing the oxidation rate by one order of magnitude.	Oct 2020	Jan 2021
9.1	30-50 variants of alkyl carbonates and amines with projected 2-3 kcal higher energy barriers in the rate-determining step of oxidative degradation.	Dec 2020	Mar 2021
11.1	Identify reaction mechanisms (reaction intermediates, rate constants/reaction orders) for nitrosation of 2 alkylcarbonate, and 2 carbamate solvents. Emphasis on identification of durability of alcohol, imine and amine functional groups.	Jan 2021	Apr 2021

Project Scope – Success Criteria

- **FY 2020:** Mechanisms of hydrolysis identified, and mitigation strategies discovered that reduces the rate of hydrolysis by 50%.



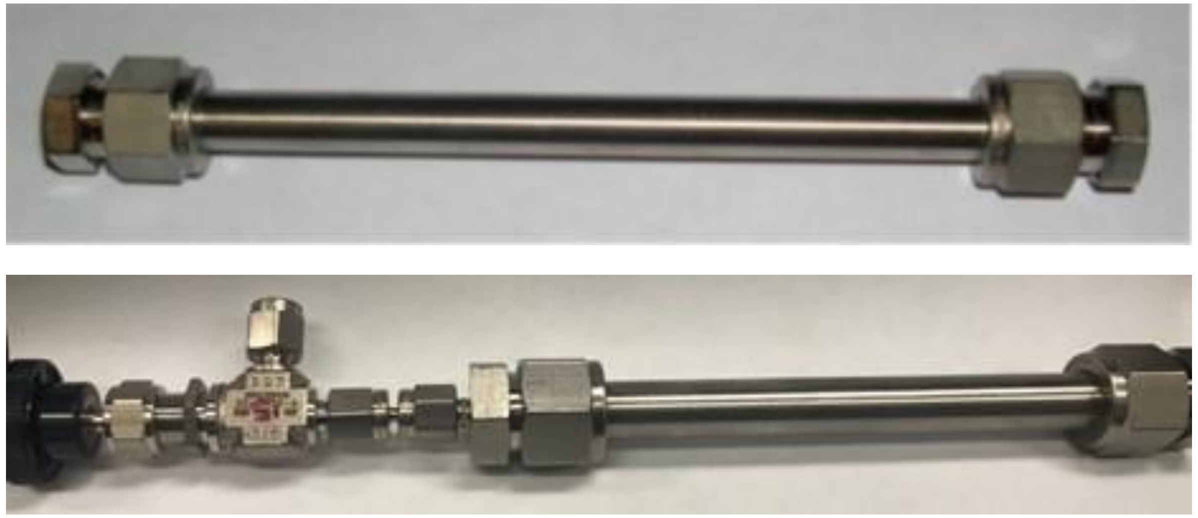
- **FY 2021:** Identify mitigation strategy that reduces the rate of oxidative degradation by 50%.

Both criterial require a 2-3 kcal/mol increase in energy barrier to shut down the reaction.

Experimental Degradation Study

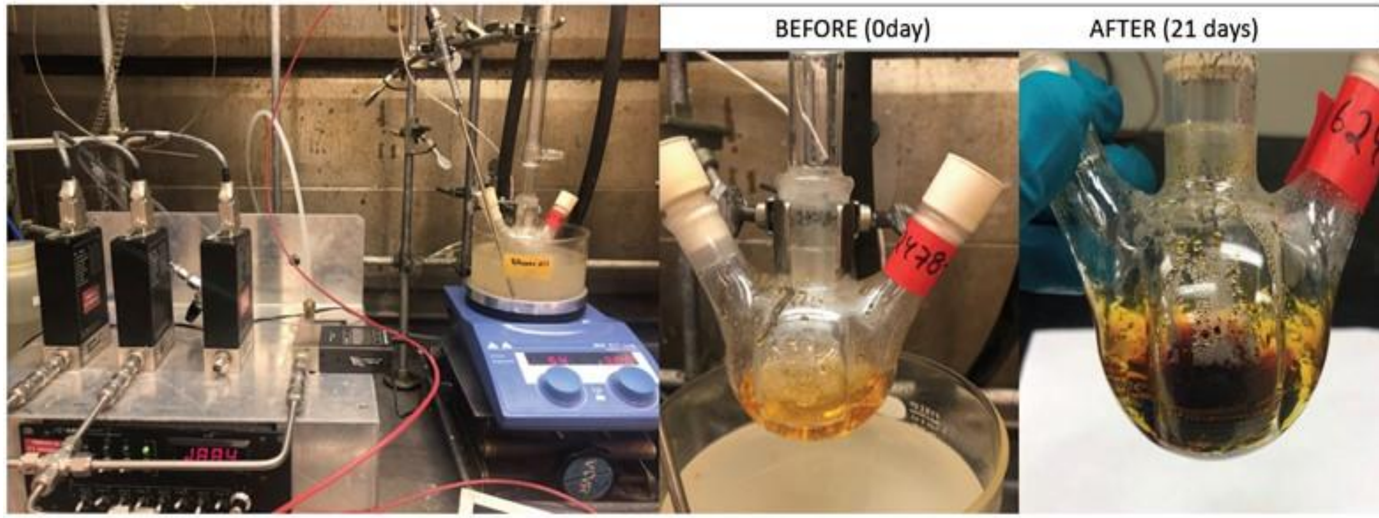
Objective: Study decomposition in absorber and stripper conditions for 5-weeks.

*Thermal degradation mimics stripper conditions.



- CO_2-free and CO_2–saturated samples
- With without water
- Six-gram aliquots in 316 stainless reactors
- Held at 117 °C for 5 weeks

*Oxidation mimics absorber conditions.



- CO_2-free and CO_2–saturated samples
- Glass reactors sparged with air and 2% CO_2 (0.35 L/min air + 7.5 mL/min CO_2) for 213 h (21 days)

- Samples were taken from the liquid phase and analyzed at weekly intervals
- Analyzed by ^1H & ^{13}C NMR, ESI-MS and LCMS

Conclusions from Degradation Study

Alkanolguanidines: ***are unlikely to meet sufficient durability***

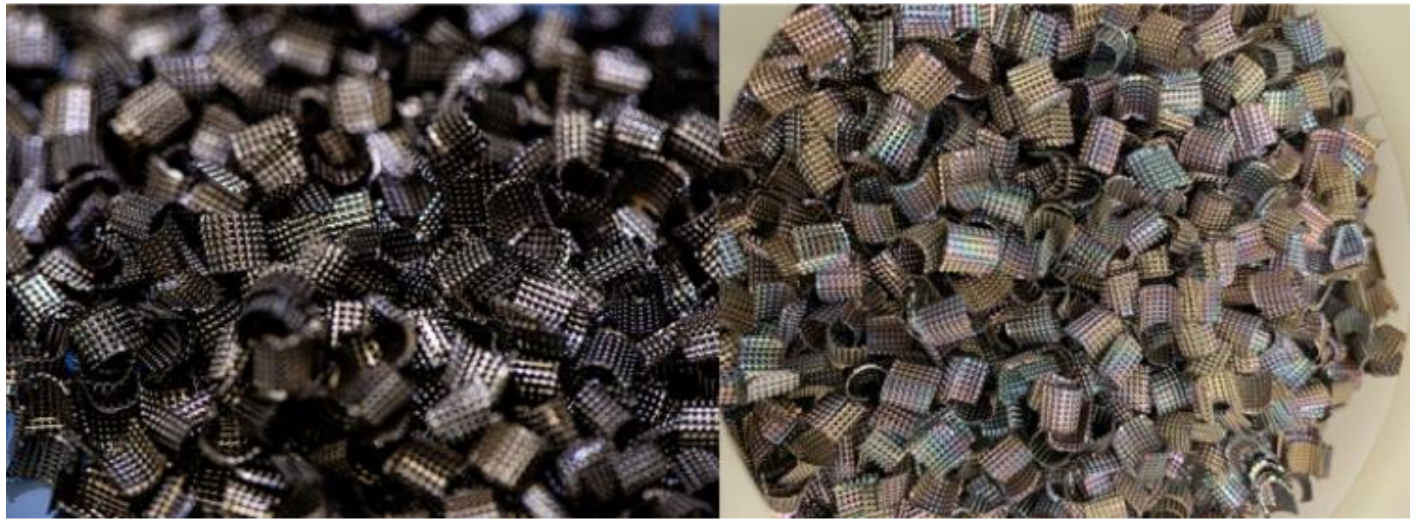
- CO_2-loaded alkanolguanidine solvents are more prone to degradation reactions.
  - *Attributed to decreases in pH, changing the acid/base properties of solvent molecules*
- Dry 1-IPADM-2-BOL showed relative stability with only ~10% degradation in air
- Guanidine cores are highly susceptible to hydrolysis, with >95% loss with 5 wt.% water
  - *Water's high dielectric constant more readily solvates cations and anions which are common in degradation reactions*
  - *Water is the 2nd–best hydrogen bond donor and acceptor, enabling more facile proton transfer reactions to occur*

Aminopyridines and diamines: ***are far more durable than aqueous MEA***

- 2-EEMPA and 2-MPMPA were found to be stable under both absorber conditions (oxidative) and stripper conditions (thermal and hydrolysis).
- Under all the conditions <1% decomposition was observed or no detectable products after at least 5 weeks of testing
- Durability correlates with testing on EEMPA by SINTEF In DOCCSS (FWP 70924)

Influence of Steel Interfaces on Degradation

- Degradation measurements of 2-EEMPA, 1-IPADM-2-BOL, and 30 wt.% MEA.
- 2-EEMPA and 30 wt.% MEA solvent samples were subjected to oxidation conditions,
  - *Neat solvent with and without* CO_2
  - *316 stainless-steel Propak™ random packing*
  - *Silcotek® (hydrophobic) silane) coated Propak™ random packing*
- ~1:1 volume ratio of solvent to packing allows comparable surface area
- Silane-coating enables a comparison between passivated and pristine steel interfaces



Propak™ ½” packings:

- Left) uncoated
- Right) Silcotek® coated

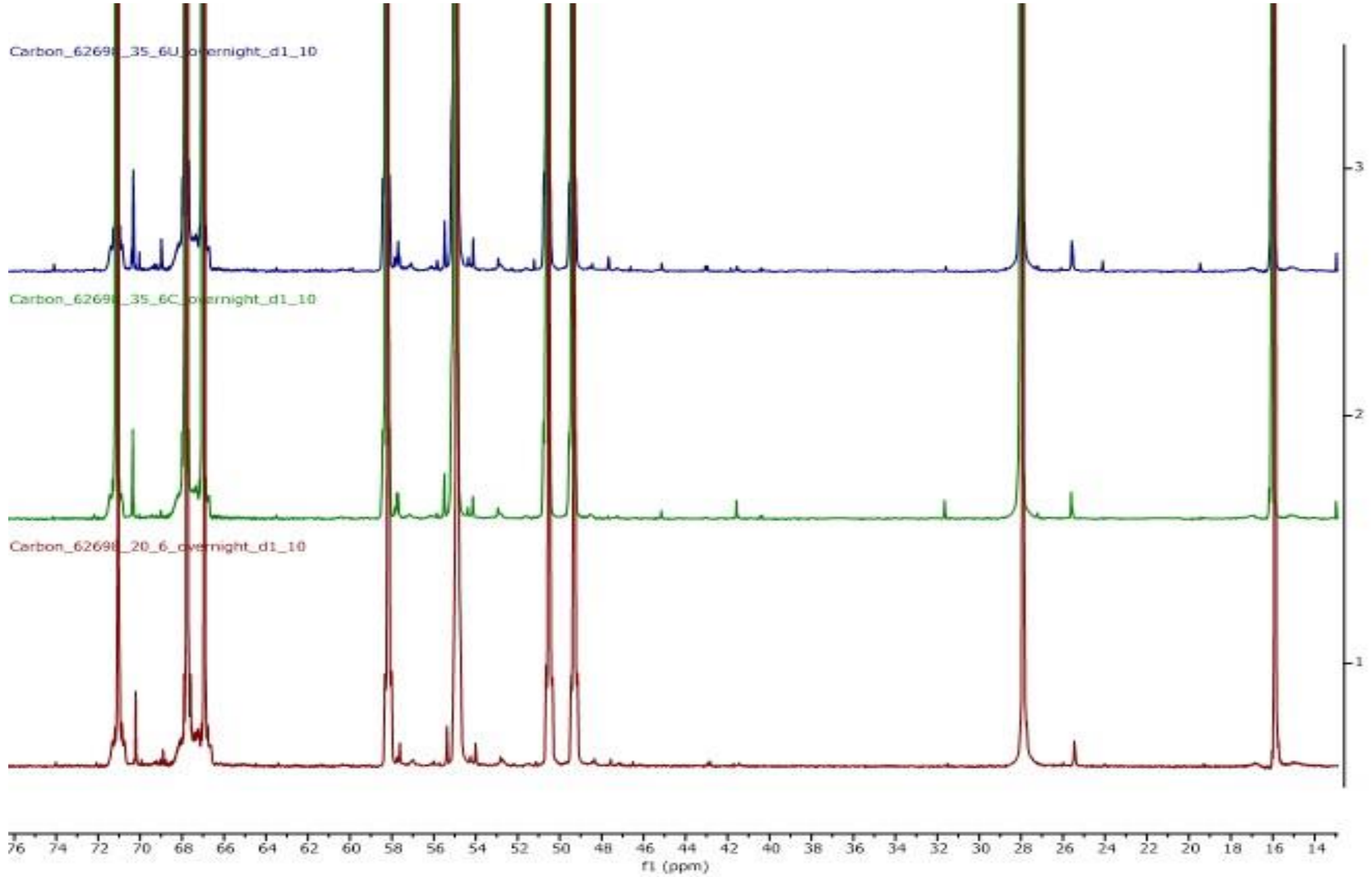
Influence of Steel Interfaces on Degradation

Chemical analysis of all degradations were performed in gas and liquid phase for samples with and without steel packing

Visual comparison of different samples of oxidatively-degraded 2-EEMPA.
Similar visual assessments were observed with 1-IPADM-2-BOL and 30 wt.% MEA.

Influence of Steel Interfaces on Degradation

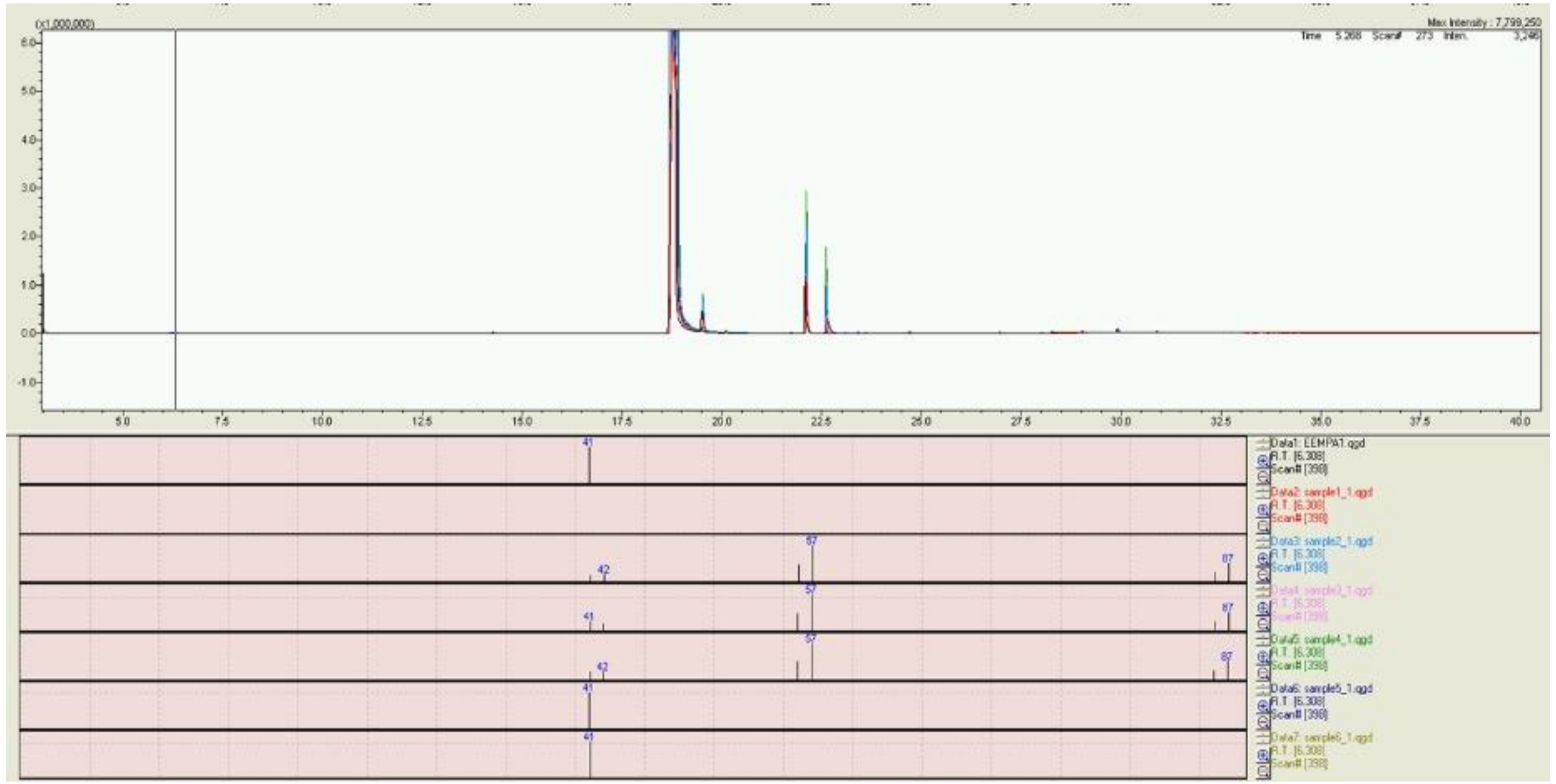
Chemical analysis of all degradations were performed in gas and liquid phase for samples with and without steel packing



Representative comparison of ^{13}C NMR spectra of degradation of 2-EEMPA during reaction **6**. Top: with uncoated 316 SS chips, middle: with Silcotek®-coated 316 SS chips, bottom: in the absence of 316 SS. Similar NMR spectra were recorded for 30 wt.% MEA.

Influence of Steel Interfaces on Degradation

Chemical analysis of all degradations were performed in gas and liquid phase for samples with and without steel packing



Representative stacked MS analyses' results of reactions of 2-EEMPA. Similar MS analysis was performed for 30 wt.% MEA.

Influence of Steel Interfaces on Degradation

Oxidative degradation conditions: 55 ˚C, 1 atm O_2, 30 days in glass.

Alkanolguanidine: 1-IPADM-2-BOL

- Has not been tested in the presence of either coated or uncoated packing due to high degradation rate in the absence of steel

Diamine: 2-EEMPA

- Degraded quickly when loaded with 9 wt.% of CO_2 in the presence of uncoated steel
  - *96% lower oxidative degradation when Silcotek® packing was substituted*
- Degraded quickly in the presence of 2.5 wt.% of H_2O in the presence of uncoated steel
  - *83% lower oxidative degradation when Silcotek® packing was substituted*

Aqueous amine: 5M (30 wt.% MEA)

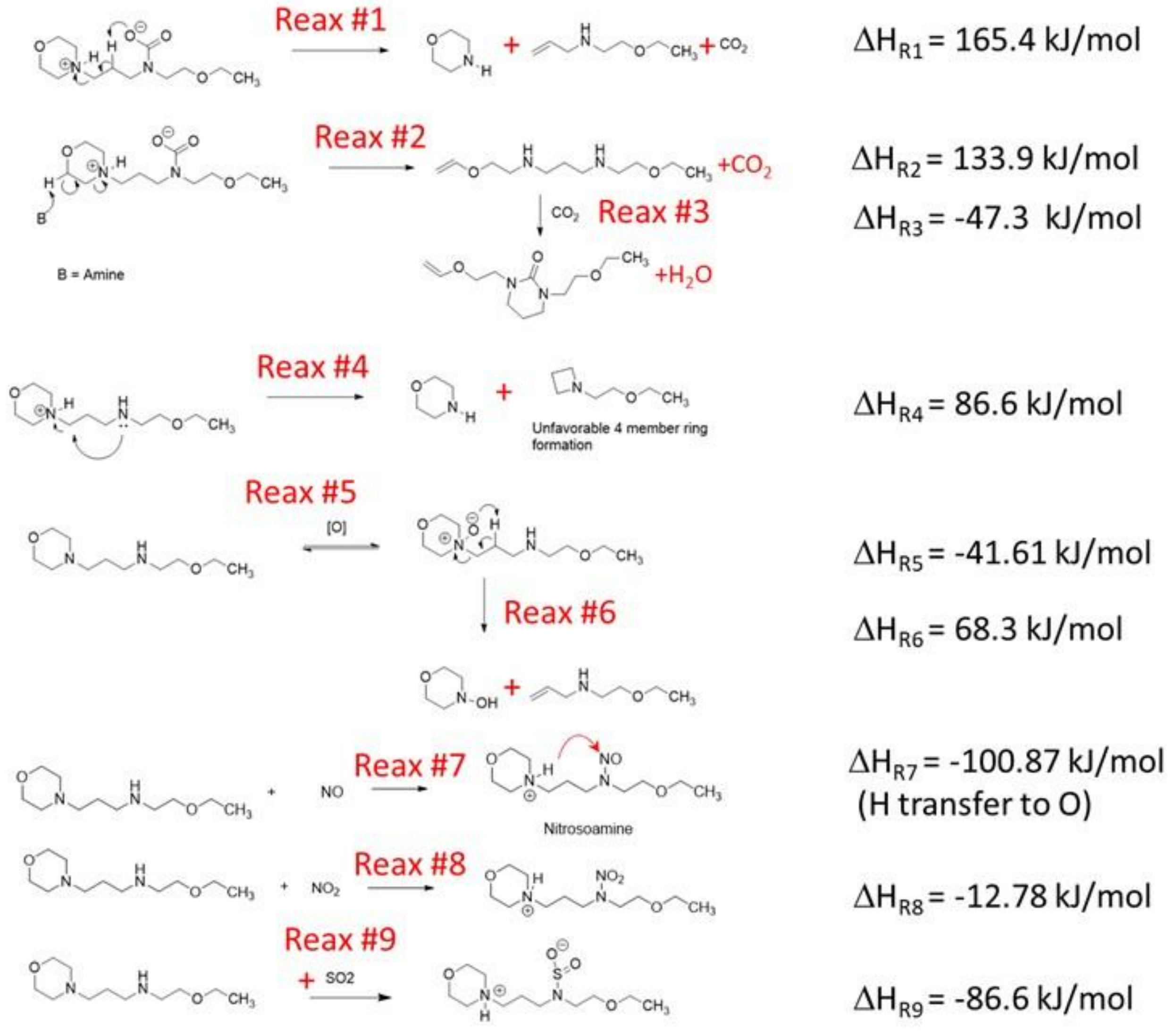
- CO_2-free MEA degraded quickly when loaded with 9 wt.% of CO_2 in the presence of steel
  - *49% lower oxidative degradation when Silcotek® packing was substituted*
- CO_2-saturated MEA exhibited 55% increase in degradation in the presence of steel
  - *Silcotek® packing showed different product speciation*
  - *Reaction suppression or reaction with silane possible*

Modeling Reactivity for All Degradations

Reaction energies of proposed mechanisms for identified chemical degradation reactions of solvents (using a dielectric model).

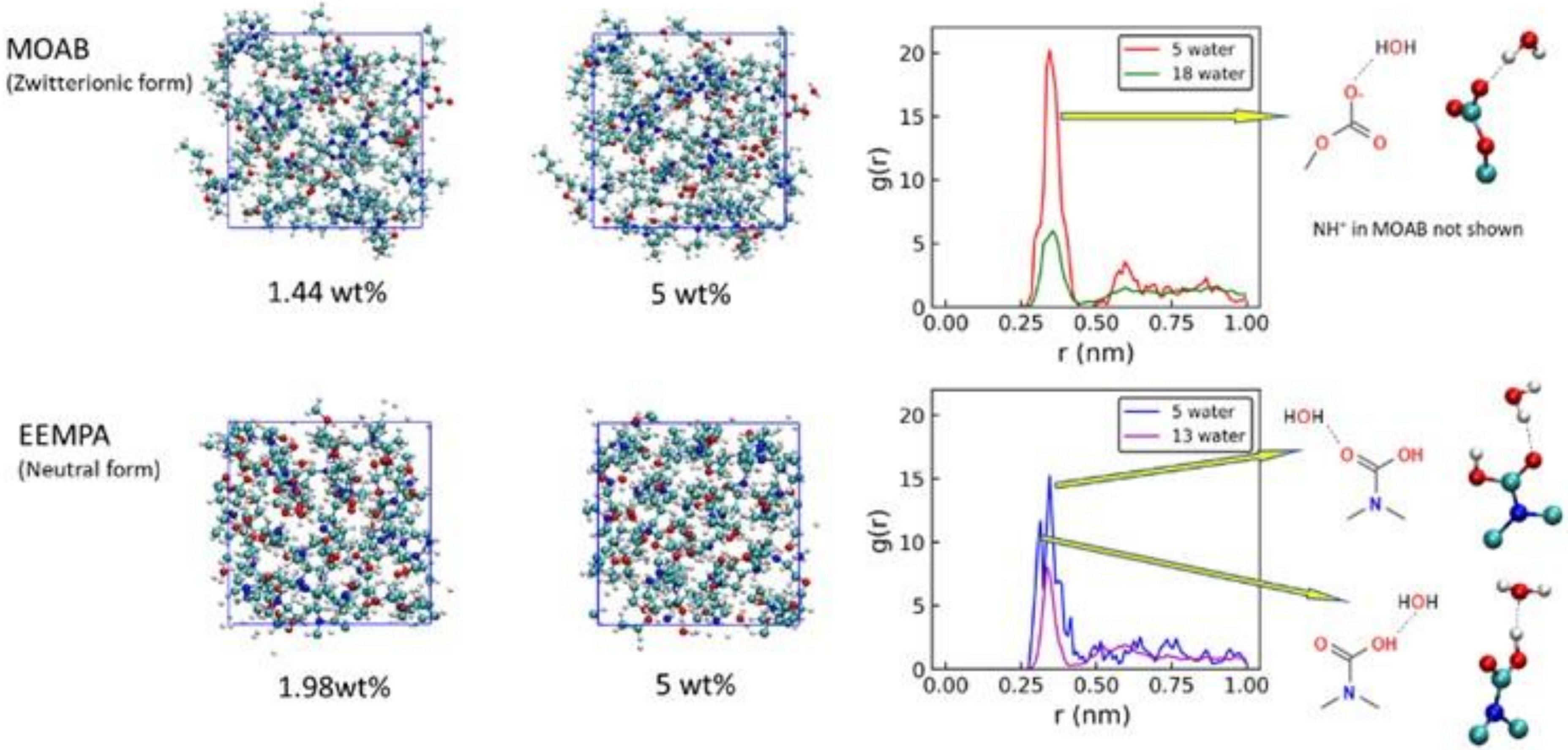
1-EEMPA is a representative solvent:

- High positive enthalpy changes implies that neat EEMPA is thermally stable, matching experimental data
- Oxidation reactions with O_2 (reactions 5 and 6), still may proceed, as the overall reaction is almost enthalpically neutral, and susceptible to become exothermic in the presence of catalysts, *i.e.* steel interfaces
- Reactions with NO and SO_2 (reactions 8 and 9) are the most reactive with solvents, again matching experimental observations of heat-stable salt (HSS) formation.



Learning Not Just *How* a Reaction Occurs, but *Why* it Occurs

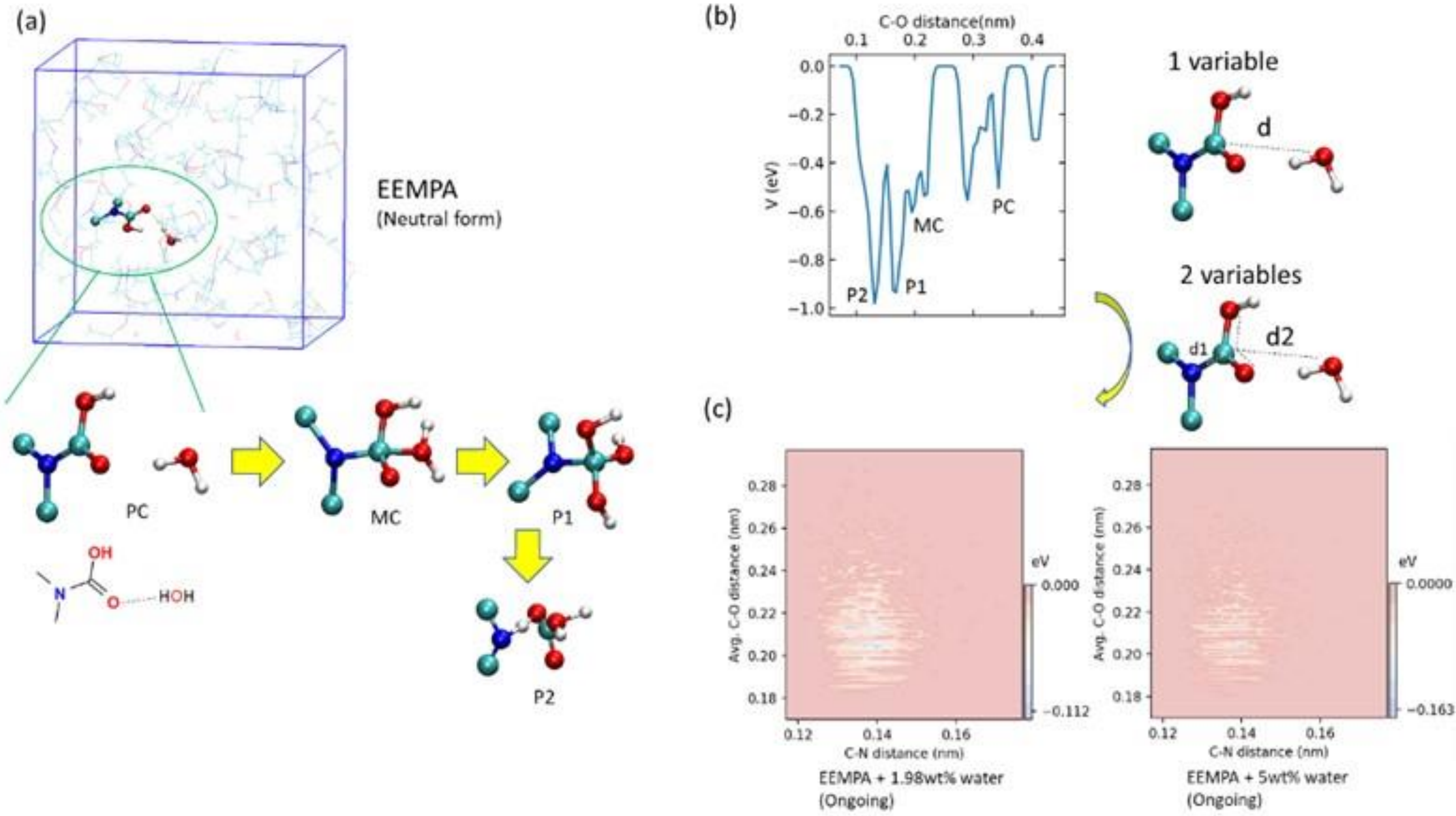
Condensed-phase calculations with with explicit solvent w/out H_2O provide a molecular picture of intermolecular interactions and insights of descriptors that guide reactivity.



- Snapshots from the simulation’s boxes of 1-BEIPADIPA-2-BOL and 2-EEMPA with two different concentration of water (~1.5-2.0 wt.% and ~5%)
- Provide the average distribution of C(CO_2) in loaded molecules and surrounding water oxygens

Building Reaction Free-Energy Landscapes

Condensed-phase calculations with w/out water allows us to identify key energy barriers and molecular descriptors accounting for collective phenomena.



- Example of hydrolysis reaction process for EEMPA identified from AIMD simulations
- C in cyan, O in red, N in blue and H in white
- Preliminary reaction free energy surface probed by (b) 1 and (c) 2 molecular descriptors

Building Reaction Free-Energy Landscapes

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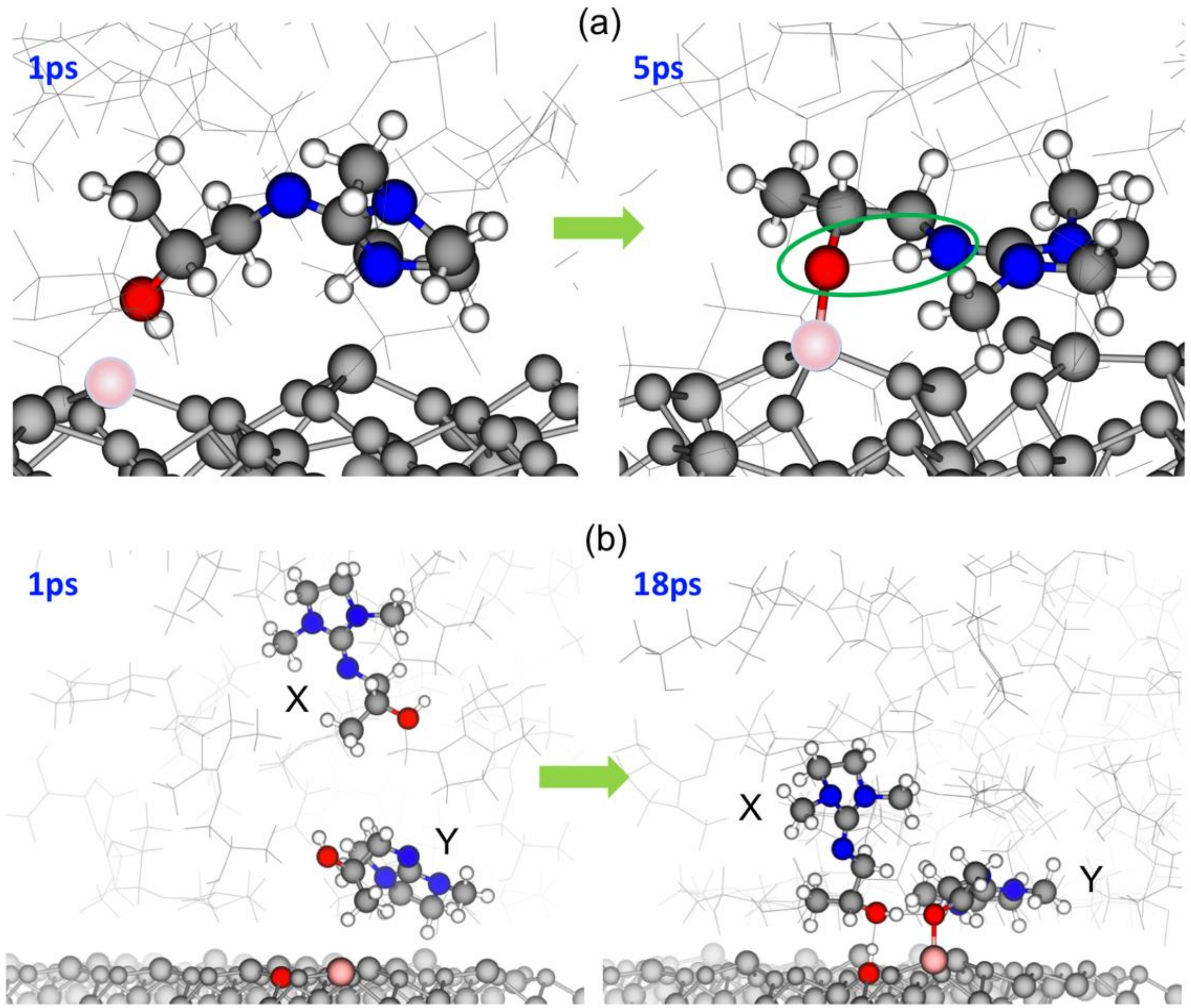
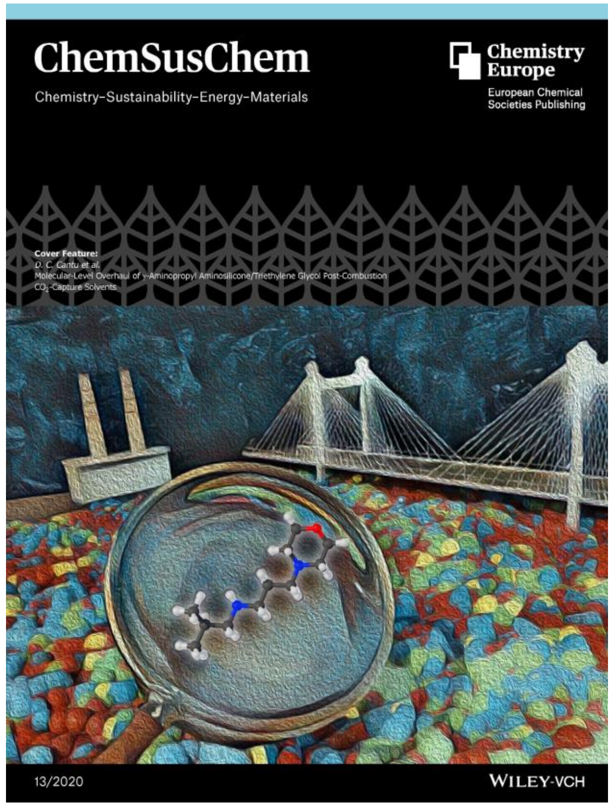


- Example of hydrolysis reaction process for EEMPA identified from AIMD simulations
- C in cyan, O in red, N in blue and H in white
- Preliminary reaction free energy surface probed by (b) 1 and (c) 2 molecular descriptors

Project Outputs

Accepted Manuscripts:

1. D. C. Cantu, D. Malhotra, M. T. Nguyen, P. K. Koech, D. Zhang, a V. A. Glezakou, R. Rousseau, J. Page, R. Zheng, R. J. Perry, D. J. Heldebrant. “Molecular-Level Overhauling of GAP/TEG Post-Combustion CO_2 Capture Solvents.” ChemSusChem., 2020, DOI: 10.1002/cssc.202000724.



ChemSusChem

Chemistry–Sustainability–Energy–Materials

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European Chemical Societies Publishing

Cover Feature:

D. C. Cantu et al.

Molecular-Level Overhaul of γ-Aminopropyl Aminosilicone/Triethylene Glycol Post-Combustion CO_2-Capture Solvents

13/2020

WILEY-VCH

Manuscripts in Process:

1. “Interfacial phenomena of water-lean solvents on carbon capture infrastructure.” This manuscript covers the interfacial phenomena and observed speciation and potential catalytic degradations of water-lean solvents on varied interfaces in Tasks 2 and 7.

Awarded United States Patents:

1. U.S. Patent No. 10,434,460, October 8, 2019, "CAPTURE AND RELEASE OF ACID GASSES USING TUNABLE ORGANIC SOLVENTS WITH AMINOPYRIDINE "
2. U.S. Patent No. 10,456,739, October 29, 2019, " CAPTURE AND RELEASE OF ACID GASSES USING TUNABLE ORGANIC SOLVENTS WITH BINDING ORGANIC LIQUIDS " .

Filed International Patents:

1. International Patent No. PCT/US2020/023153 filed March 17, 2020, “Novel Diamine Solvent System for CO_2 Capture.”

Summary Slide

- Water-lean solvents more durable than aqueous solvents for thermal & oxidative degradations
  - *Due to fundamental differences in pH, charge solvation, dielectric, and H-bonding*
- Alkanolguanidines are less robust than diamines in all degradations
- Molecular simulations are showing critical insights into reactivity and why many CO_2-loaded solvents are more prone to degradation,
  - *Primary degradations are linked to alkylcarbonate and carbamate moieties.*
  - *Hydrolysis shows an inverse correlation of enthalpy of hydrolysis and enthalpy of CO_2 binding, implying suppression through molecular refinement is possible by reducing CO_2 affinity.*
- Steel interfaces are not chemically inert to solvents, acting catalysts for degradations
  - *True for all formulations, aqueous and water-lean*
  - *Passivating steel interfaces increases solvent lifetime, enabling reduced make-up rates*
  - *Product distribution changes when steel packings are present, coated or uncoated.*
  - *Suggests other decomposition products (e.g. oxidation via NOx) could be controlled*

Future Testing

Continuing our understanding of solvent degradations for SOx and NOx.

- Apply reactive models for oxidation, nitrosation
  - *Calculate ab initio of hydrolysis and oxidation reactions of alkanol guanidine and diamine derivatives*
  - *Calculate activation energy barriers for chemical degradations with stainless-steel interfaces*
- Expand reactivity towards heat-stable salts from SO_x
  - *PSAR regeneration viable?*
    - ✓ *2-EEMPA has shown SO_x release at 130 ˚C with polydimethylsiloxane antisolvent*
- Expand reactivity towards heat-stable salts and nitrosamines from NO_x
  - *PSAR regeneration viability*
    - ✓ *2-EEMPA has shown NO release at 51˚C and NO_x release at 53˚C with polydimethylsiloxane antisolvent*
  - *Assess whether stainless-steel interfaces promote nitrosamine formation*
    - ✓ *Potential mitigation of nitrosamines for 2˚ amines (2-AMP, piperazine, EEMPA)*

Appendix

- These slides will not be discussed during the presentation, but are mandatory.

Organization Chart


Vanda Glezakou


Roger Rousseau


Manh Nguyen


Difan Zhang


Phillip Koech

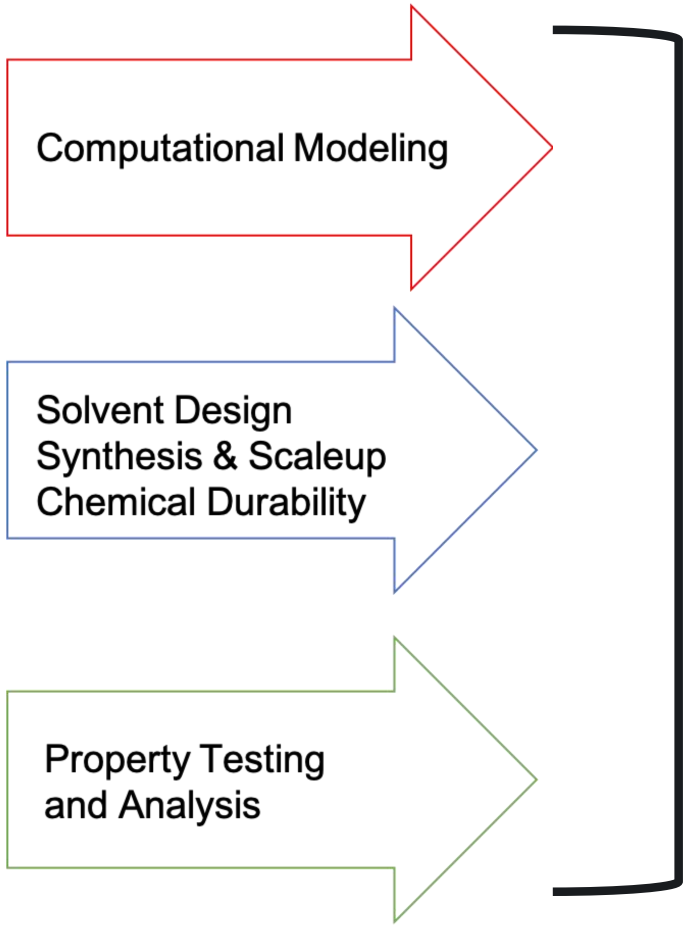

Deepika Malhotra


Kat Grubel


David Heldebrant


Richard Zheng


Andy Zwoster

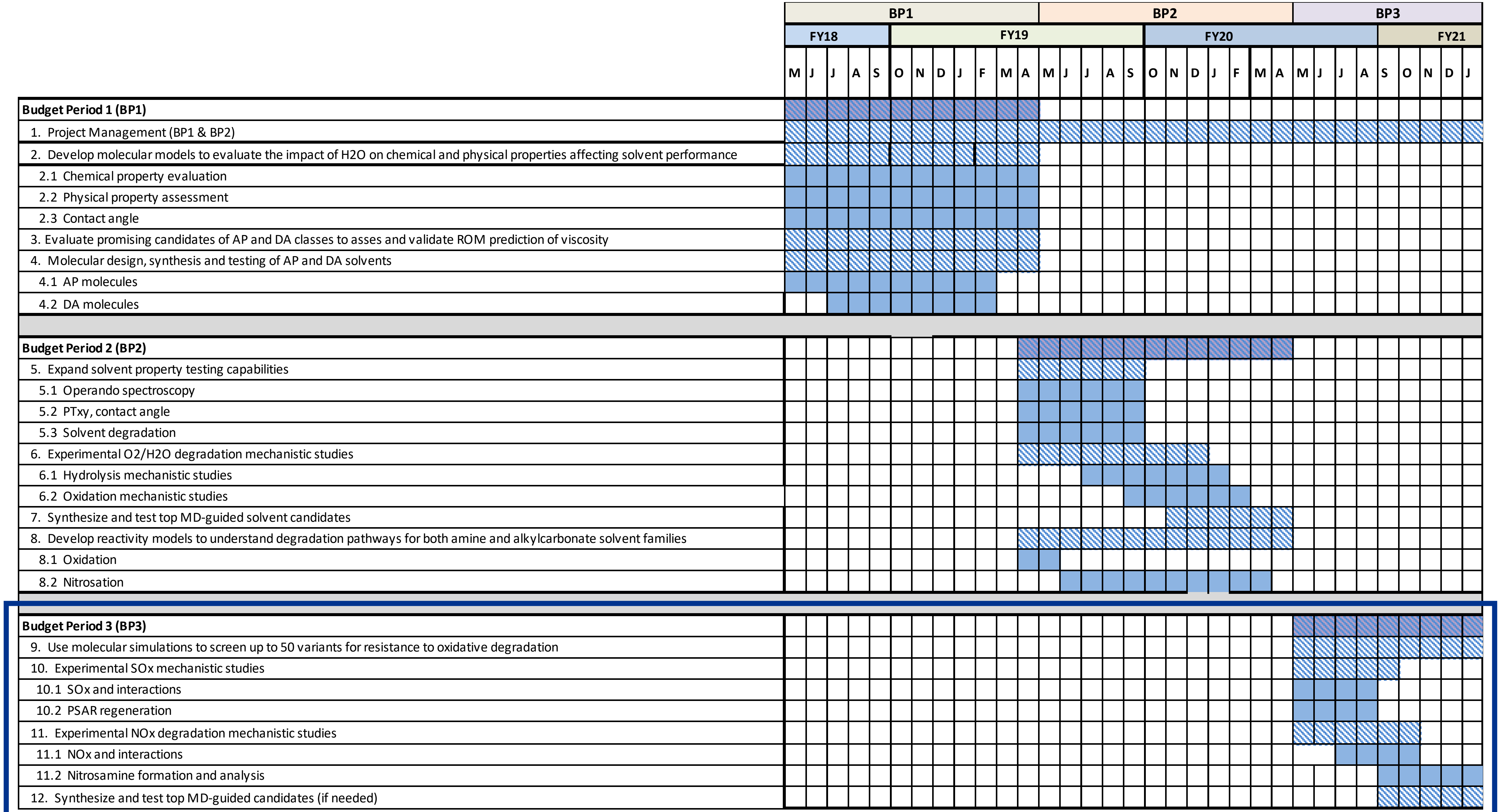

Computational Modeling

Solvent Design
Synthesis & Scaleup
Chemical Durability

Property Testing
and Analysis

PM
Andy Aurelio

Project Gantt Chart



	BP1												BP2												BP3								
	FY18					FY19												FY20											FY21				
	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J
Budget Period 1 (BP1)	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																					
1. Project Management (BP1 & BP2)	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
2. Develop molecular models to evaluate the impact of H2O on chemical and physical properties affecting solvent performance	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																					
2.1 Chemical property evaluation	■	■	■	■	■	■	■	■	■	■	■	■																					
2.2 Physical property assessment	■	■	■	■	■	■	■	■	■	■	■	■																					
2.3 Contact angle	■	■	■	■	■	■	■	■	■	■	■	■																					
3. Evaluate promising candidates of AP and DA classes to asses and validate ROM prediction of viscosity	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																					
4. Molecular design, synthesis and testing of AP and DA solvents	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																					
4.1 AP molecules	■	■	■	■	■	■	■	■	■	■																							
4.2 DA molecules			■	■	■	■	■	■	■	■																							
Budget Period 2 (BP2)												▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨									
5. Expand solvent property testing capabilities												▨	▨	▨	▨	▨	▨																
5.1 Operando spectroscopy												■	■	■	■	■	■																
5.2 PTxy, contact angle												■	■	■	■	■	■																
5.3 Solvent degradation												■	■	■	■	■	■																
6. Experimental O2/H2O degradation mechanistic studies												▨	▨	▨	▨	▨	▨	▨	▨	▨													
6.1 Hydrolysis mechanistic studies															■	■	■	■	■	■	■												
6.2 Oxidation mechanistic studies																	■	■	■	■	■	■											
7. Synthesize and test top MD-guided solvent candidates																			▨	▨	▨	▨	▨	▨									
8. Develop reactivity models to understand degradation pathways for both amine and alkylcarbonate solvent families												▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨									
8.1 Oxidation												■	■																				
8.2 Nitrosation														■	■	■	■	■	■	■	■	■	■										
Budget Period 3 (BP3)																									▨	▨	▨	▨	▨	▨	▨	▨	▨
9. Use molecular simulations to screen up to 50 variants for resistance to oxidative degradation																									▨	▨	▨	▨	▨	▨	▨	▨	▨
10. Experimental SOx mechanistic studies																									▨	▨	▨	▨	▨				
10.1 SOx and interactions																									■	■	■	■					
10.2 PSAR regeneration																									■	■	■	■					
11. Experimental NOx degradation mechanistic studies																									▨	▨	▨	▨	▨	▨			
11.1 NOx and interactions																											■	■	■	■			
11.2 Nitrosamine formation and analysis																													■	■	■	■	■
12. Synthesize and test top MD-guided candidates (if needed)																													▨	▨	▨	▨	▨