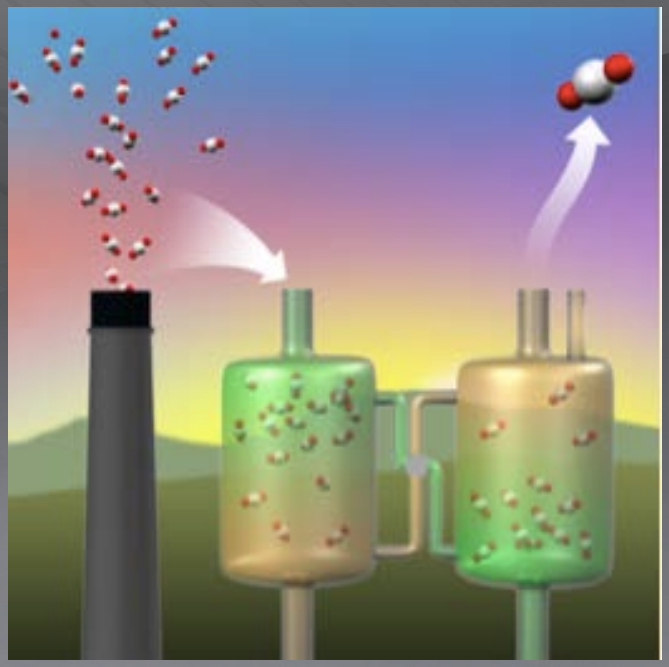

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Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration (FWP-70924)

DAVID J. HELDEBRANT

NETL CO_2 CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
AUGUST 24, 2017

U.S. DEPARTMENT OF
ENERGY

PNNL FY16 at a glance

Pacific Northwest
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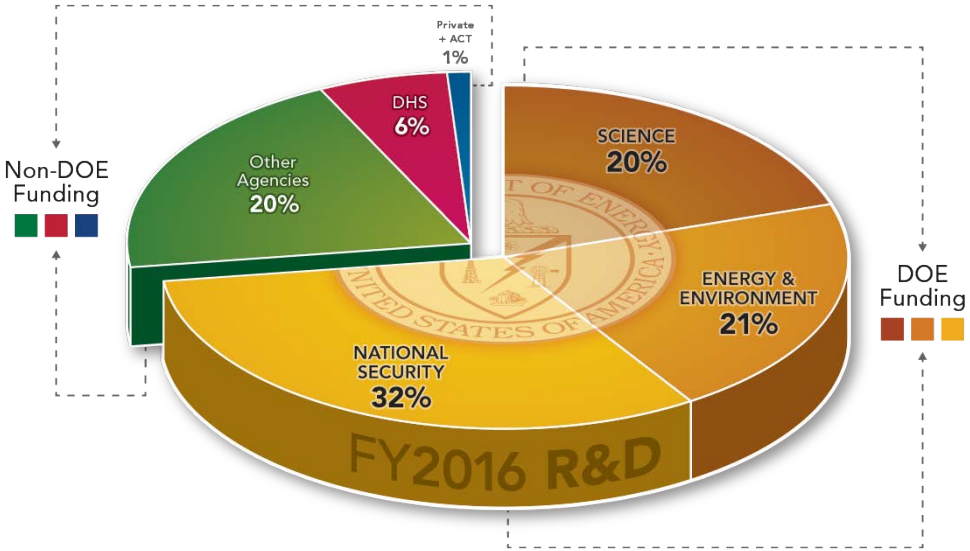
- $920.4M in R&D expenditures
- 4,400 scientists, engineers and non-technical staff
- 104 U.S. & foreign patents granted
- 2 FLC Awards, 5 R&D 100
- 1,058 peer-reviewed publications



Project Goals and Objectives

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Goals

- Comprehensive physical and thermodynamic property testing of 1-BEIPADIP-2-BOL
- Project the energetics (e.g. reboiler duty, parasitic load) and preliminary cost analysis using Aspen Plus Modelling
- Develop technology that meets DOE's cost and performance baselines for post-combustion CO_2 capture.
- Collaborations with industry, national lab and academia through the Carbon Capture Simulation for Industry Impact ($CCSI^2$) program.
- Transfer to industry

Objectives

- Scale-up low-viscosity CO_2BOL derivative (1-BEIPADIP-2-BOL).
- Perform testing and evaluation through laboratory scale to inform techno-economic assessment of solvent performance towards DOE's target capture cost of $30 per metric ton of CO_2.
- Identify data needs and collect necessary data to support future scale-up of the solvent manufacturing and capture processes.

CO_2-Binding Organic Liquids (CO_2BOLs)

"Water-lean" organic switchable ionic liquid solvent system.

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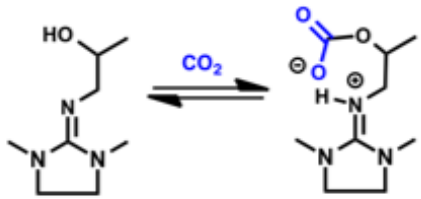
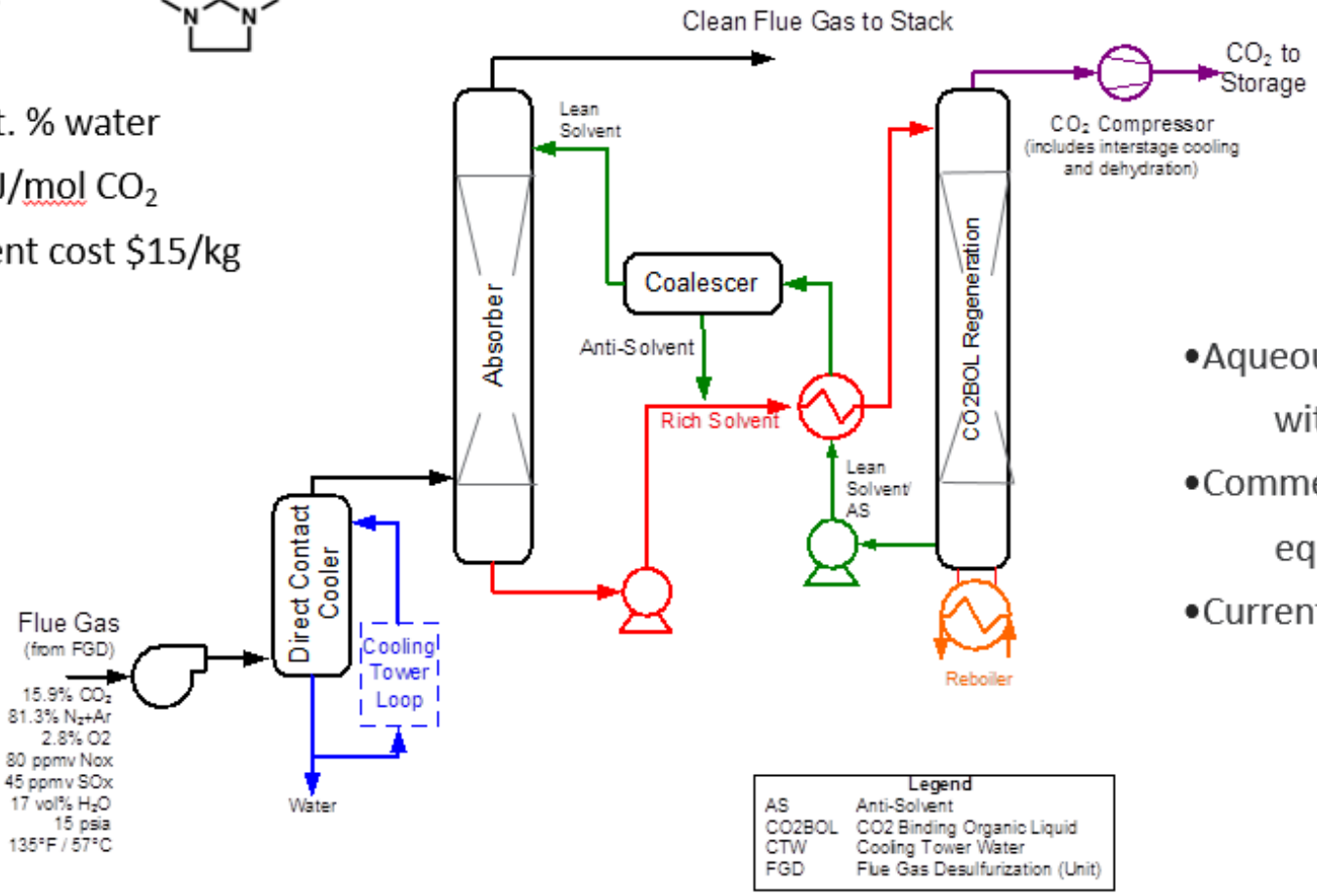


- ~5 wt. % water
- -80 kJ/mol CO_2
- Current cost $15/kg



- Aqueous amines design with added PSAR
- Commercially available equipment
- Currently un-optimized

Nature, (2005), 436, 1102; Ind. & Eng. Chem. Res. (2008); 47, 3, 539, Energy Environ. Sci., (2008), 1, 487; *RSC Adv., (2012),* 3, 566-572; *Energy Environ. Sci (2013),* 6, 2233 – 2242; *Energy Fuels, (2016), 30,* 1192–1203;

Polarity-Swing Assisted Regeneration (PSAR)

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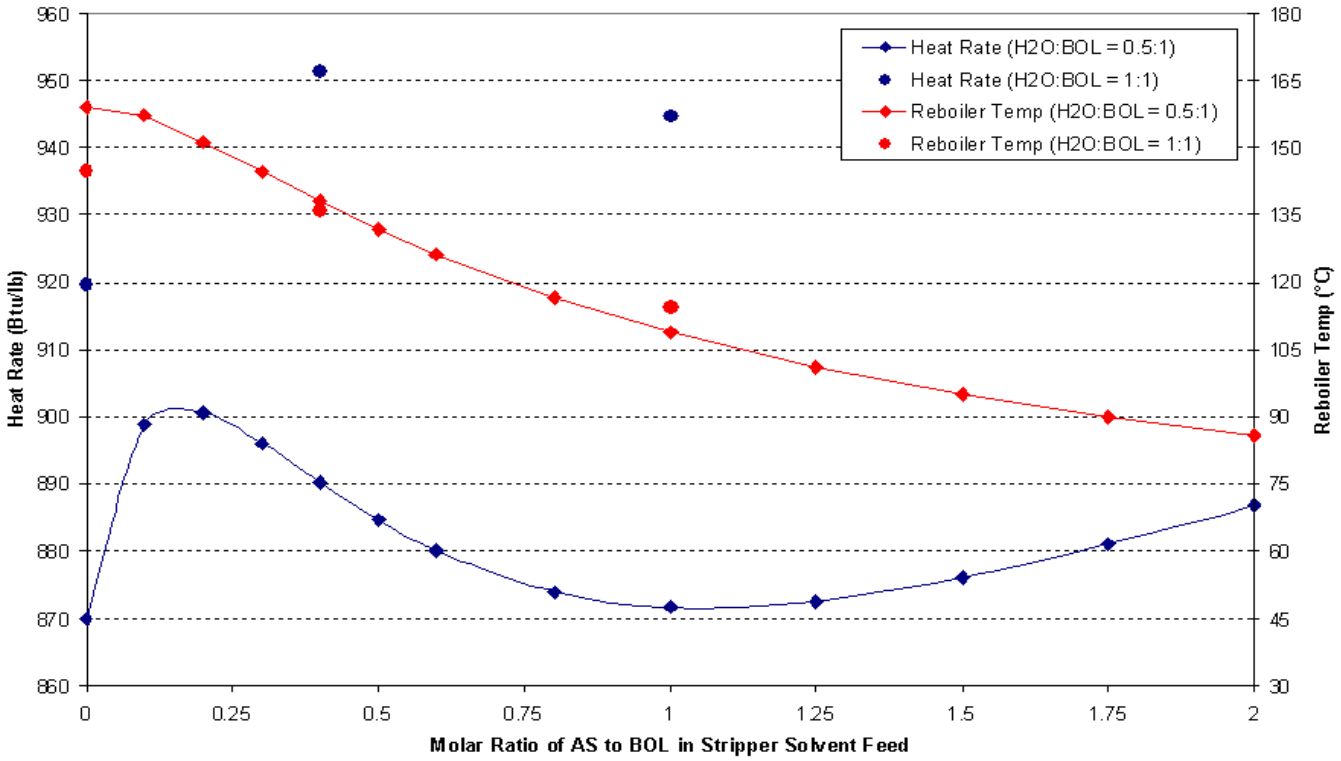
Maintains Reboiler Heat Duty but decreases T_{regen} by destabilizing the CO_2 carrier.

NETL baseline: 1520 btu/lb CO_2



- Addition of hexadecane “antisolvent” equivalents
- 72 ˚C decrease in reboiler temperature
- Reboiler heat duty remains unchanged
- Sensitive to water

Energy Environ. Sci. ***(2013)***, 6, 2233 – 2242. U.S Patent NO: 9,707,508

Polarity-Swing Assisted Regeneration (PSAR)

May Increase Net Power Output by 102 Mwe (550 Mwe baseline).

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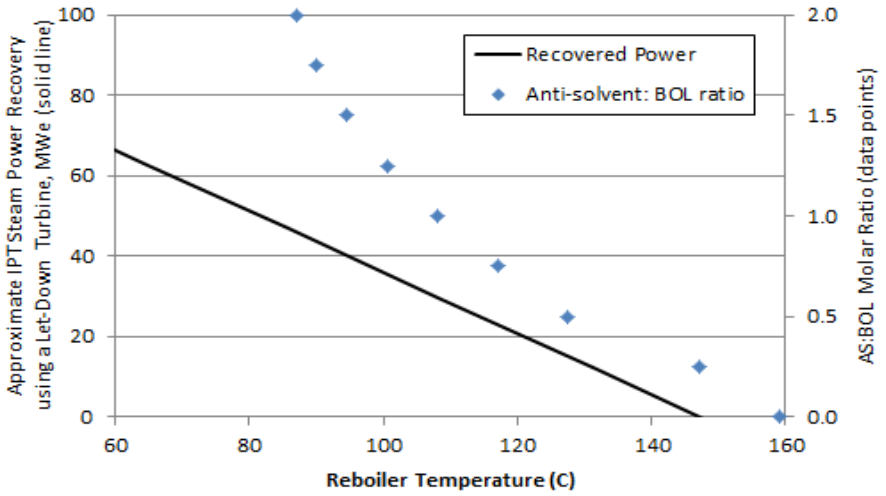

- Extract power via a let-down turbine before passing the lower temperature steam to the reboiler
- Uses more steam than directly condensing IP steam from the plant power cycle but the power generated more than compensates.

Antisolvent Loading (Molar Equivalent)	Regeneration Temperature (°C)	Net Electric Power Produced (MWe)	Parasitic Load
0	159	594	25%
0.5	132	603	23%
1	109	621	21%
2	86	637	19%
TBD[1]	65	652	17%

[1]Based on projections of upper critical solution temperature

Energy Environ. Sci. ***(2013)***, 6, 2233 – 2242, U.S Patent NO: 9,707,508.
Assumes 20 cP *rich*-solvent

CO_2BOL/PSAR Catch-22

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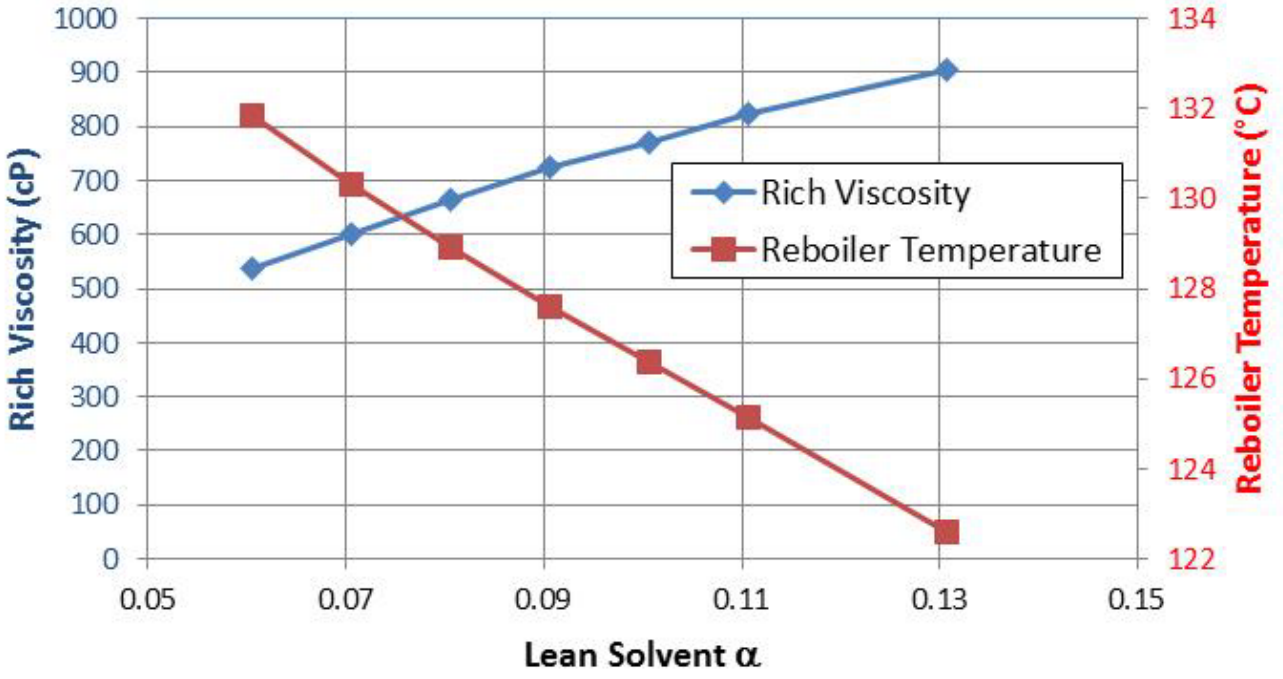
High rich-solvent viscosity negates the benefits of PSAR.



- Rich viscosity limits reboiler temperature and process performance
- Reduced viscosity allows higher α, which reduces $T_{reboiler}$ and reduces circulation rate
- Power plant efficiency benefit becomes significant when $T_{reboiler}$ < 100 ˚C

Energy Fuels, **2016**, *30* (2), pp 1192–1203

CO_2BOL Solvent Class… Where we Left Off

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Process projected to be highly energy efficient but limited by viscosity.

- 27% lower reboiler duty
- 2.1% higher net plant efficiency
- 2x's CAPEX
- Potential to meet DOE target

	NETL Case 10* – MEA capture	CO_2BOL/PSAR IPADM-2-BOL	CO_2BOL/PSAR IPADM-2-BOL 20 cP Theoretical**
Rich solvent viscosity (40 ˚C)	10	>353	20
Estimated Reboiler Duty (BTU/lb CO_2)	1520	1107	870
Net Plant Efficiency (HHV)	25.4%	27.5%	29.5%
Cost of CO_2 captured ($/tonne)	60	63	39

Energy Fuels, **2016**, *30* (2), pp 1192–1203

Viscosity Depends on Hydrogen Bonds Orientation

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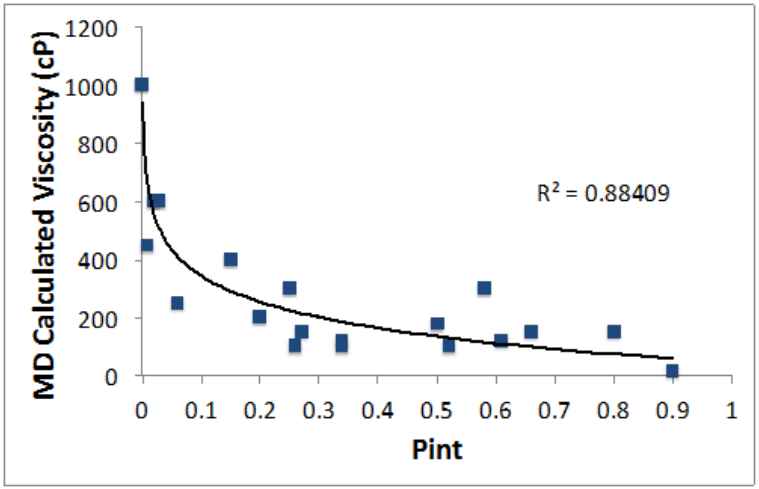
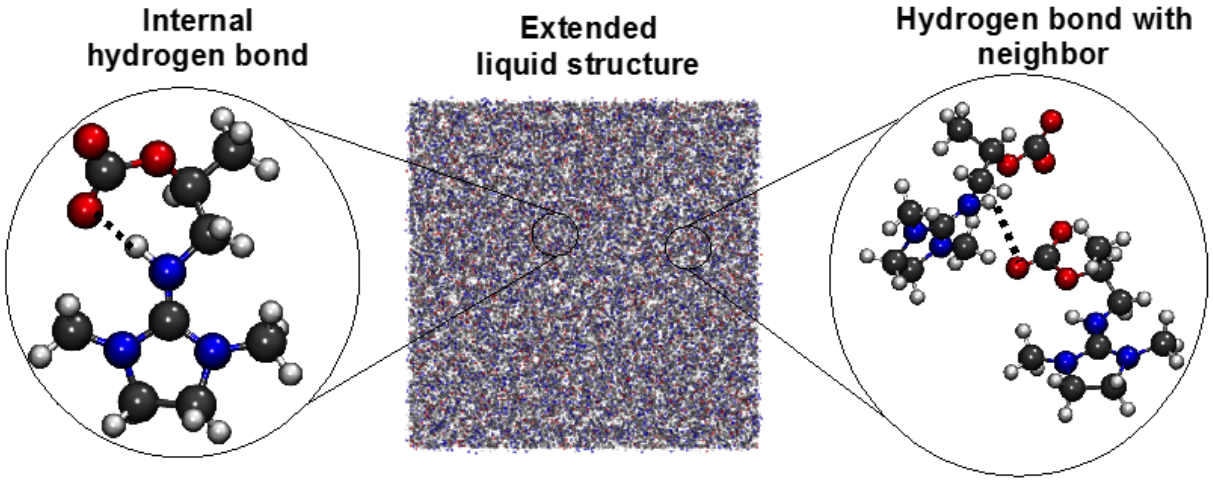
% of internal H-bonding (P_{int}) is the biggest descriptor of viscosity.

25% mol loading	100% zwitterion	
system	viscosity (cP)	% internal H-bond
EODM-2-BOL	45.5	92
IPADM-2-BOL	149.5	34
IPATFMM-2-BOL	328.5	13



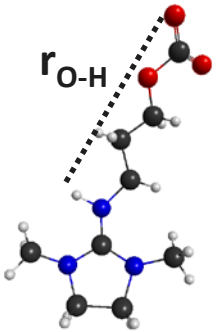


J. Phys. Chem. Lett., 2016, 7, pp 1646–1652

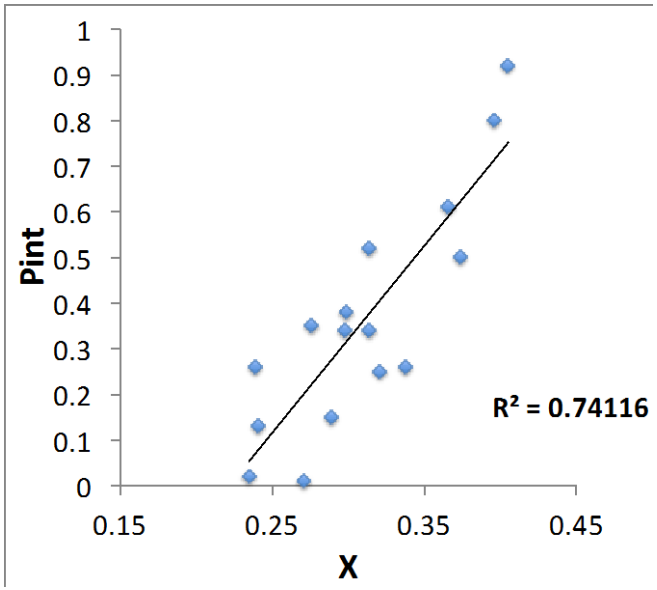
P_{int} From an Optimized Structure

Viscosity can be predicted without time intensive synthesis or modeling.

- If $r_{O-H} > 2.0$ Å, then $P_{int} = 0.001$

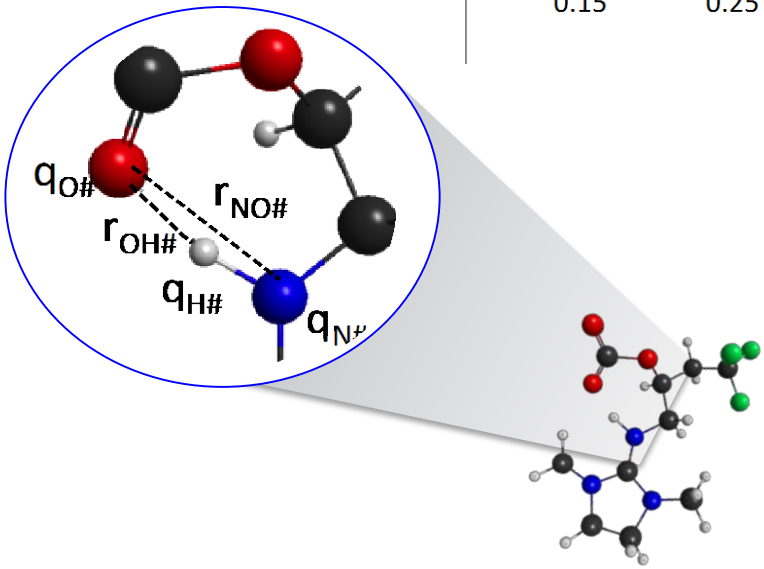


- If $r_{O-H} < 2.0$ Å, then
- Difference between electrostatic repulsion (NO) and attraction (OH)



$$P_{int} = c_1 X + c_2$$

$$X = \frac{q_N q_O}{r_{NO}} - \frac{q_O q_H}{r_{OH}}$$



J. Phys. Chem. Lett., 2016, 7, pp 1646–1652

Designing 3rd Generation CO_2BOLs

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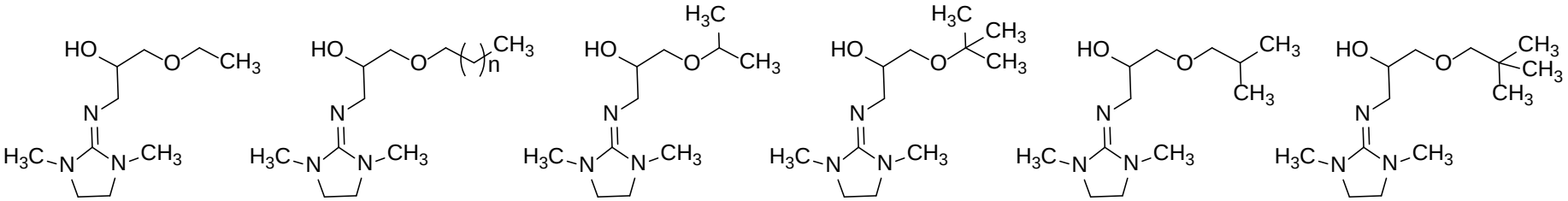
500 Candidate molecules down-selected by the reduced model.



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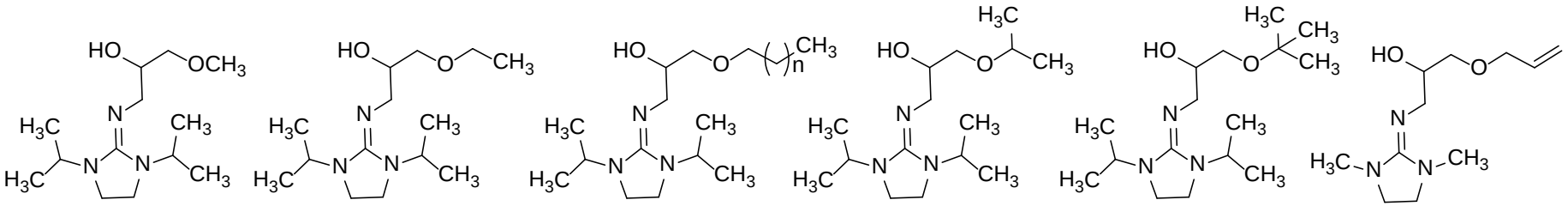

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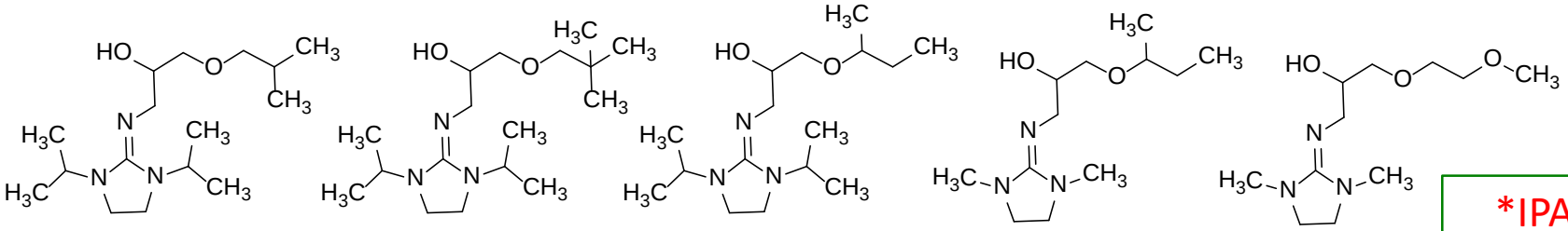

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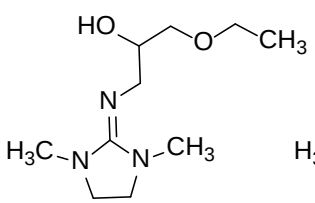

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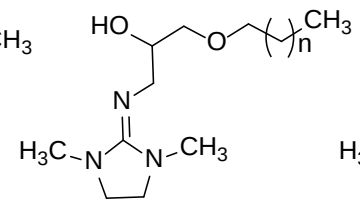

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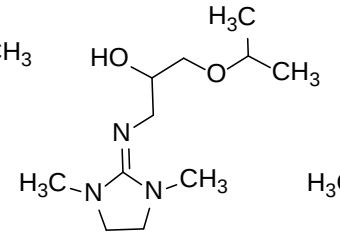

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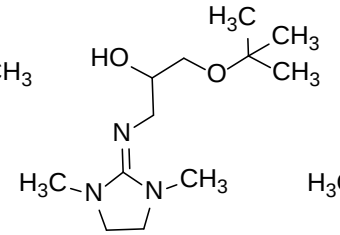

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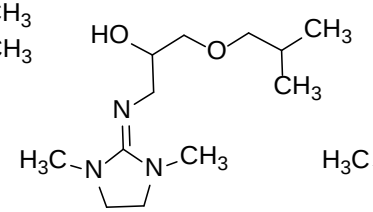

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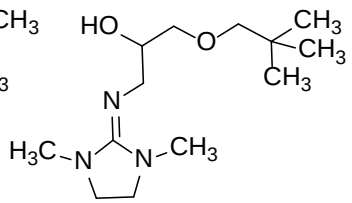

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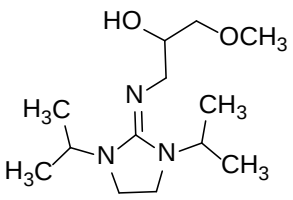

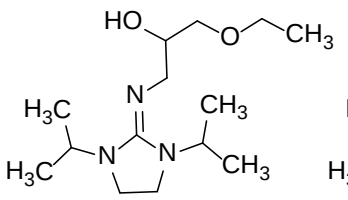

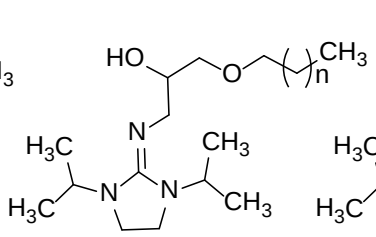

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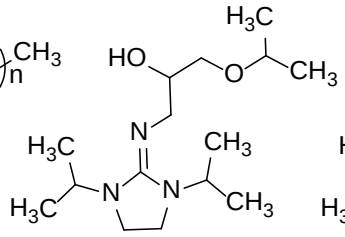

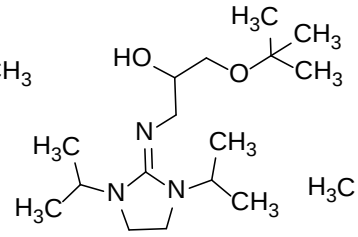

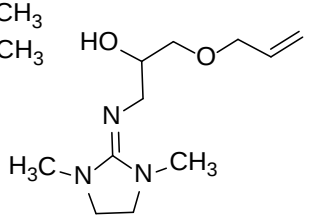

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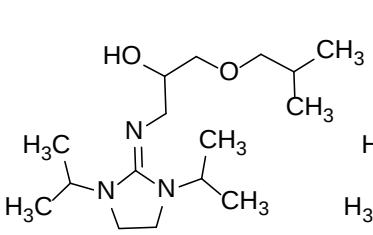

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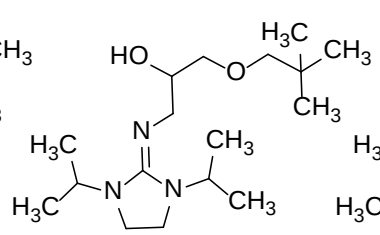

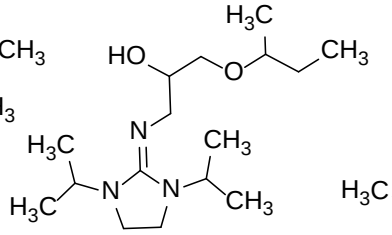

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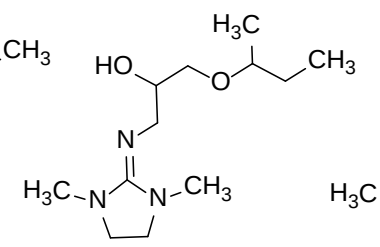

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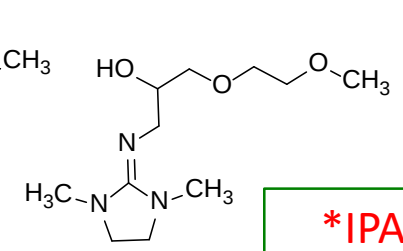

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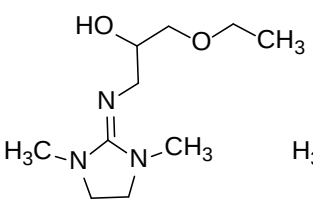

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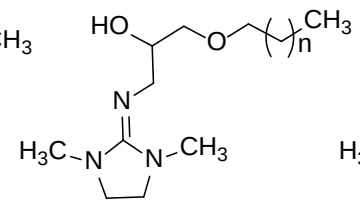

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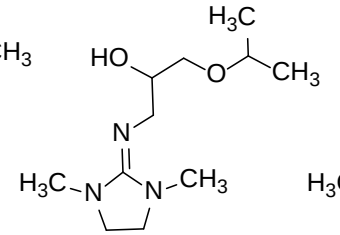

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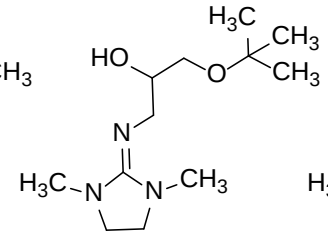

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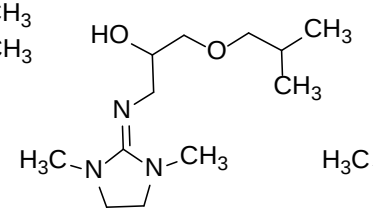

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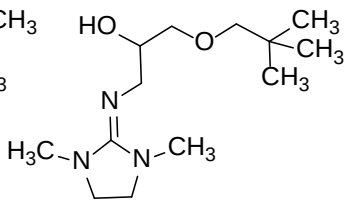

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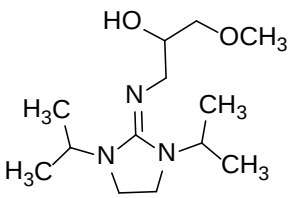

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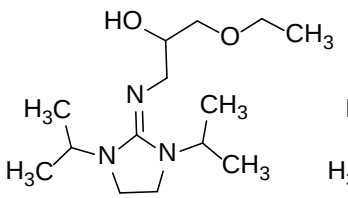

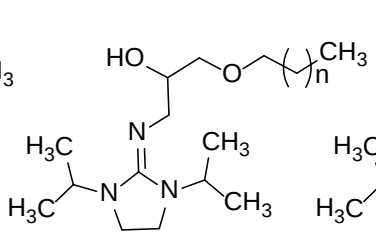

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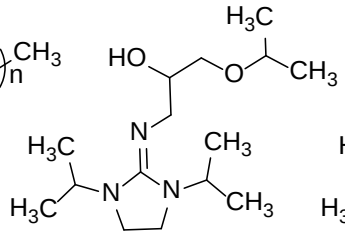

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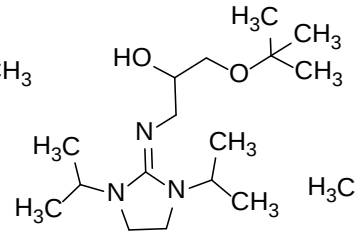

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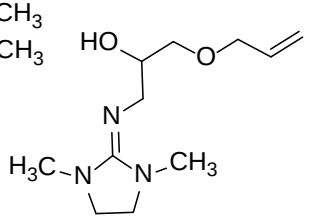

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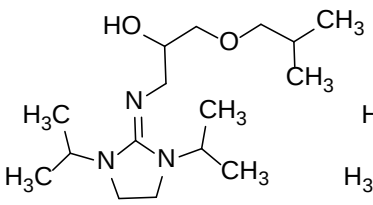

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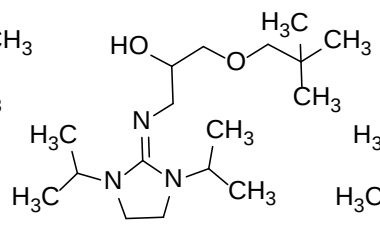

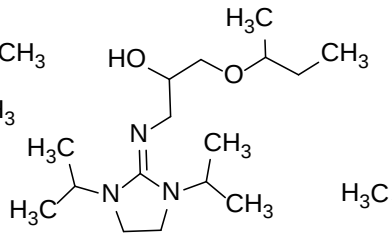

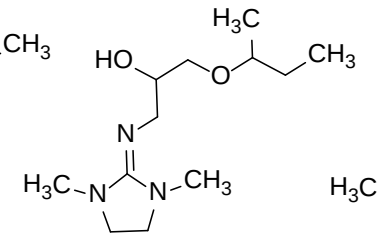

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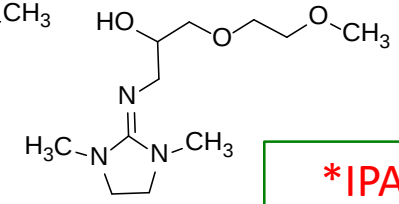

198

*IPADM-2-BOL = 150 cP

Designing 3rd Generation CO_2BOLs

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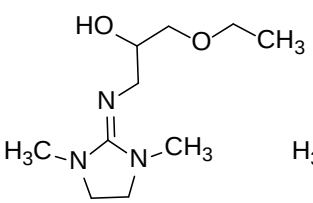
500 Candidate molecules down-selected by the reduced model.



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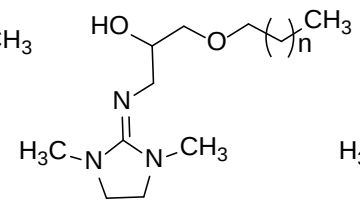

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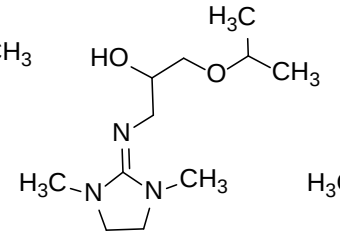
94,139



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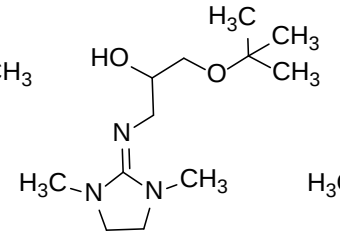

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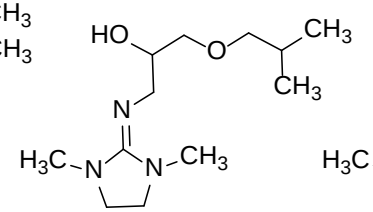

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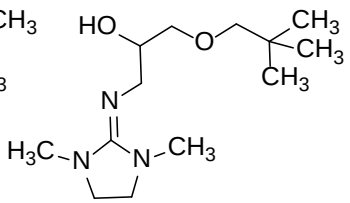

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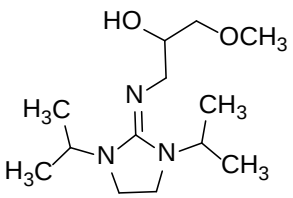

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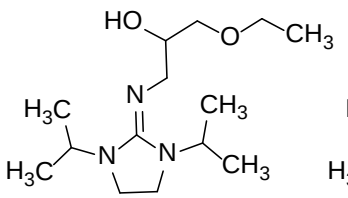

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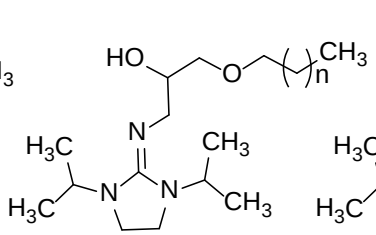

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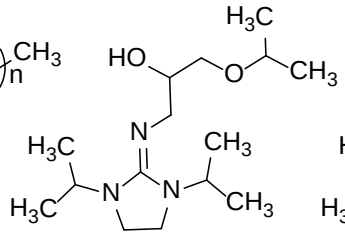

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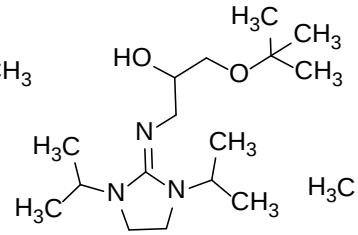

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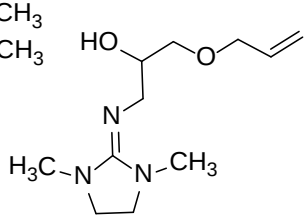

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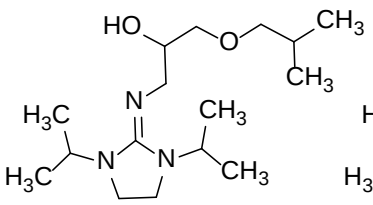

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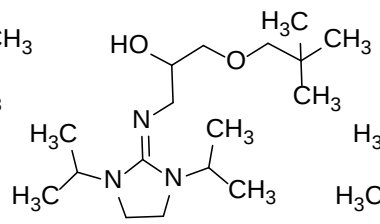

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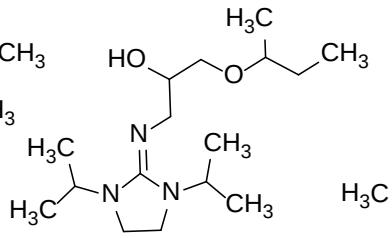

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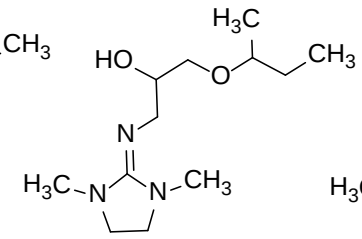

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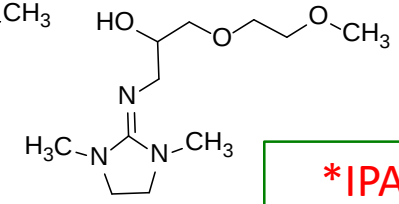

198

*IPADM-2-BOL = 150 cP

High P_{int} Favors Neutral Alkylcarbonic Acid

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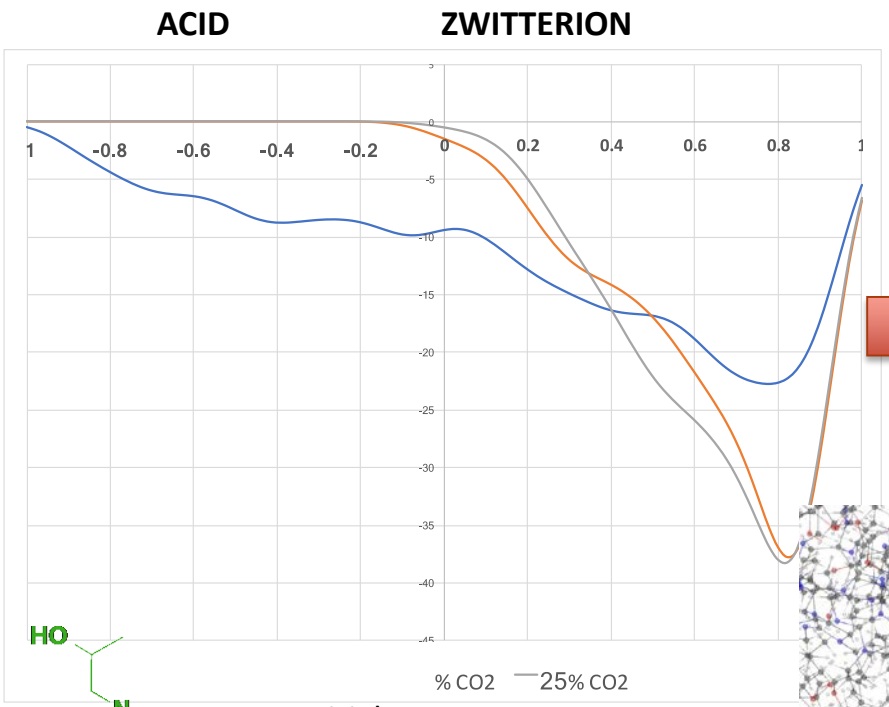
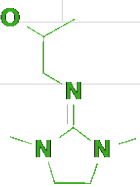
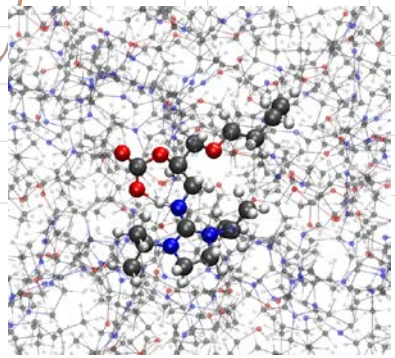
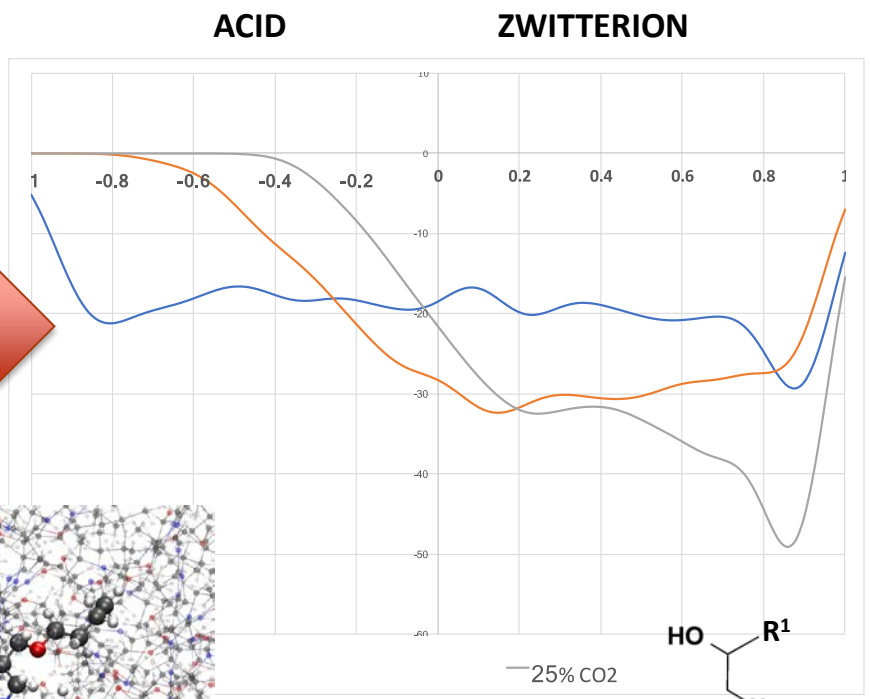
Internal H-bonding begins to favor "neutral" forms of capture, reducing the concentration of ions in solution.



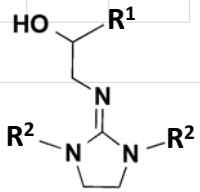


Initial





After 10 ps



Malhotra *et al., Manuscript In Preparation.*

Predicted Solvent Structure of Final Derivatives

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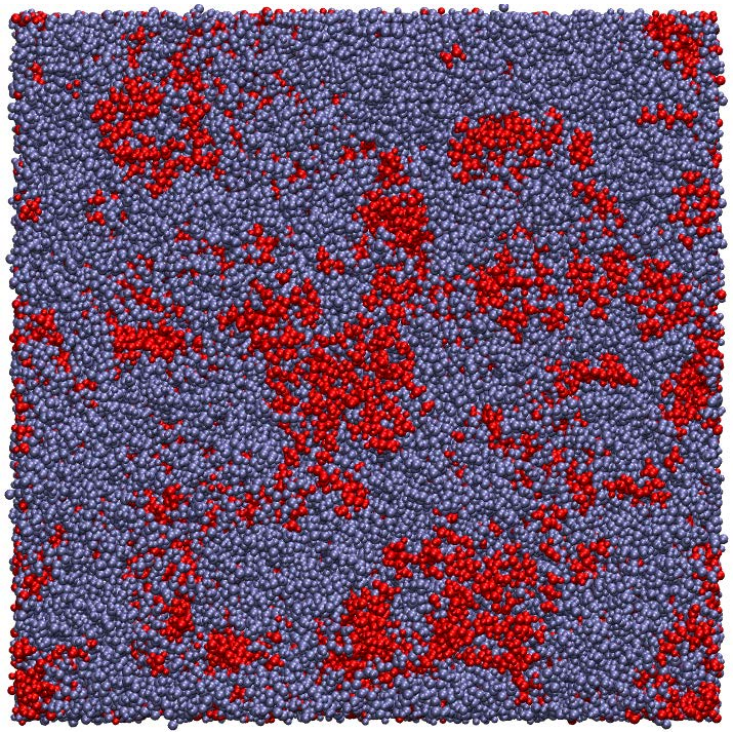
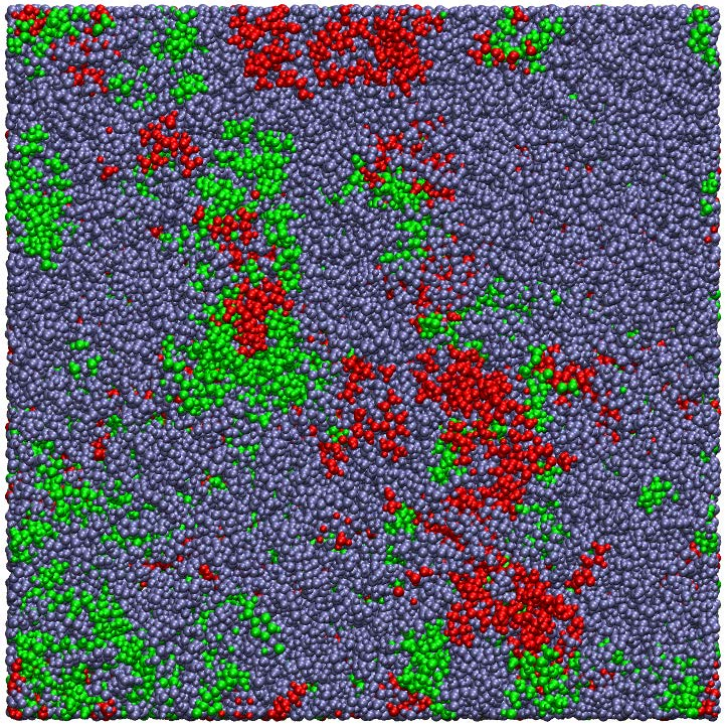
Solvents retain heterogeneous structure with reduced ionicity, still allowing for PSAR.



25% CO_2 loading, all Zwitterion



25% CO_2 loading, 1:1 acid:Zwitterion

Malhotra *et al.*, *Manuscript In Preparation.*

High P_{int} and Neutral Capture Combined

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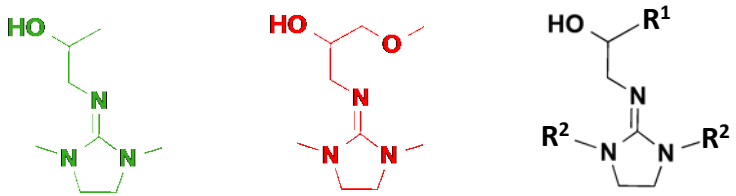
New derivatives are 98% lower in viscosity.



IPADM-2-BOL @ 40 mol% CO_2
MEIPADM-2-BOL @ 35 mol% CO_2
BEIPADIPA-2-BOL @ 42 mol% CO_2

CO_2BOL Generations

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High P_{int} and Neutral Capture Combined

Pacific Northwest NATIONAL LABORATORY
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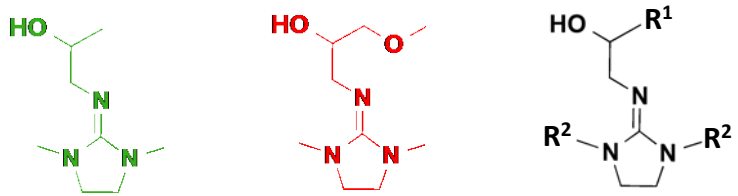
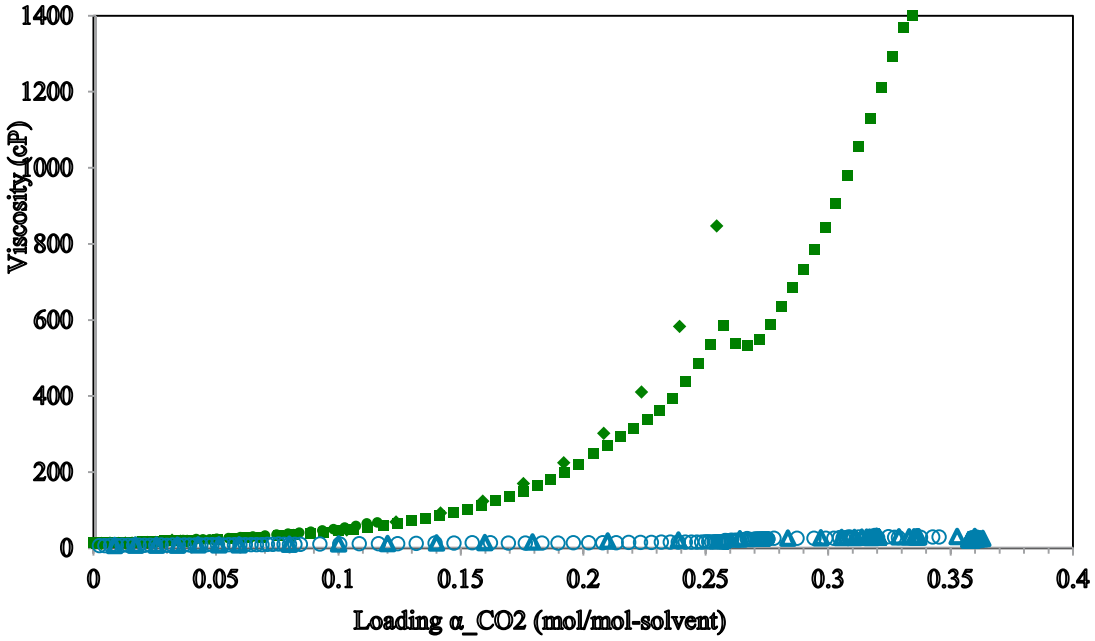
New derivatives are 98% lower in viscosity.



IPADM-2-BOL @ 40 mol% CO_2
MEIPADM-2-BOL @ 35 mol% CO_2
BEIPADIPA-2-BOL @ 42 mol% CO_2



CO_2BOL Generations

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3rd Generation Derivative Properties

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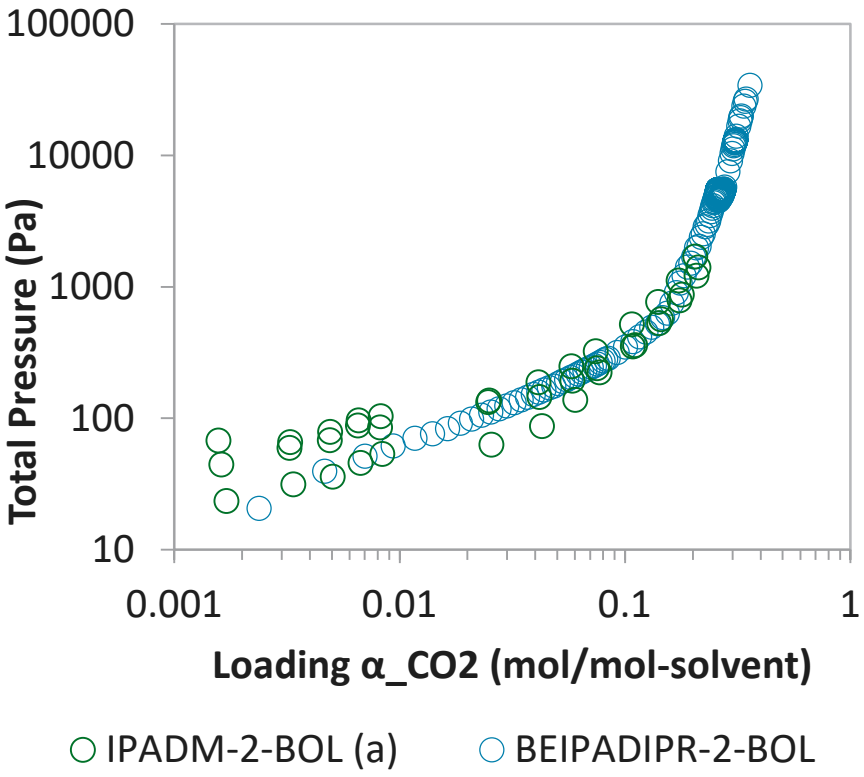
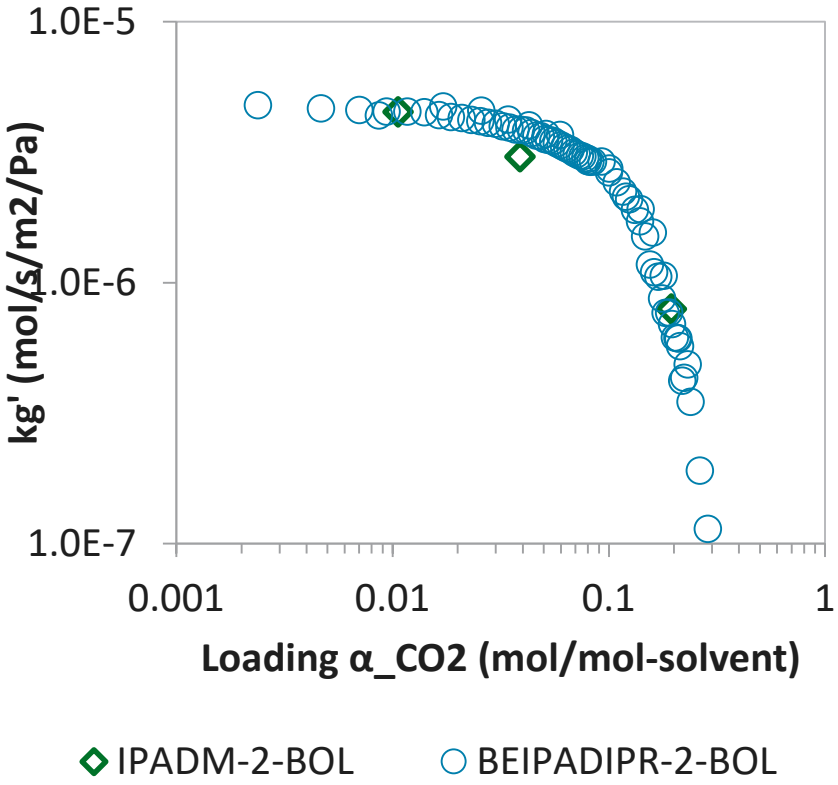
PVT testing shows physical and thermodynamic properties are retained.





- Comparable P* at 40 ˚C to IPADM-2-BOL at 40 ˚C
- Identical mass transfer of CO_2 (*kg'*) to IPADM-2-BOL at 40 ˚C

Malhotra *et al., Manuscript In Preparation.*

CO_2BOL Solvent Class… Where We Are Now.

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Revised formulation is projected to be close in performance to theoretical case.

Potential:

- 40% lower reboiler duty
- 4% higher net plant efficiency
- Meet DOE's $40/tonne metric

	NETL Case 10* – MEA capture	CO_2BOL/PSAR IPADM-2-BOL	CO_2BOL/PSAR IPADM-2-BOL 20 cP Theoretical**	CO_2BOL/PSAR BEIPADIP-2-BOL
Rich solvent viscosity (40 ˚C)	10	>353	20	36
Estimated Reboiler Duty (BTU/lb CO_2)	1520	1107	870	TBD
Net Plant Efficiency (HHV)	25.4%	27.5%	29.5%	TBD
Cost of CO_2 captured ($/tonne)	60	63	39	TBD

Whyatt *et al., Manuscript In Preparation.*

CO_2BOL Solvent Class… Where We Are Now.

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CO_2BOLs/PSAR have a higher percentage of theoretical minimum work than aqueous amines.

$$W_{eq} = W_{heat} + W_{pump} + W_{comp} \quad *$$

$$W_{heat} = \eta_{stm-tb}\left(\frac{T_{stm,sat} - T_{sink}}{T_{stm,sat}}\right) Q_{reb} \qquad W_{pump} = \frac{\dot{V}_{rich}(P_{strp} - 1\ bar)}{\eta_p}$$

$$W_{comp}\left(\frac{kJ}{mol\ CO_2}\right) = 15.3 - 4.6 lnP_{in} + 0.81(lnP_{in})^2 - 0.24(lnP_{in})^3 + 0.03(lnP_{in})^4$$

$$1\ bar \leq P_{in} \leq 149\ bar$$

2nd gen amines =~36 kJ/mol	Theoretical Minimum Work*	Recreated NETL Case 10 MEA capture[1]	CO_2BOL/PSAR IPADM-2-BOL 356 cP[1]	CO_2BOL/PSAR IPADM-2-BOL 20 cP Theoretical[1]**	CO_2BOL/PSAR BEIPADIP-2-BOL 36 cP
RAW (kJ/mol CO_2)	18.2	44.1	35.6	27.4	TBD
% minimum	100%	41.3%	51.1%	66.4%	TBD

1. *Energy Fuels,* (2016), 30, 1192–1203. *Energy Environ. Sci.,* (2013), 6, 2233. CO_2BOL cases include 13 MW refrigeration duty.
*Lin, Y. J., Doctoral dissertation, U. T. Austin, 2016. ** Theoretical minimum, not experimentally observed.

Project Objectives and Major Tasks

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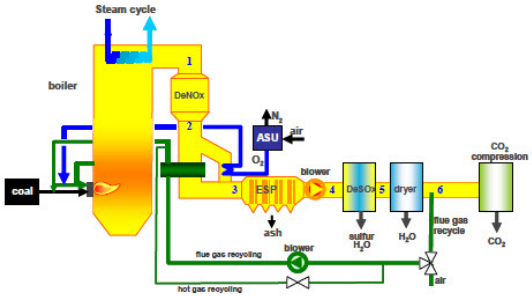
Funding: $2,792,000 / 30 months

Solvent Scale-up

Parametric testing: O_2, SO_x, NO_x, H_2O

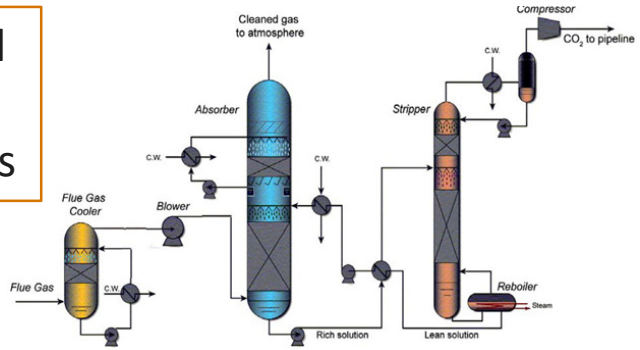


Kinetic Testing

Techno-economic Assessment

aspentech

Absorber and Stripper Configurations



Industry Handoff

DOCCSS Solvent Program Plan

Pacific Northwest NATIONAL LABORATORY

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7/17/2017 – 12/31/2019

	FY17				FY18				FY19			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1. Project Management												
2. Solvent Physical Property Measurements												
3. Solvent Synthesis												
4. Initial Techno-Economic Projections												
5. Laboratory Continuous Flow System Redesign, Retrofitting and Testing												
6. Initial CCSI2 Engagement												
7. Initial Industry Outreach												
8. Solvent Durability Measurements												
9. Laboratory Continuous Flow System Testing												
10. Final Techno-economic Projections												
11. Data Needs for Future Process Scale-Up												
12. Final CCSI2 Engagement												
13. Final Industry Outreach												

Industry Partnering Focus

CCSI-2 Partnering Opportunities

Acknowledgements

U.S. DEPARTMENT OF ENERGY

NETL

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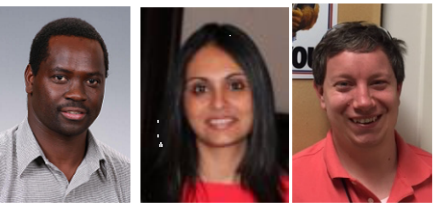
PNNL Team

Solvent Design
Chemical Durability
Synthesis & Scaleup

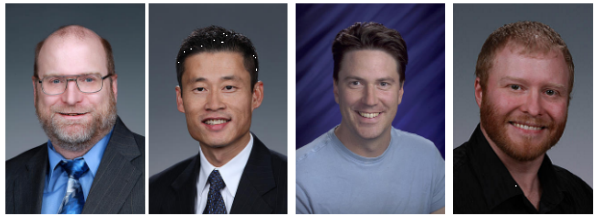


Dr. Phillip Koech
Dr. Deepika Malhotra
Dr. Jordan Page

Advisory Computational Modeling

Dr. Vanda Glezakou
Dr. Roger Rousseau

Parametric Materials Testing & Analysis



Greg Whyatt
Dr. Feng Zheng
Andy Zwoster
Dr. David Heldebrant

Process Modeling Performance Projections

Mark Bearden
Charles Freeman

Collaborators

Lawrence Livermore National Laboratory

CCSI^2 Carbon Capture Simulation for Industry Impact

FLUOR®

Dr. Josh Stolaroff

Dr. Michael Matuszewski

Dr. Paul M. Mathias