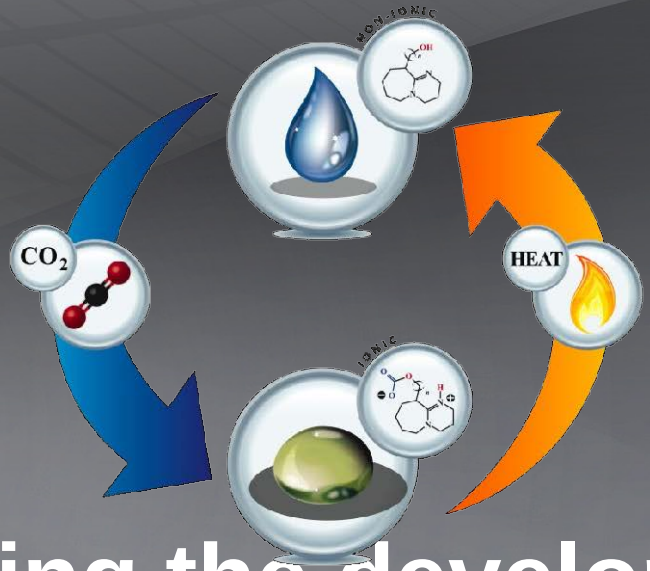


Accelerating the development of transformational solvent systems for CO_2 separations

FWP 65872

DAVID J. HELDEBRANT

NETL CO_2 CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
AUGUST 11, 2016

PNNL at a Glance

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

FY15:
$955 MILLION
in R&D expenditures

FY15:
4,400 STAFF

98
R&D 100 AWARDS

81
Tech transfer AWARDS

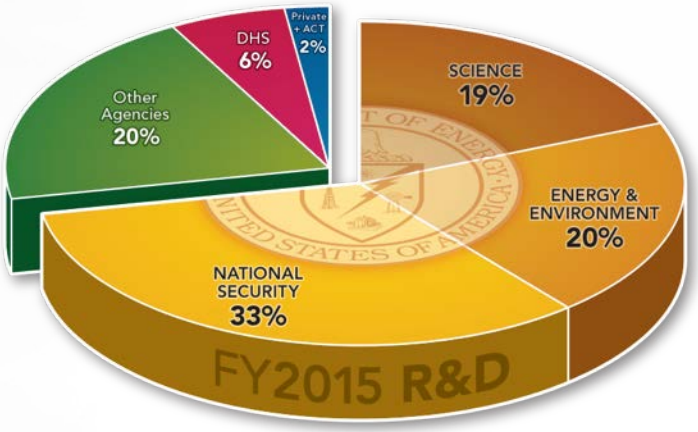
Intellectual property and startups

Average
ONE
INVENTION
per day

Average
ONE
PATENT
per week

822
LICENSES
since 1970s

170+
BUSINESSES
started with
PNNL IP
or executives



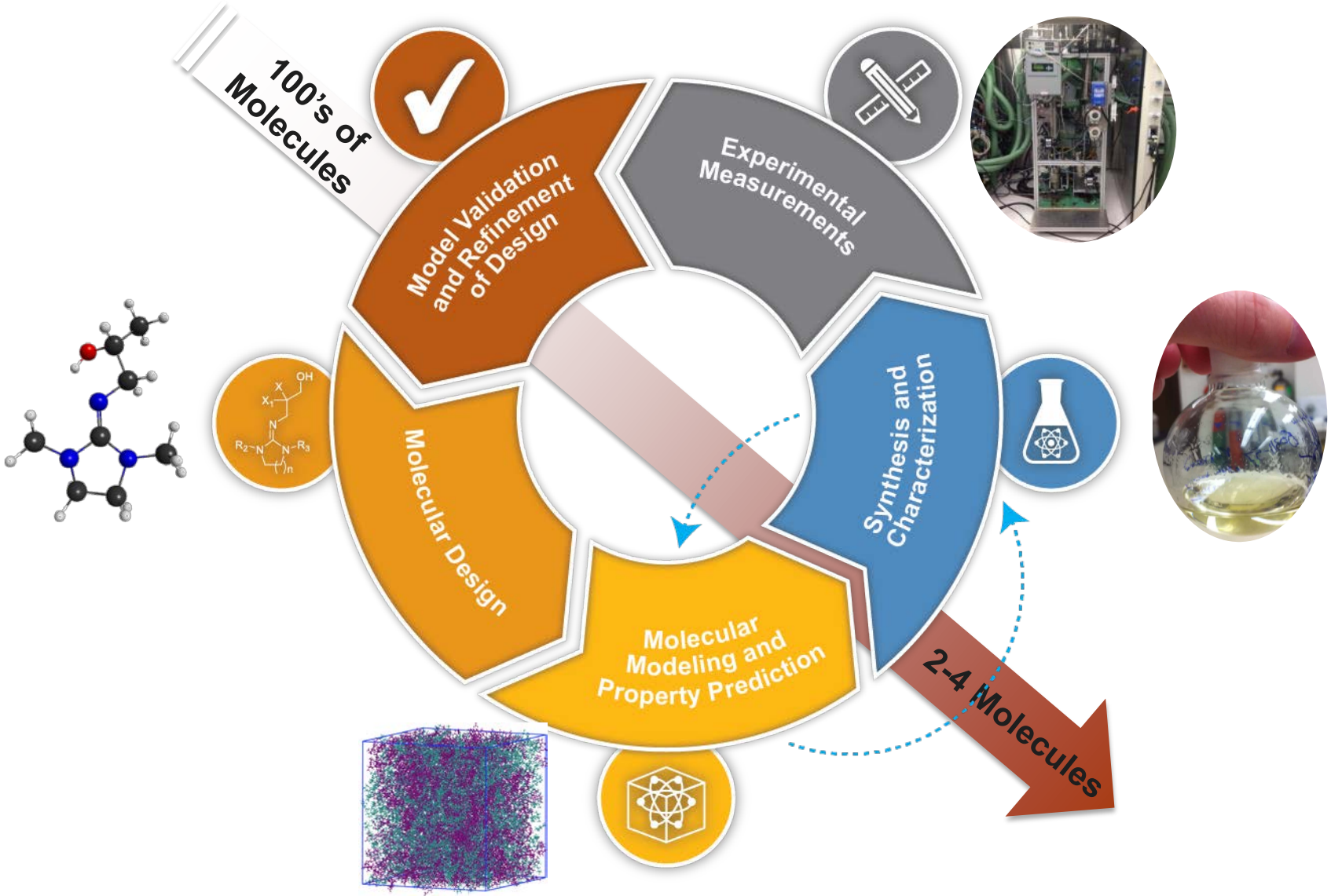
U.S. DEPARTMENT OF
ENERGY

Overview: Integrating Molecular Design, Synthesis & Testing For Multiple Platforms

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

***Aiding DOE's transformational solvent portfolio address the grand challenge of viscosity**



Project Goals and Objectives

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Objective

- Enable advanced solvent designs for all water-lean solvents up DOE's TRL readiness scale to enable large scale testing and deployment by year 2030.

Goals

- Develop a reduced order viscosity model that can predict key solvent physical and thermodynamic properties
- Down-select hundreds of candidate molecules to 2-4 viable derivatives
- Design testing devices for expedited testing of candidate solvents
- Collect necessary additional thermodynamic and kinetic data to validate models
- Partner with technology owners to advance the field of water-lean solvents

Project Schedule and Major Tasks

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Funding: $2,561,000 / 24 months

May 2014

May 2016

Fundamental Science

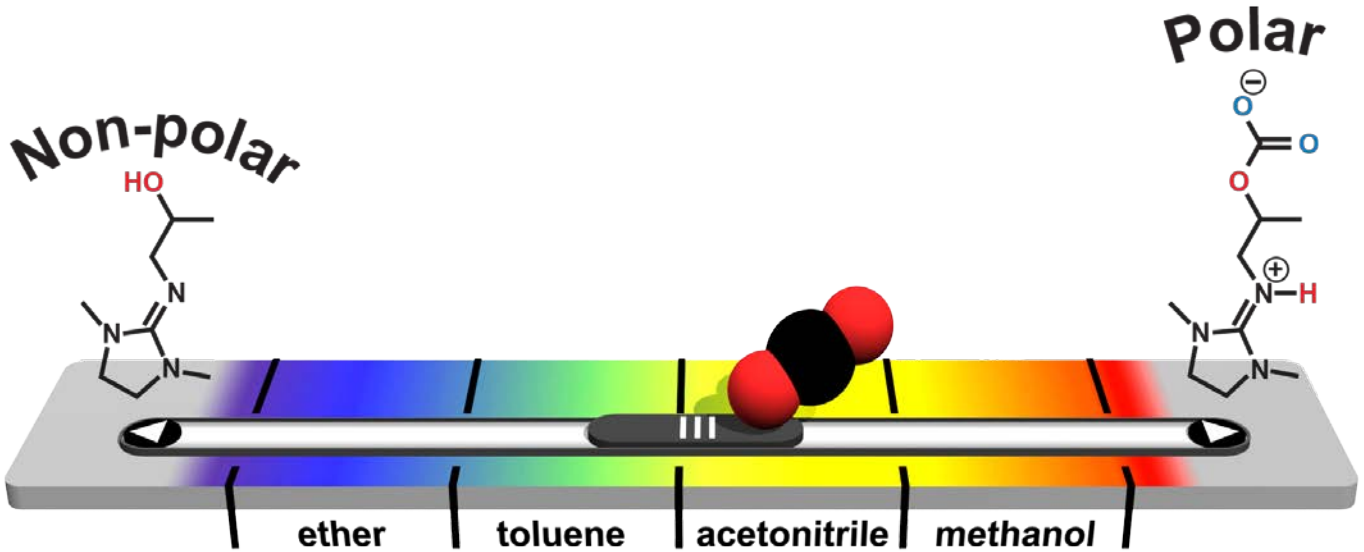
- **BP 1** (May 2014-May 2015)
  - 1. Project management ☑
  - 2. Molecular development ☑
    - Design 200 molecules from current formulation ☑
    - Construct physical property prediction model ☑
    - Predict physical and thermodynamic properties ☑
    - Revise performance targets ☑
  - 3. Synthesis and characterization of candidate molecules ☑
    - Synthesize promising candidates from Task 2 ☑
    - Measure material physical and thermodynamic properties ☑

Applied Science and Testing

- **BP 2** (May 2015-September 2016)
  - 1. Project management ☑
  - 4. Measure key process physical and thermodynamic data
    - Kinetics, vapor-liquid equilibria
  - 5. Process performance projections
  - 6. Alternative synthetic methodology identified ☑
  - 7. Translation of capabilities to other solvent platforms
    - Collaboration with GE on GAP-1 aminosilicones

Case Study:
CO_2-Binding Organic Liquids (CO_2BOLs)

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



*Nile Red Solvatochromatic Polarity Scale

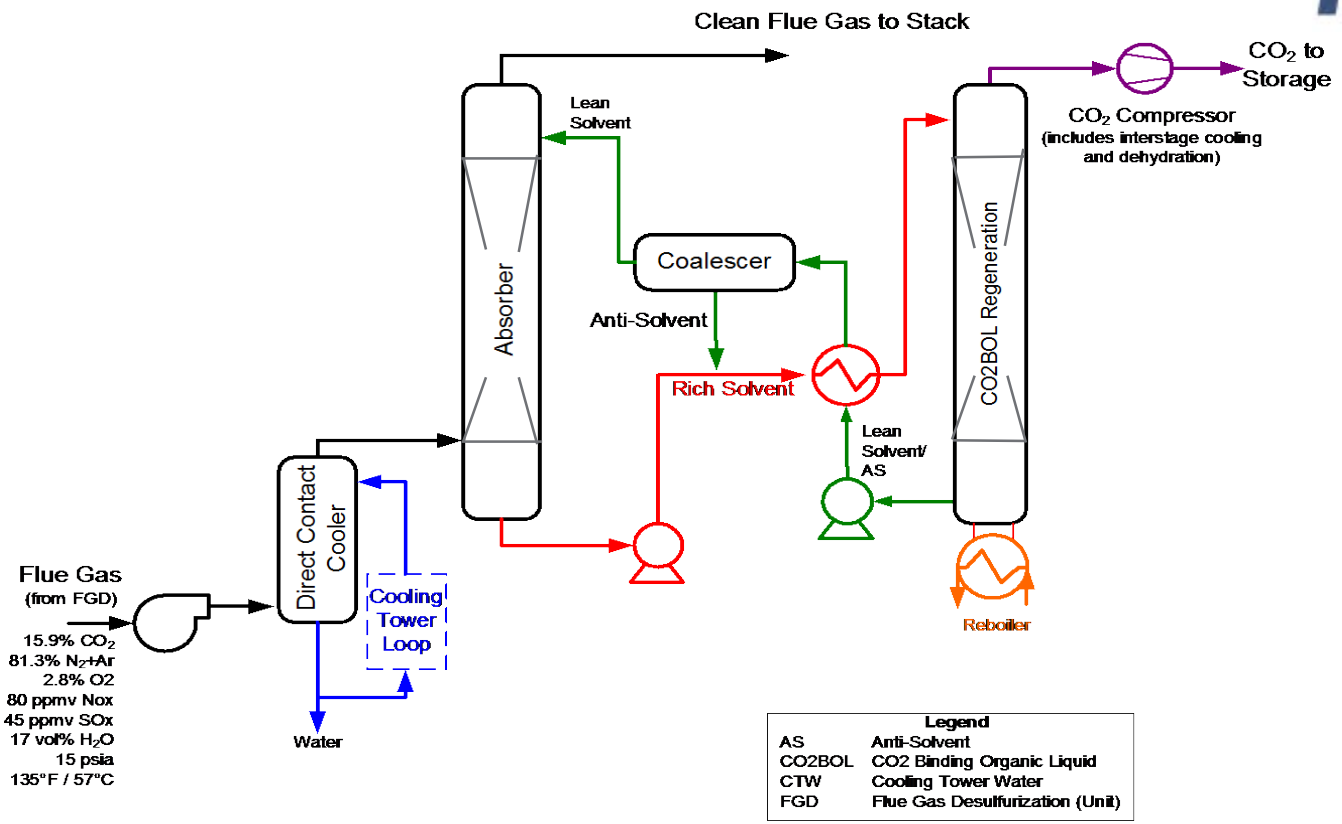
- "Water-lean" organic switchable ionic liquid solvent system
  - Optimal water level in circulating solvent estimated
    - (~5 wt. % water confirmed by simulation)
  - Heat of solution -80 kJ/mol (similar to amines @ -85 kJ/mol)
  - CO_2BOL material projected at ($35-70/kg)

Jessop *et al. Nature,* **2005**, *436, 1102;* Phan et al. *Ind. & Eng. Chem. Res.* **2008**, *47, 3, 539;* Heldebrant et al. *Energy Environ. Sci.*, **2008**, 1, 487; Koech *et al. RSC Adv.,* **2012**, 3, 566; Mathias et al. *Energy. Environ. Sci.* **2013**, 6, 2233.

CO_2BOL/PSAR Conceptual Configuration

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

FLUOR®



- Similar to aqueous amine systems except:
  - Coalescing tank
  - Antisolvent loop
  - Water management equipment
- Commercially available equipment and infrastructure

CO_2BOLs/PSAR Could be Energetically Viable With Lower Solvent Viscosities

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

FLUOR®

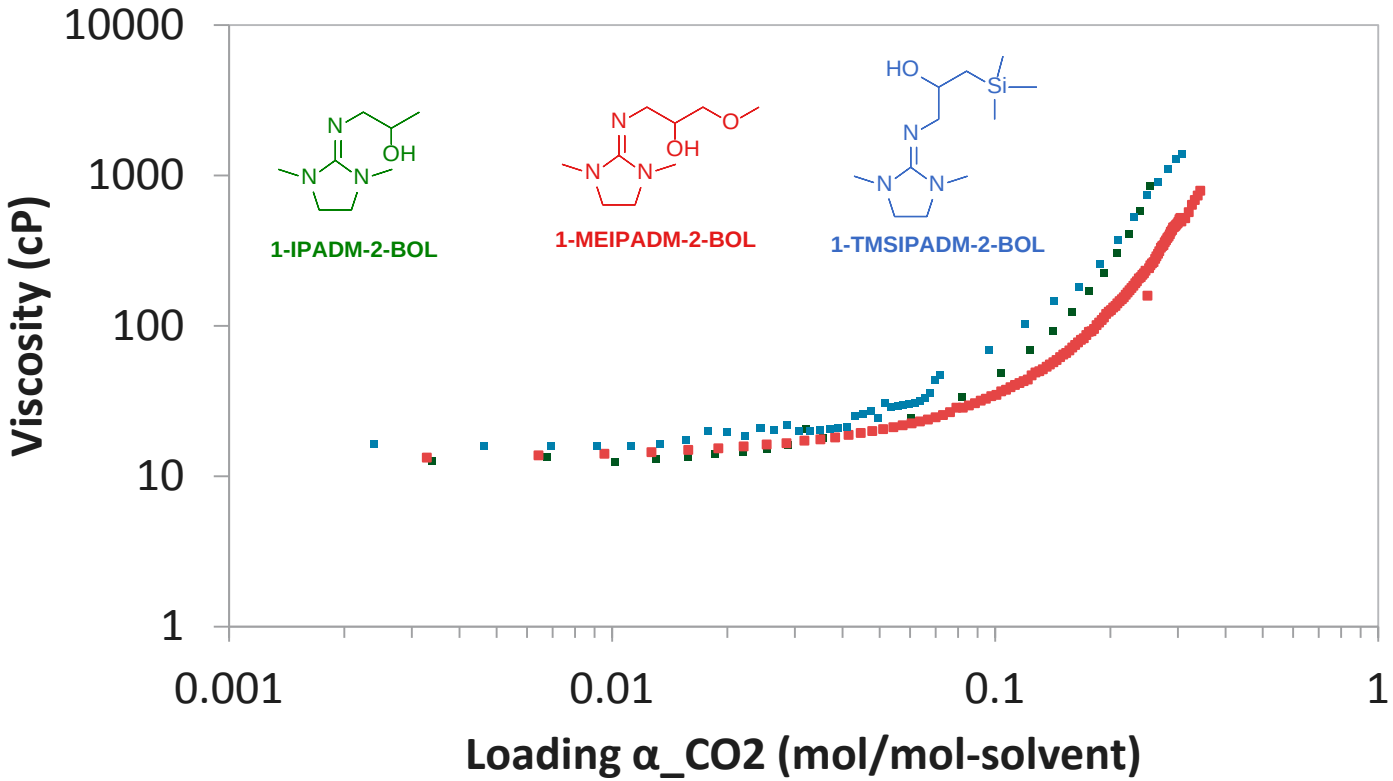
	MEA (Recreated NETL Case 10)	CO_2BOL/PSAR (356 cP)	CO_2BOL/PSAR (578 cP)	CO_2BOL/PSAR (20 cP Target)
Rich solvent loading (mol CO_2/mol solvent)	0.49	0.28	0.34	0.50
Temperature Required for Regeneration (°C)	120	104	104	85
Estimated Reboiler Duty (BTU/lb CO_2)	1,520	1,107	965	870
Increase in Net Electric Power over Case 10 (%)	0	7	9	16

- Viscosity limits the possible *rich* solvent CO_2 loadings and reboiler duty
- If a 20 cP target were achieved:
  - Reboiler duties as low as 870 btu/lb CO_2, (57% of Case 10)
  - 16% increase in net power at an equivalent coal feed rate

Mathias *et al.*, *Energy Fuels*, **2016**, 30, 1192

Cycle-1 Showed Significant Reductions in Viscosity

- Down-selected from >350 molecules to 13 variants for each viscosity reducing factor
  - Internal H-bond and cation charge solvation (ether) show most promise
- 60% reduction in viscosity for MEIPADM-2-BOL
- Experimental data used to validate molecular models



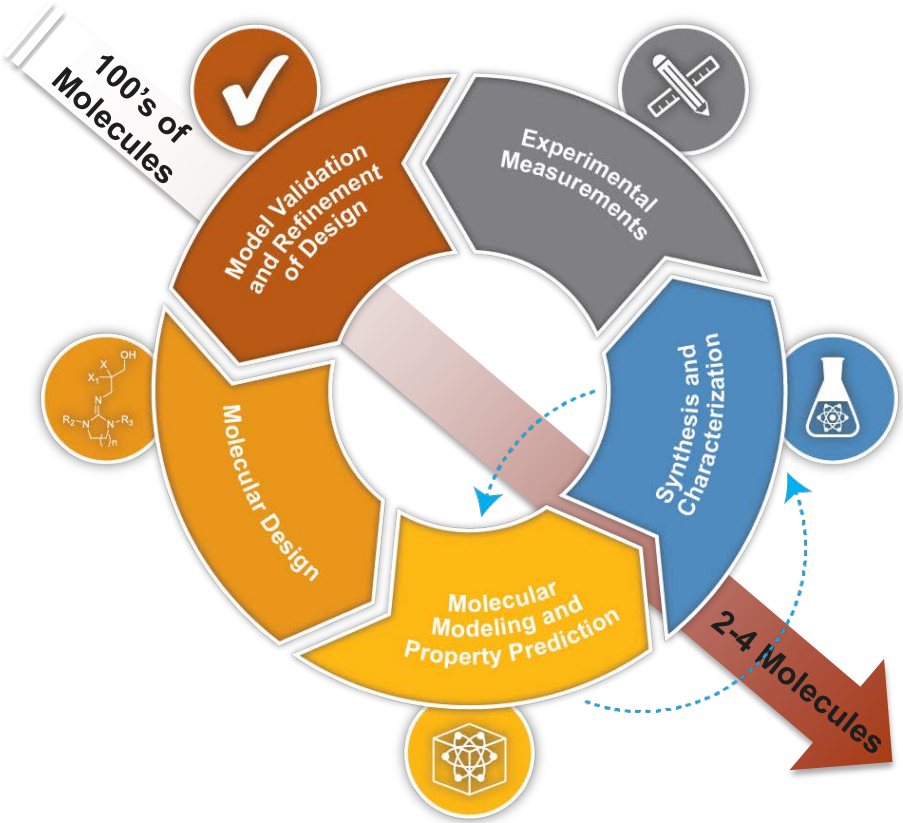
3,000 cP for IPADM-2-BOL @ 50 mol% CO_2 loading
1,100 cP for MEIPADM-2-BOL @ 50 mol% CO_2 loading

Manuscript In Preparation

Technical Approach: CO_2BOL Solvent Class Cycle-2

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

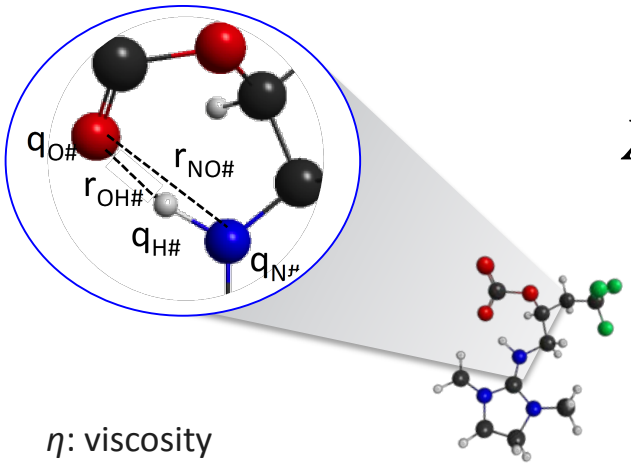
Using PNNL's infrastructure for 2nd level refinement of CO_2BOLs



- Down-select variants from Cycle-1 derivative
- Use reduced viscosity model that enables viscosity prediction off an optimized structure
- Perform comprehensive solvent property testing using ΔPVT cell

Reduced Model Is Qualitatively Predicting Viscosity From Optimized Structures

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

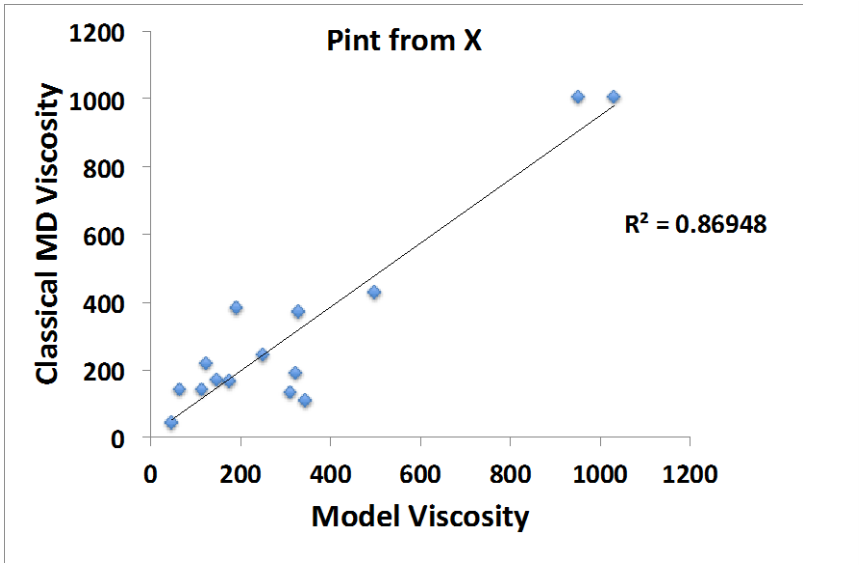


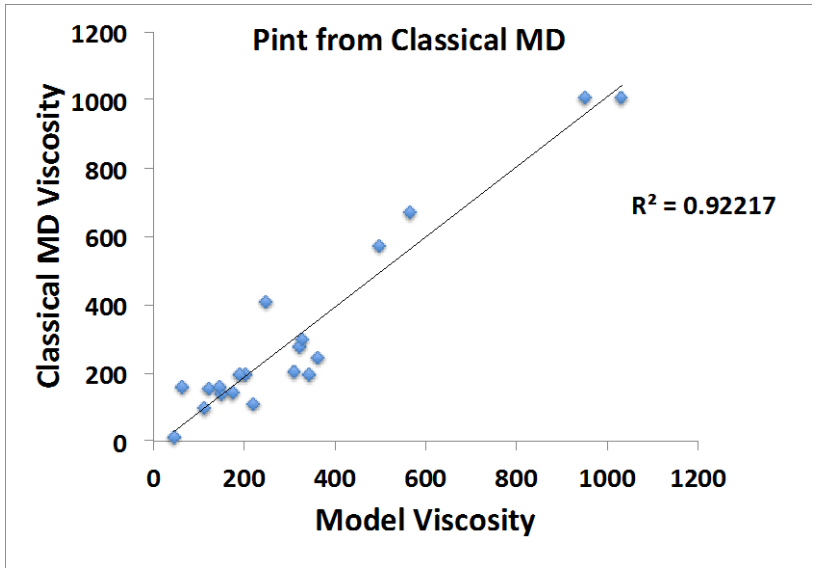
$$X = \frac{q_N q_O}{r_{NO}} - \frac{q_O q_H}{r_{OH}} \quad (1)$$

$$P_{int} = c_1 X + c_2 \quad (2)$$

$$\eta = c_1 \ln\left(\frac{P_{int}}{1 - P_{int}}\right) \exp\left(c_2 L\right) \quad (3)$$

η: viscosity
P_{int}: percent internal hydrogen bond, calculated as a function of X
L: mol percent CO_2 loading
c_1 & c_2: constants to obtain the viscosity magnitude in cP, varied to fit the *experimental* data for at 0 and 25 mol% CO_2





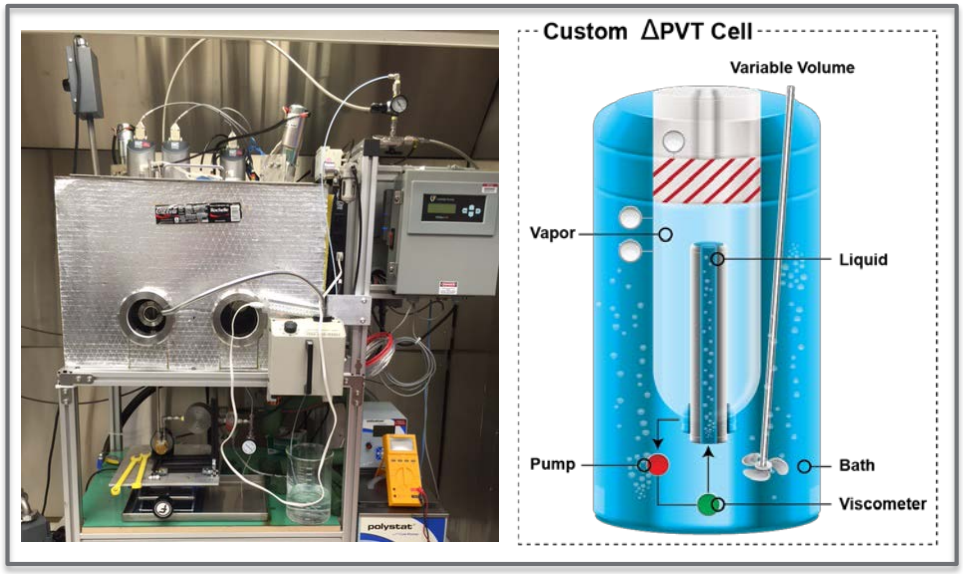
J. Phys. Chem. Lett., **2016**, 7, pp 1646–1652, Cantu *et al. Submitted*, **2016**

PNNL's Custom ΔPVT Cell Enables Rapid Screening

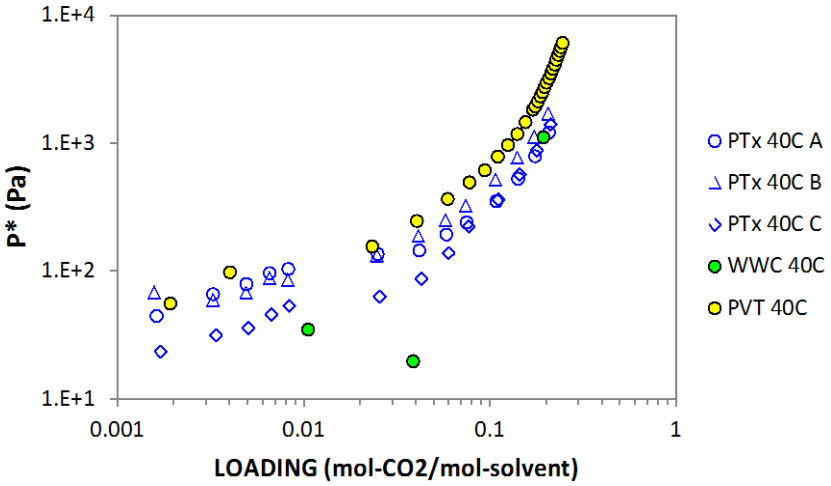
***Standardized Measurements on ~40 mL scale**

Pacific Northwest NATIONAL LABORATORY

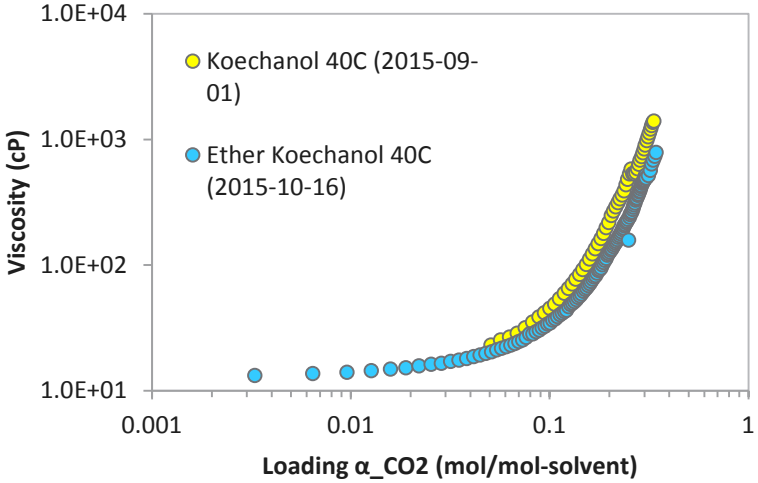
Proudly Operated by Battelle Since 1965



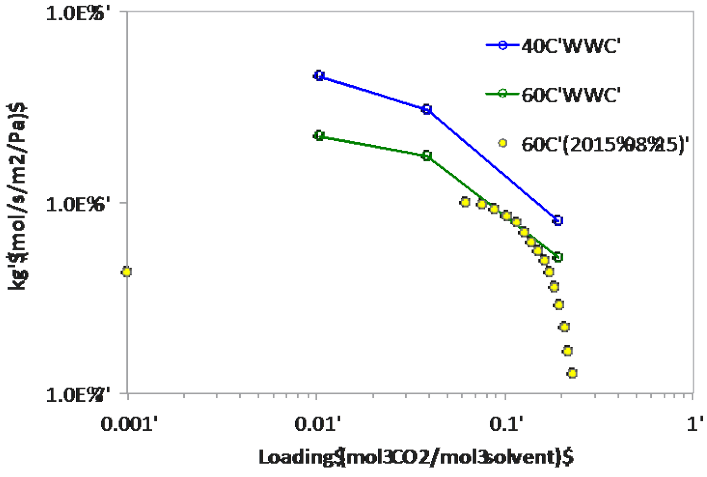
- PT_x Capability Capability Matches VLE



- Flow-through viscometer measures cP as a function of CO_2 loading



- Miniaturized wetted wall contactor can extract qualitative *kg´* data



Applying Molecular Design Towards CO_2BOL Cycle-2

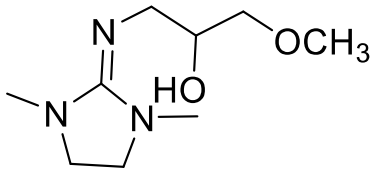
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

What we learned from Cycle-1:

- High degree of internal hydrogen bonding
- Ether groups for cation charge solvation
- Potential for neutral capture

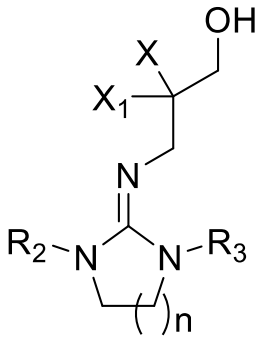
Viscosity Modifying Factors:

- Fine tuned electronics for acid/base equilibria
- Steric crowding to reduce stacking



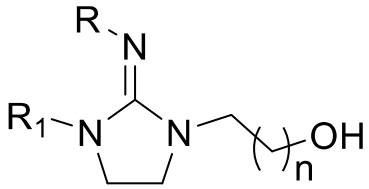
1-MEIPAD-2-BOL

Electronic Effects



X and X_1= F, Cl, CF_3, (EWG) or OMe, CH_2NMe_2, (EDG) and R_2=R_3=Me, CF_3, CF_3CF_2, OMe with n=1, 2, 3

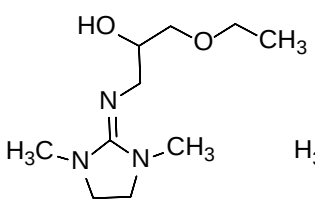
Steric Effects



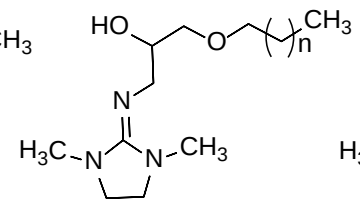
R=Pr, *i*-Pr, Bu, *t*-Bu
R_1=Me, Et, *i*-Pr
with n=1, 2, 3

Reduced Model Predicts ~90% Reduction for Multiple Derivatives (@ 25 mol% CO_2)

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

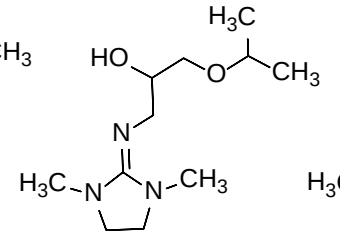


275

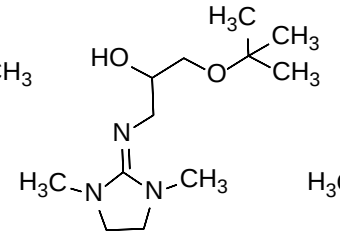


n = 1, 2

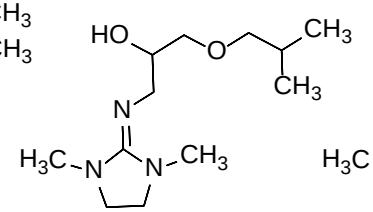
94,139



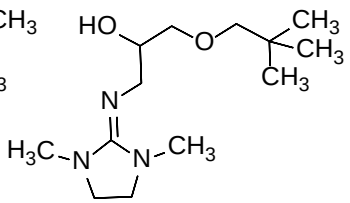
228



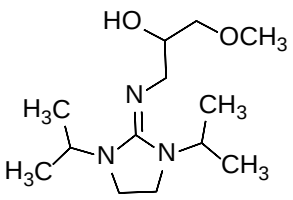
170



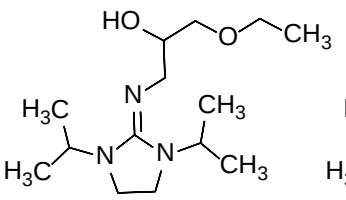
111



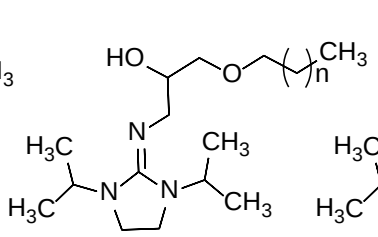
146



36

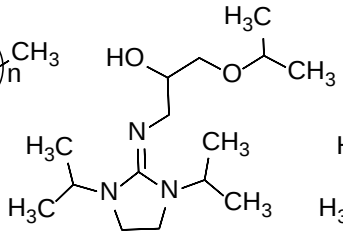


13

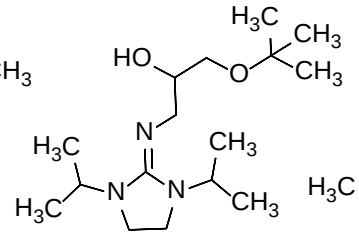


n = 1, 2

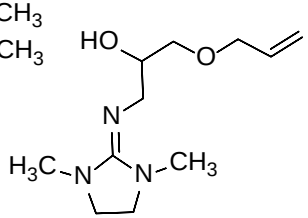
n/a, 14



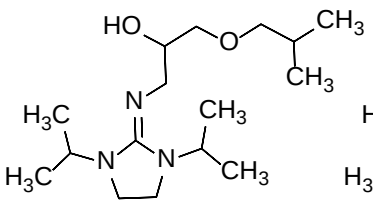
33



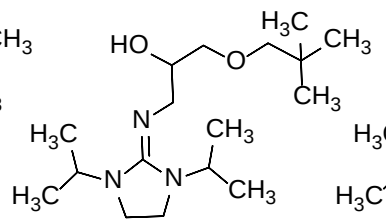
29



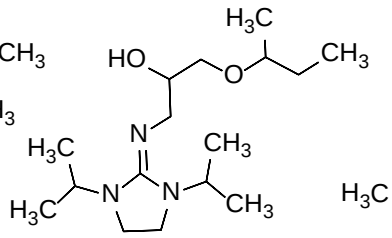
n/a



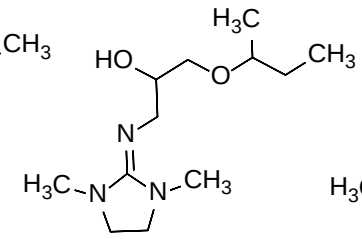
14



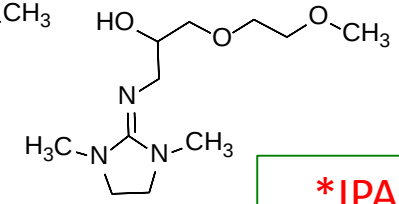
n/a



14



145



198

*IPADM-2-BOL = 150 cP

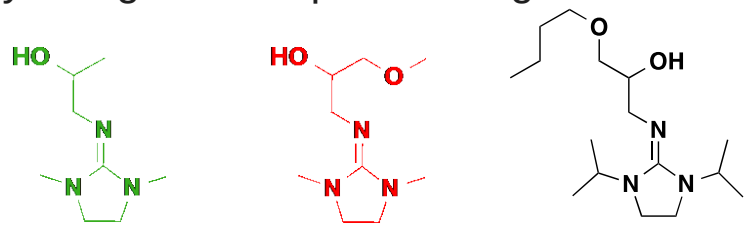
Synthesis & Testing of Cycle-2 Derivatives Confirms Significant Viscosity Reduction

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

- Synthesizing 4 variants of MEIPADM-2-BOL with ether and isopropyl moieties
  - 90% reduction predicted @ 25 mol% CO_2, 40 ˚C
- BEIPADIPA-2BOL currently being scaled up for testing

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



100 Molecules → **2-4 Molecules**

Malhotra *et al., Manuscript In Preparation*

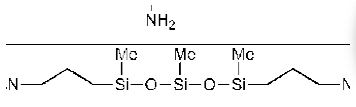
Integrating Molecular Design, Synthesis & Testing For Aminosilicone Solvents

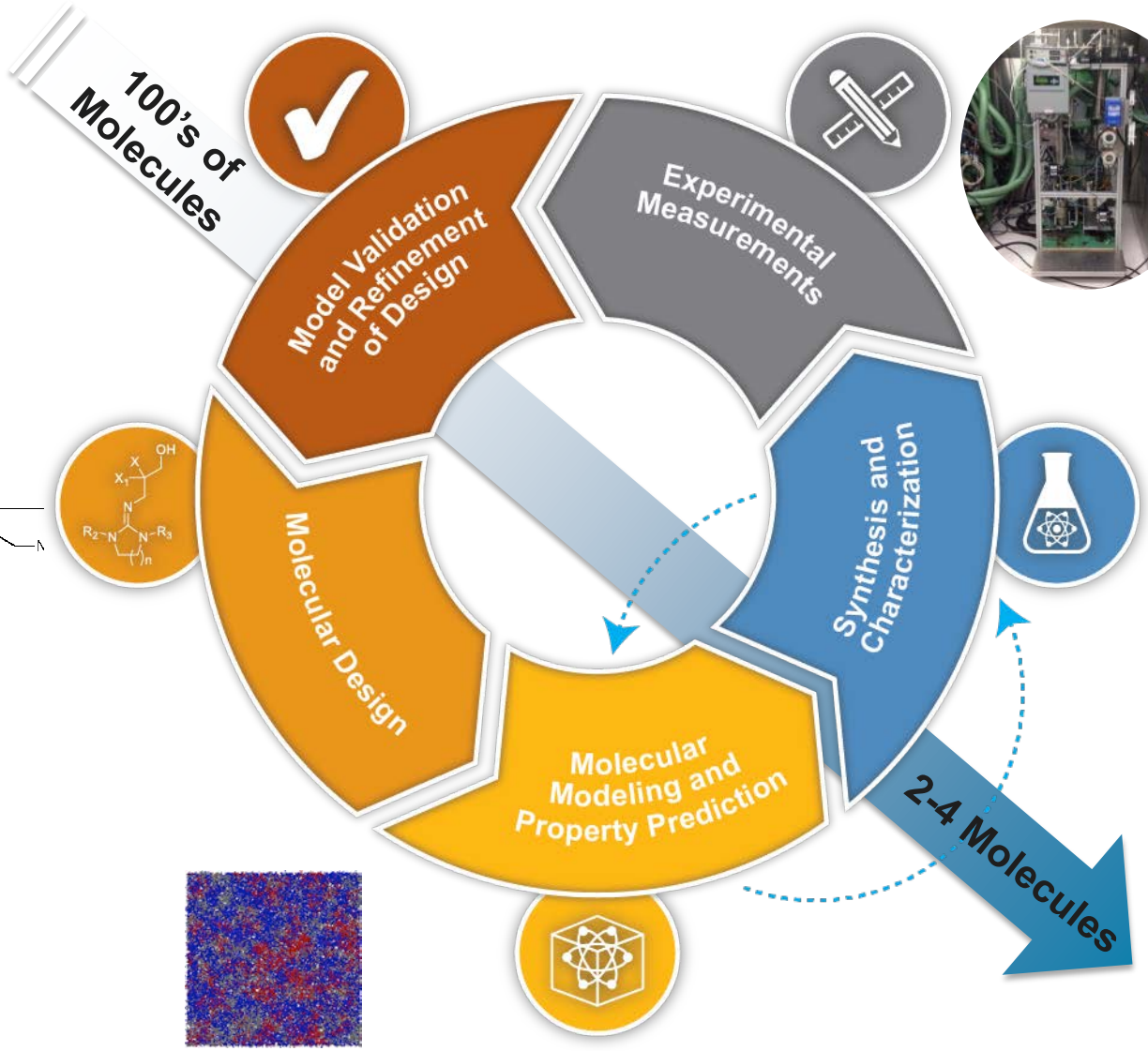
Pacific Northwest NATIONAL LABORATORY

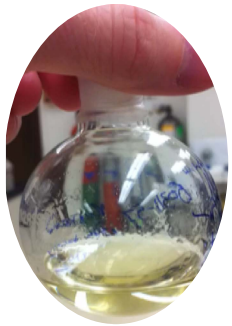
Proudly Operated by Battelle Since 1965

***Collaboration with GE Global Research**

GE Global Research



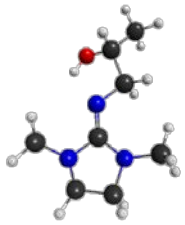




All Non-Aqueous Solvents May Have "Heterogeneous" Molecular Structure

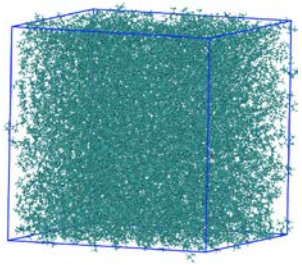
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

CO_2BOL Solvent Class: (100% Concentrated)

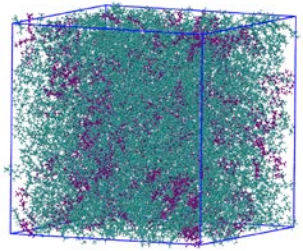


IPADM-2-BOL

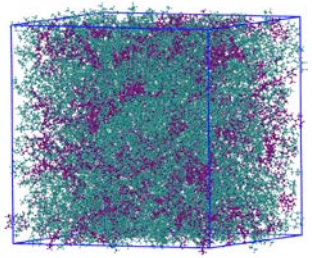
IPADM-2-BOL (0% CO_2)



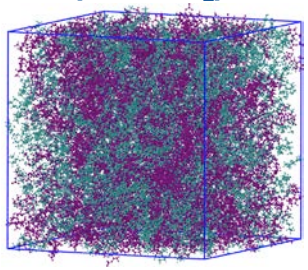
IPADM-2-BOL (15% CO_2)

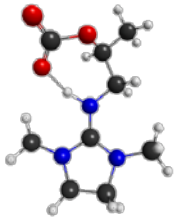


IPADM-2-BOL (25% CO_2)



IPADM-2-BOL (50% CO_2)



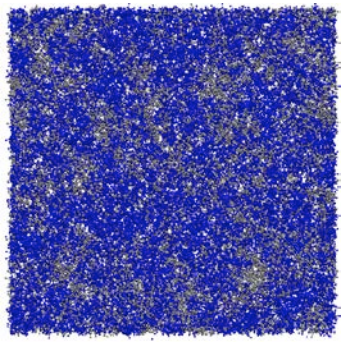


CO_2-loaded IPADM-2-BOL

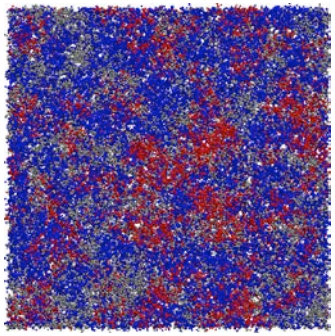
- Different solution and interfacial properties
- Changes as a function of CO_2 loading

Aminosilicone Solvent Class: (Triethylene Glycol co-Solvent)[2]

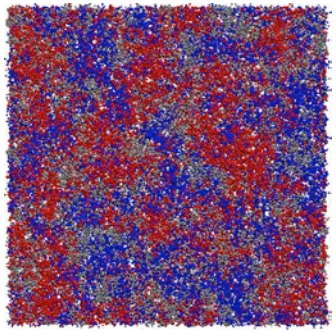
GE Global Research



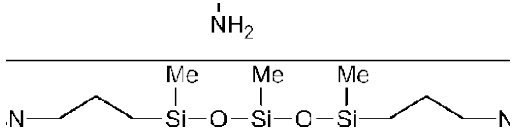
GAP-0/TEG 0% CO_2



GAP-0/TEG 25% CO_2



GAP-0/TEG 50% CO_2



CO_2-GAP-0: red

GAP-0: blue

TEG: silver

- TEG may not be dissolving GAP carbamates
- Potential for different co-solvent

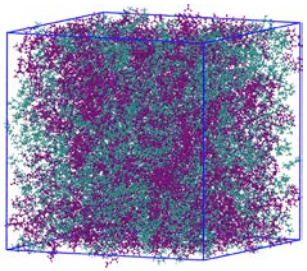
1) Mathias et al *Energy Procedia,* **2015***;* Cantu *et al. J. Phys. Chem. Lett.* **2016**, *7,* 1646. 2) *Manuscript in preparation*

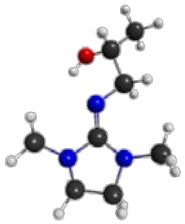
Heterogeneous Molecular Structure May Account for Similar Materials Performance

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

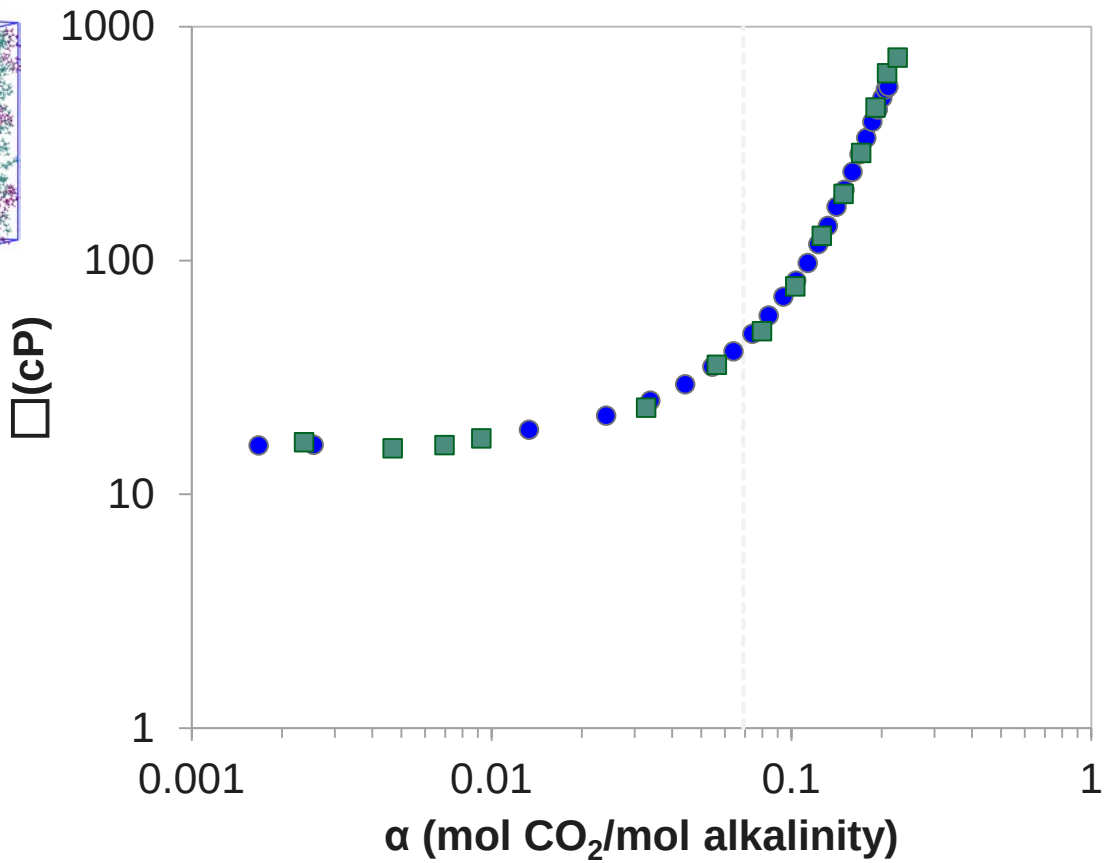
GE Global Research

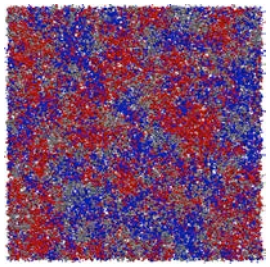
- CO_2BOLs and aminosilicones show similar predicted solvent structure and viscosity profiles as a function of CO_2 loading





IPADM-2-BOL





GAP-1/TEG

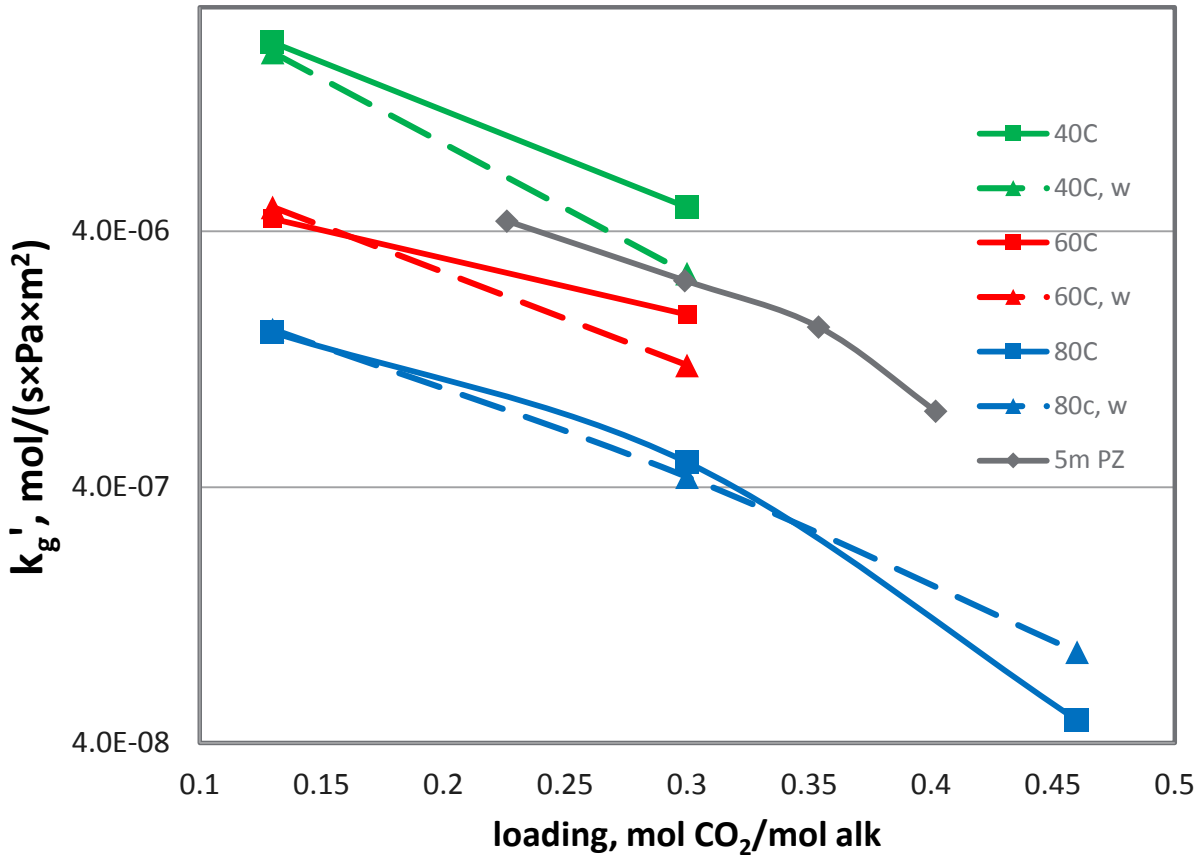
1) Mathias et al *Energy Procedia,* **2015***;* Cantu *et al. J. Phys. Chem. Lett.* **2016**, *7,* 1646. 2) Malhotra *et al. Manuscript in preparation*

Mass Transfer of GAP-1/TEG is Inverse With Temperature

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

GE Global Research

- Inverse k_g' with temperature observed
  - Similar to IPADM-2-BOL[1]
- Follows trend of physical solubility of CO_2 driving liquid-stage kinetics



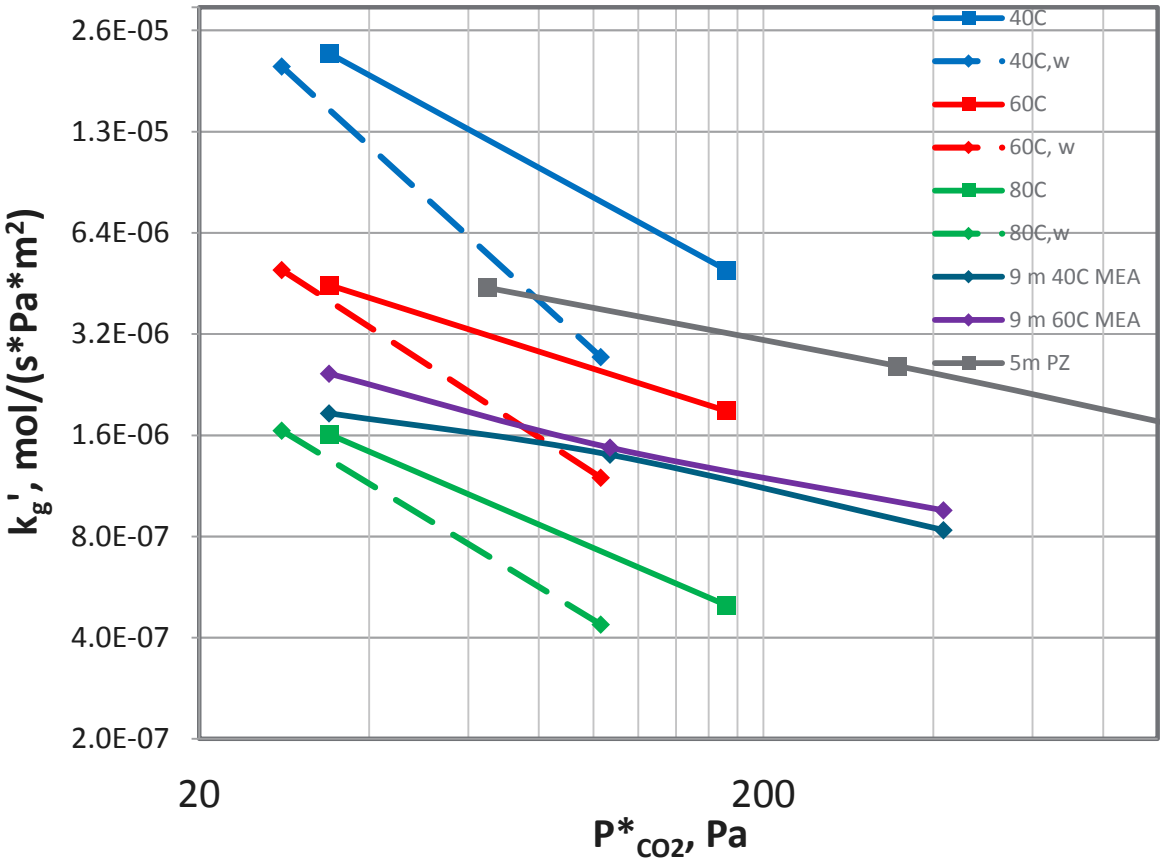
1) Whyatt *et al. ChemSusChem*, **2015,** *8*, (21), 3617, 2) Whyatt *et al.*, Manuscript *in preparation*

Mass Transfer of GAP-1/TEG is Greater Than MEA & Piperazine

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

GE Global Research

- k_g' of GAP-1 is twice that of 8 m PZ and 6 times that of 9 m MEA
  - 100 Pa of P^*_{CO2} at 40 ºC
- Non-aqueous k_g' *values* larger at higher solution viscosities[1]



1) Whyatt *et al. ChemSusChem*, **2015,** *8*, (21), 3617, 2) Whyatt *et al.*, Manuscript *in preparation*

Strategies of Refinement of GAP-1 Derivatives

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

GE Global Research

GAP-1/TEG shows enhanced kinetics compared to aqueous solvents though viscosity can still be lowered

Near Term

- Identify co-solvents that dissolve ionic clusters
- Identify potential diluents to breakup ionic clustering

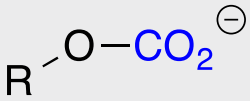
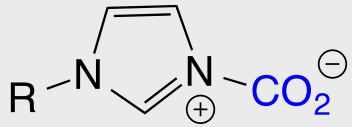
Long Term

- Apply findings from CO_2BOL solvent class to refine GAP derivatives
  - Promote internal H-bonding
  - Add ether groups for charge solvation
  - Increase steric bulk
  - Optimize acid/base equilibria

Benefits of Technology to the Program

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- An approach that can benefit all solvent classes
- Rapid modeling and testing of all CO_2 binding mechanisms
- Detailed understanding of molecular level interactions and how they impact performance

	Alkylcarbonate-Derived	Carbamate-Derived	Imidazole-Derived
			
Property	(CO_2BOLs)	(RILs, Aminosilicones, TSILs, Phase-Change)	(imidazole, carbene, AHA ILs)
Internal H-Bonding			
Molecular Stacking			
Steric Crowding			
Optimized Thermo-chemistry			
Quantify k_g'			

KEY | **Current Work** | **Projected Translation**

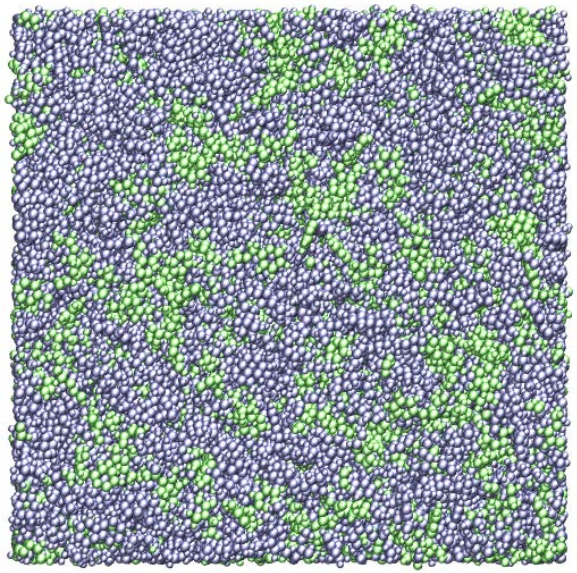
Next Steps: FY17 Work Scope

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

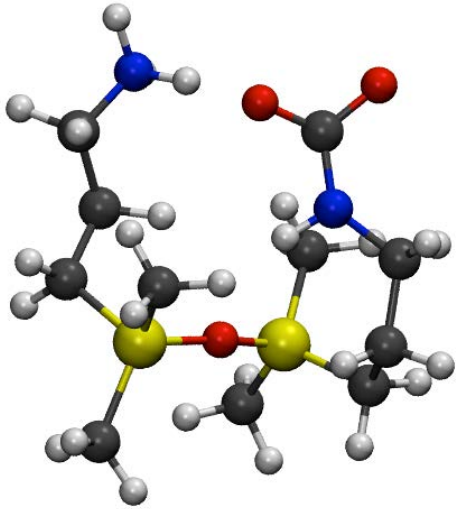
Three parallel efforts at each level of testing and development

Solvent Class #3 Molecular Development Cycle 1



Development of model
Initial solvent screen

Aminosilicone Molecular Development Cycle 2



Molecular-level refinement
Reduce viscosity by up to 90%

CO_2BOL/PSAR Continuous Flow Testing for TEA

Validate performance
\$40/ton CO_2 target

Acknowledgements

Funding: US Department of Energy Office of Fossil Energy FWP 65872

Andy Aurelio, Lynn Brickett, John Litynski

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

Dr. Phillip Koech

Dr. Vanda Glezakou
Dr. Roger Rousseau

Dr. Feng Zheng

Solvent Design
Retrosynthetic-analysis
Synthesis & Scaleup

Computational Modeling
Physical property projections

Materials Testing & Analysis

Process Modeling
Performance Projections

Dr. Deepika Malhotra

Dr. David Cantu

Greg Whyatt
Charles Freeman

Andy Zwoster

Mark Bearden

FLUOR®

*Advisory process engineering, thermodynamics:
Dr. Paul M. Mathias

GE Global Research

Dr. Robert Perry
Tiffany Westendorf
Benjamin Wood

Lawrence Livermore National Laboratory

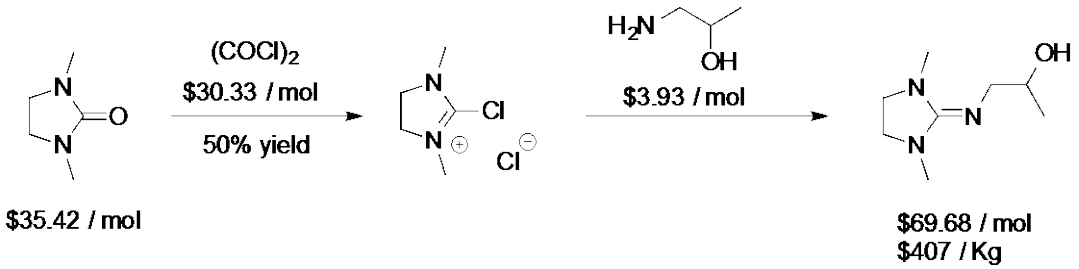
Dr. Josh Stohlaroff,
Dr. John Vericella

EPRI ELECTRIC POWER RESEARCH INSTITUTE

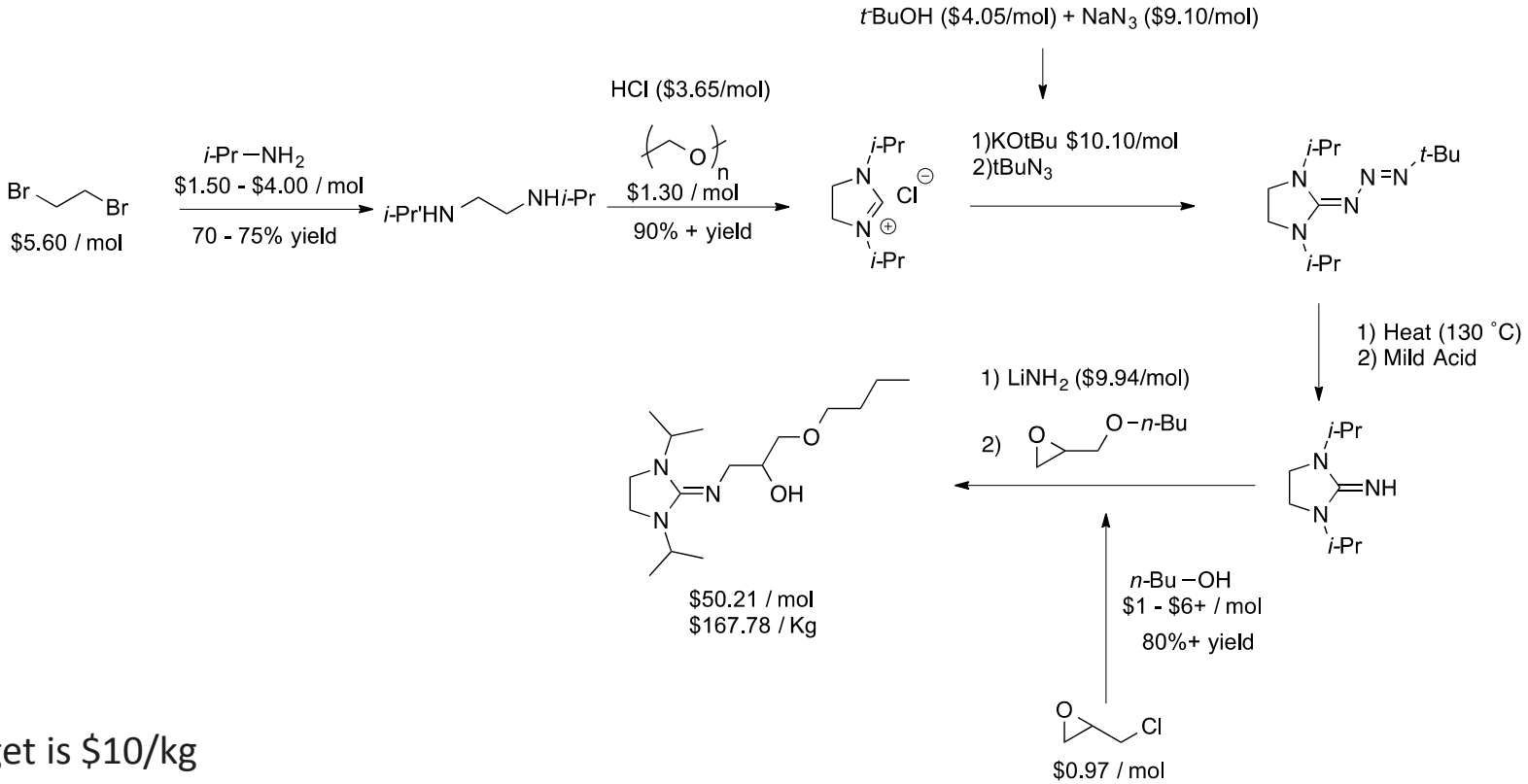
Abhoyjit Bhown

Revised Synthetic Pathway and Cost for Optimal Derivative May Achieve Cost Targets

- IPADM-2-BOL costs $407/kg, but projected $35/kg at tonnage scale



- BEIPADIPA-2-BOL costs $168/kg, but projected at $12/kg at tonnage scale

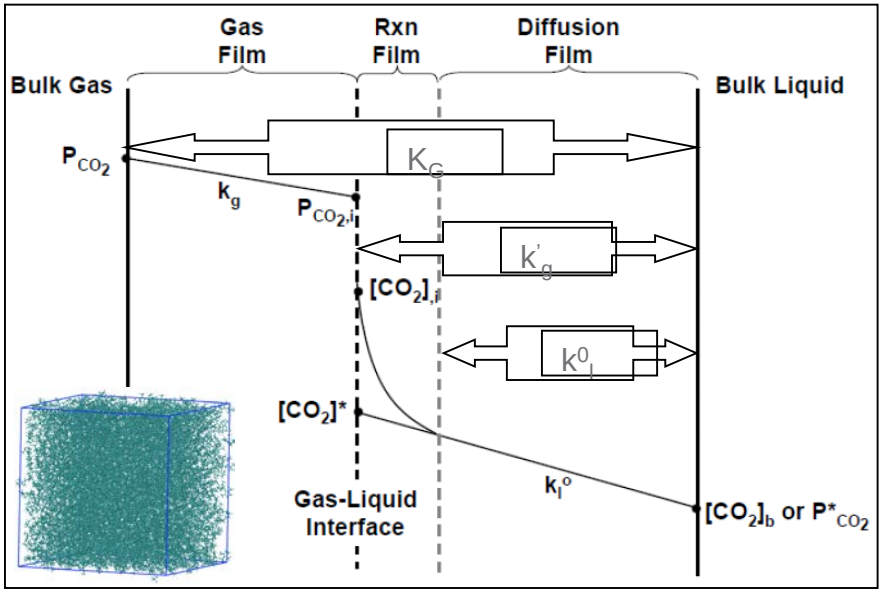


*Cost target is $10/kg

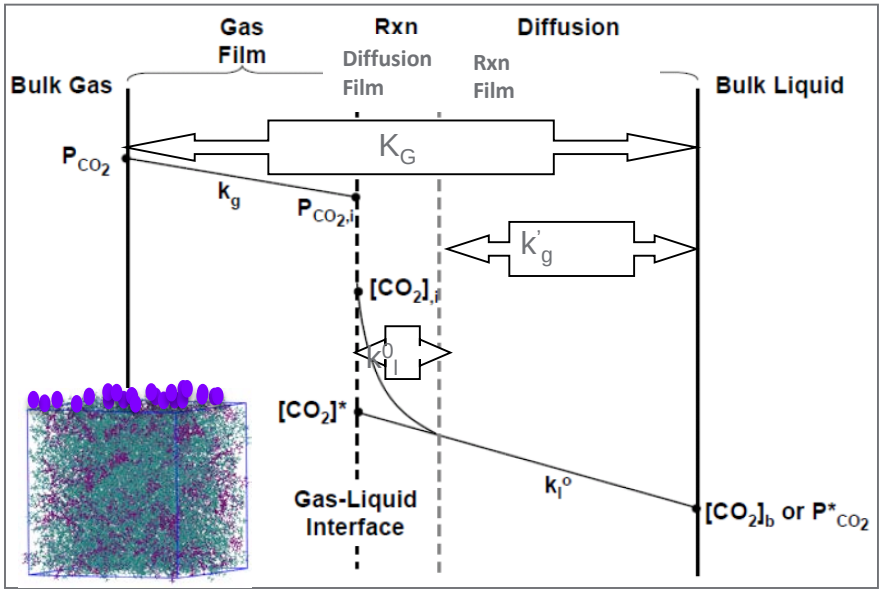
Impacts of a Heterogeneous Solvent Structure - Collaboration With CCSI

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965



Aqueous Profile



CO_2BOL Profile

- Aqueous solvents have a reactive interface, a diffusion film, then bulk liquid.[1]
- CO_2BOLs have a diffusion film (passivated interface) followed by a reaction film, then bulk liquid.[2]
- Potential new diffusion routes and mechanisms of CO_2 and CO_2-containing ions
- Different contactor or packing may be needed New film theories needed to quantify this behavior

1. Dugas, R.. Ph.D. Dissertaion UT Austin (2009), 2. Liauw *Analyst* **2013**, *138*, 819-824, 3.

Utilizing A Heterogeneous Solvent -Collaboration With CCSI

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Gradient packing to adjust to changing fluid
  - Changes in fluid properties: contact angle, surface tension and viscosity
  - Changes in packing: Structured to random, packing material

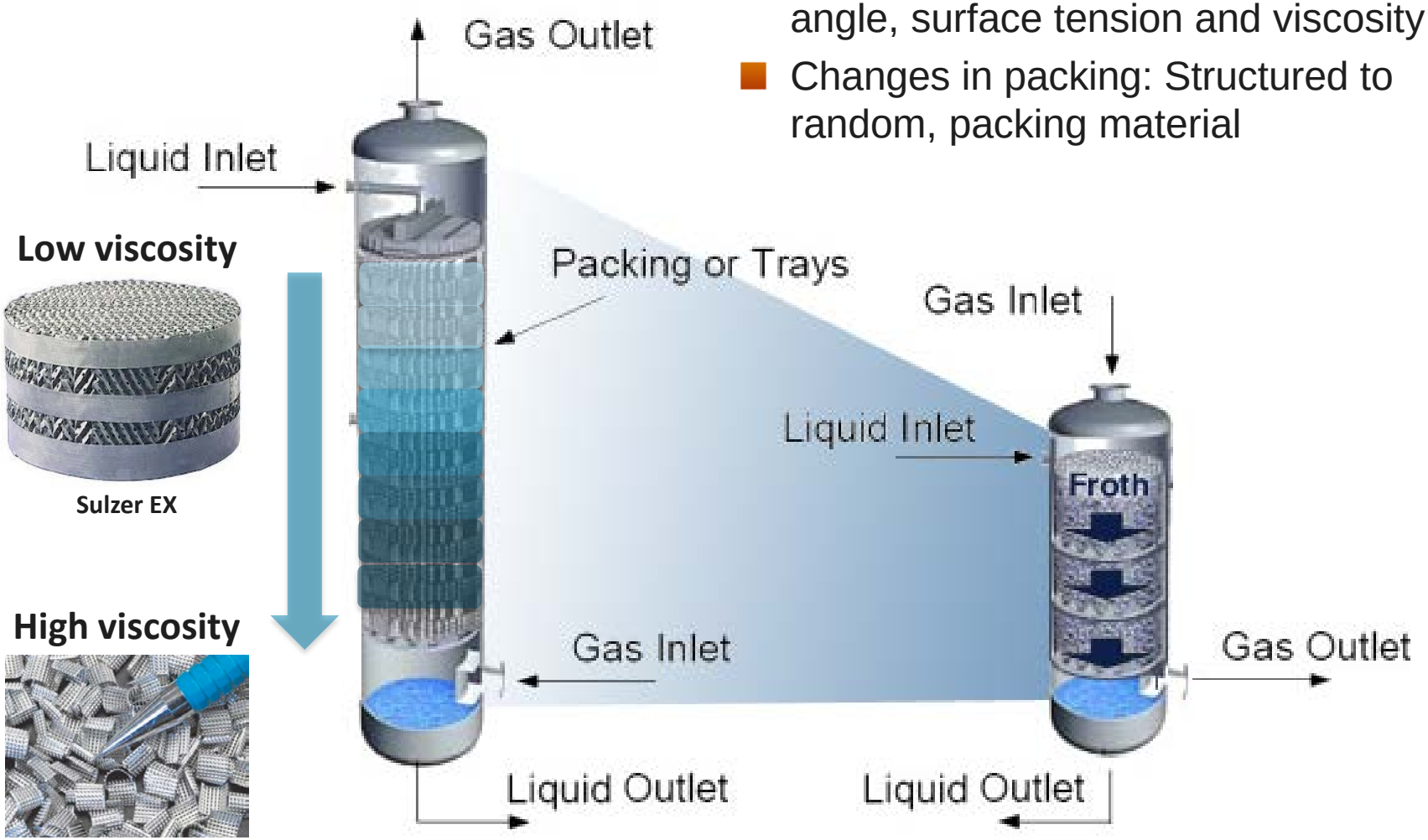


Image taken from: http://www.wes-worldwide.com