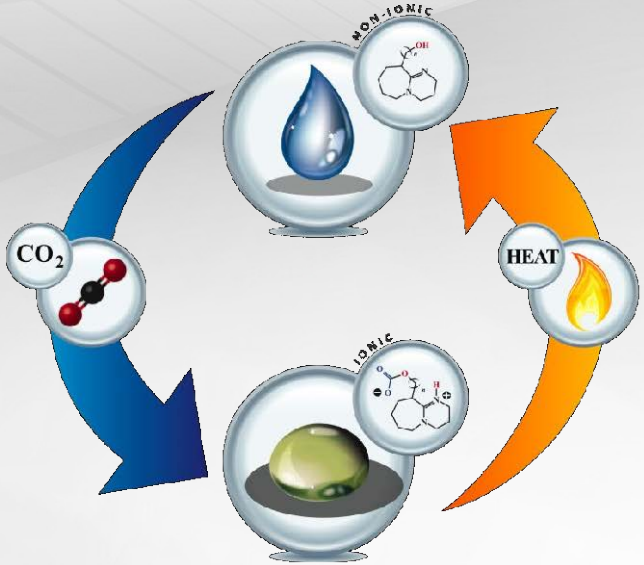
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



Accelerating the development of transformational solvent systems for CO_2 separations

DAVID J. HELDEBRANT

NETL CO_2 CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
JUNE 24, 2015

U.S. DEPARTMENT OF ENERGY

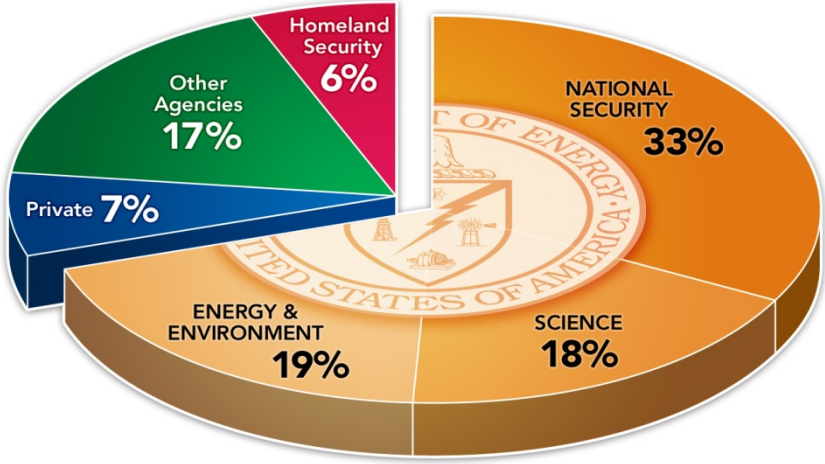
Pacific Northwest National Laboratory: *Battelle-managed and mission-driven*

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

FY13 Facts

- *$936 million in R&D expenditures*
- *More than 4,300 staff*
- *2000+ users & visiting scientists*
- *1,168 peer-reviewed publications*
- *36 patents*



- Mission-driven collaborations with government, industry, academia
- Operated by Battelle since 1965
- DOE's top-performing lab for 7 years

Interdisciplinary teams at Pacific Northwest National Laboratory address many of America's most pressing issues in energy, the environment and national security through advances in basic and applied science. For more, visit PNNL's News Center, or follow PNNL on Facebook, LinkedIn and Twitter.

Why Water-Lean & Concentrated Solvents?

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Benefits:

- Reduced reboiler duty from boiling and condensing water
- Lower sensible heat
- Different thermodynamic and physical properties
- May use existing 1st gen solvent infrastructure

Limitations:

- Some advanced solvents have not yet demonstrated water tolerance
- Full dehydration impractical
- Cost challenges with a custom solvent
- Viscosity increase as a function of CO_2 loading

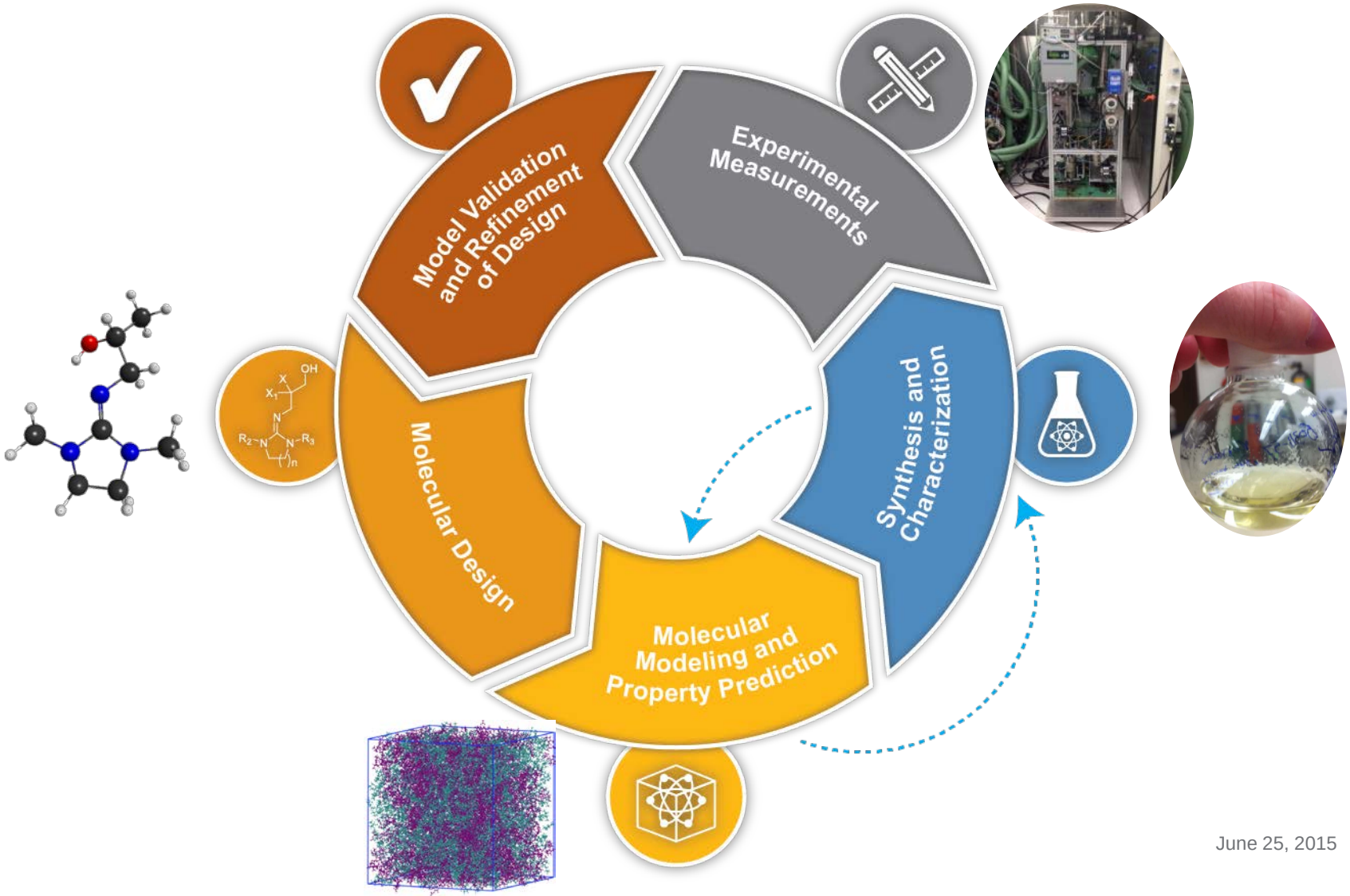
Image taken from www.separatinosnow.com

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

Goals

- Develop tools for viscosity prediction and solvent design methodologies for reducing viscosity across all transformational solvent platforms.
- Develop cost-effective synthesis methodologies to bring solvent costs ~ $10/kg.
- Verify the performance of the model, and reduce viscosity of current formulations by >400 cP.
- Enable advanced solvent designs for advancement up DOE's TRL readiness scale to enable large scale testing and deployment by year 2030.

Objectives

- Develop a viscosity model that can predict key solvent physical and thermodynamic properties.
- Collect necessary additional thermodynamic and kinetic information for a library of compounds.
- If budget and time permitting use continuous flow testing data to make robust energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system.
- Apply the viscosity model and molecular design principles to other solvents in DOE's post-combustion solvent portfolio.

Project Schedule and Major Tasks

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Funding:1.76 million/ 24 months

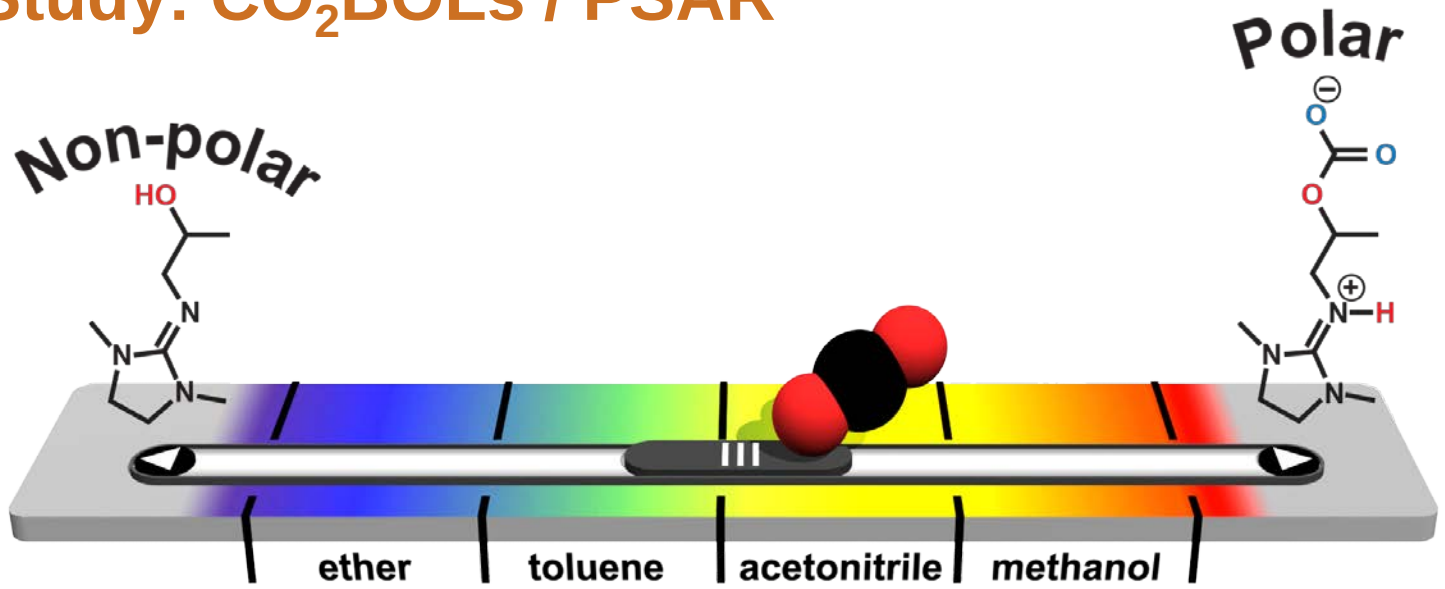
Fundamental Science

- **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-May 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
  - Translation of capabilities to other solvent platforms

Case Study: CO_2BOLs / PSAR



*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
  - CO_2BOL material projected at ($35-70/kg)
- Polarity-Swing Assisted Regeneration
  - Co-injection of non-polar "antisolvent" destabilizes the CO_2-rich form enhancing CO_2 release.

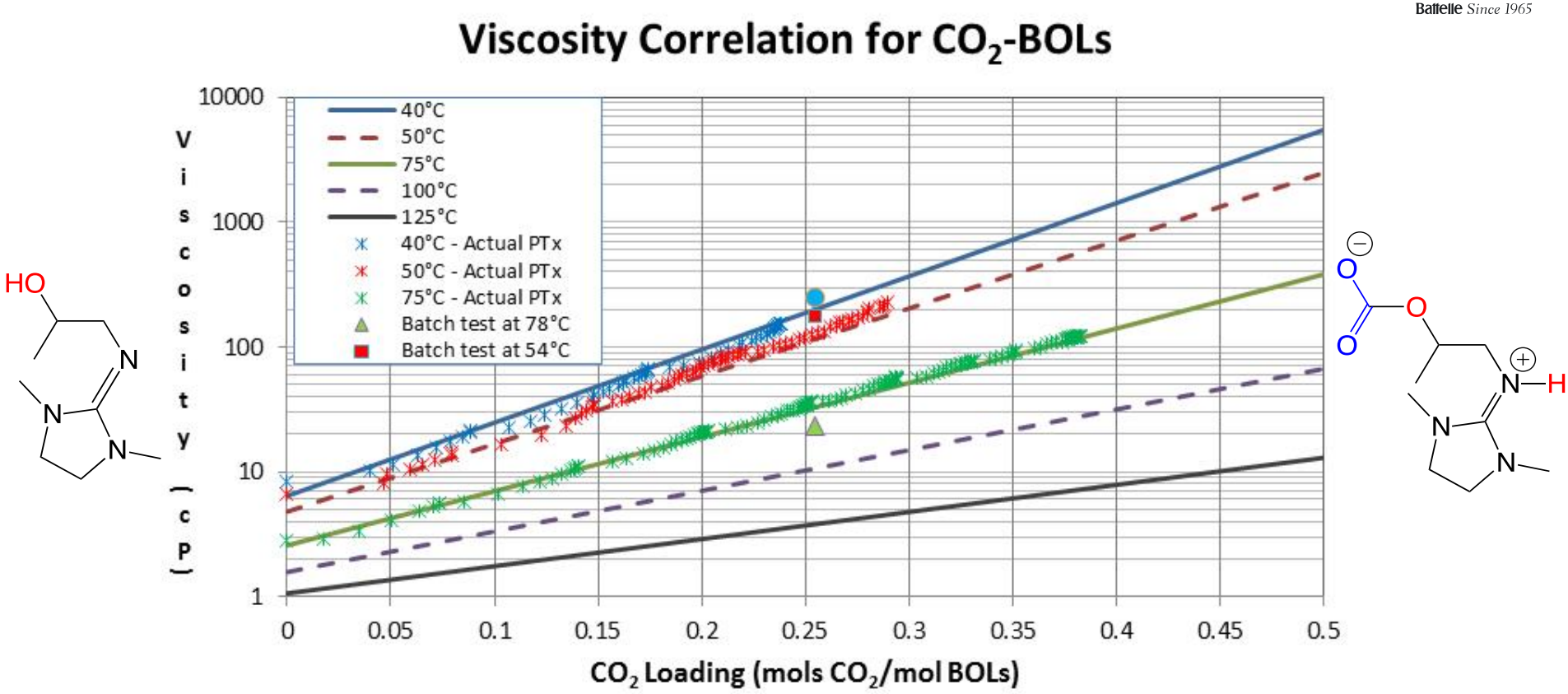
*Nature, (**2005**), 436, 1102; Ind. & Eng. Chem. Res. (**2008**); 47, 3, 539, Energy Environ. Sci.*, *(**2008**)*, 1, 487
*RSC Adv., (**2012**)*, 3, 566-572, *Energy. & Env. Sci. (**2013**)*, 6, 2233 - 2242

CO_2BOL Viscosity

FLUOR®

Pacific Northwest NATIONAL LABORATORY

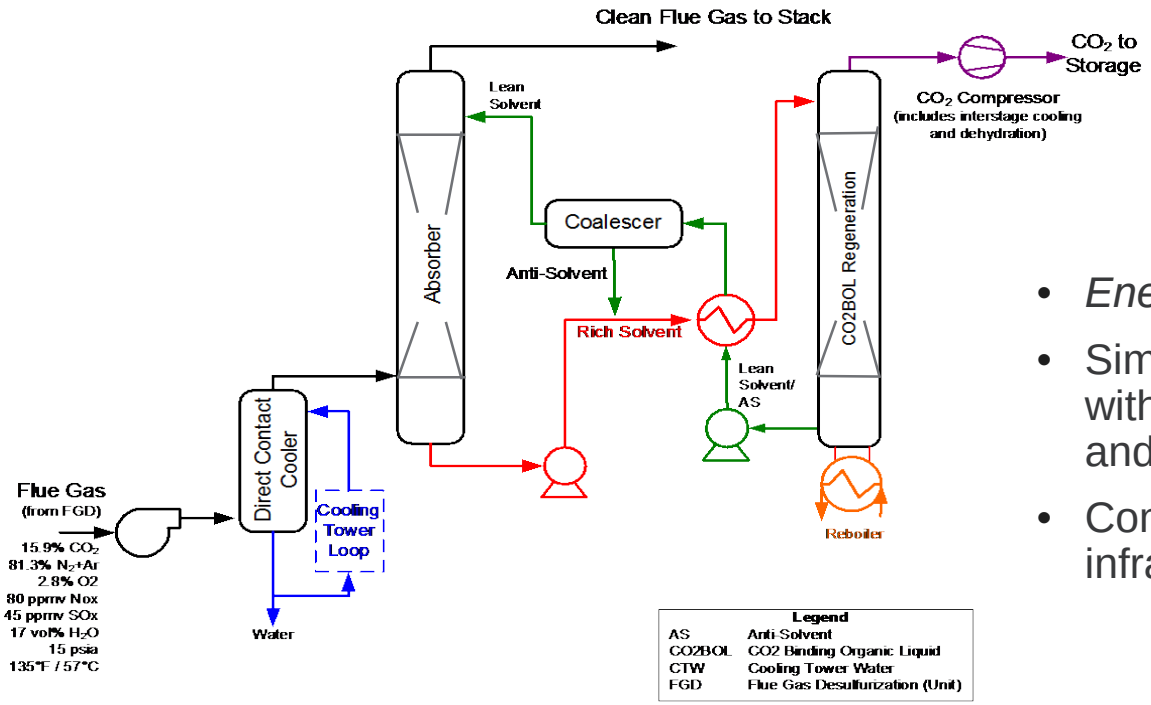
Battelle Since 1965



- Points are measured data and lines are model fits
- Water does not precipitate bicarbonate salts
- Viscosity with 10% water (worst case loading) has a minor impact
- Equilibrium model projections of current formulation (0.25 LEAN -0.5 RICH) would be 200-3,000 cP

*RSC Adv., (**2012**)*, 3, 566-572

CO_2BOL/PSAR Conceptual Configuration



Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

FLUOR®

- *Energy. & Env. Sci. (**2013**)*, 6, 2233
- Similar to aqueous amine systems albeit with coalescing tank, antisolvent loop, and water management equipment
- Commercially available equipment and infrastructure

Process Model Results

		Case 2	Case 4	20 cP Target Equilibrium Case
Lean Solution Loading	mol CO2/mol BOL	0.0807	0.0807	0.2615
Rich Solution Loading	mol CO2/mol BOL	0.2867	0.3339	0.5737
Delta Loading	mol CO2/mol BOL	0.206	0.2532	0.3122
Lean solution circulation rate	kg/hr	6004440	4878290	4387408
CO2 removed	kg/hr	297957	297957	299188
lean solution rate per kg CO2 removed	kg/kg CO2	20.15	16.37	14.66
RICH viscosity	cP	356	577	20
Reboiler Temperature	°C	103.8	103.6	86
heat rate	kcal/kg CO2 removed	615.5	548	442.3
heat rate	btu/lb CO2 removed	1107.9	986.3	796
Relative heat rate		1	0.89	0.72

Manuscript in preparation

Why CO_2BOLs as a Case Study

- Comprehensive data available of all transformational solvents is lacking
  - Complete thermodynamic, kinetic and bench scale data available
  - Water tolerance established (5 wt% steady state)
  - Estimated low evaporative losses
  - Comparable Ecotoxicity (rainbow trout) to MEA
    - CO_2BOL (180), MEA (150mg/L)

- Process reviewed and guided by the Fluor Corporation
  - New ASPENplus equilibrium and kinetic models constructed by Fluor.
  - Viscosity increases consistent with prior results, but capture performance not impeded as much as anticipated.
  - Current formulation of BOL shows acceptable performance, but less viscous derivatives will show enhanced performance.
  - Prior thermodynamic model projections consistent with observed bench scale performance.

- **Other transformational (water-lean) solvent systems will behave similarly to CO_2BOLs**

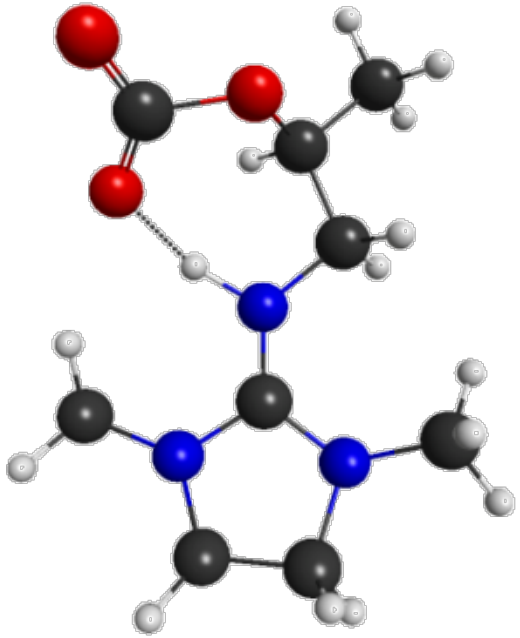
Applying Molecular Design Towards CO_2 Capture

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

What we need

(*specific for each solvent class*):

- Guanidine-based CO_2BOLs
  - High basicity needed for >90% CO_2 capture with acceptable solvent recirculation rates
- Cyclic base core to prevent hydrolysis



Viscosity Modifying Factors:

- Steric crowding
- Fine tuned electronics
- Cation-anion interactions
- Effect of hetero-atoms and charge solvation
- H-bonding orientation and strength

Applying Molecular Design Towards CO_2 Capture

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

What we need

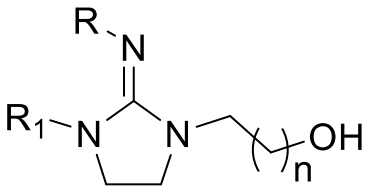
(*specific for each solvent class*):

- Guanidine-based CO_2BOLs
  - High basicity needed for >90% CO_2 capture with acceptable solvent recirculation rates
- Cyclic base core to prevent hydrolysis

Viscosity Modifying Factors:

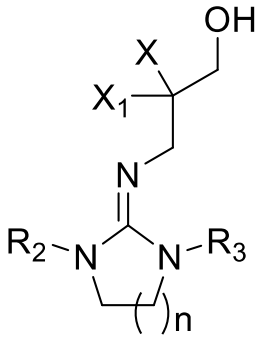
- Steric crowding
- Fine tuned electronics
- Cation-anion interactions
- Effect of hetero-atoms and charge solvation
- H-bonding orientation and strength

Steric Effects



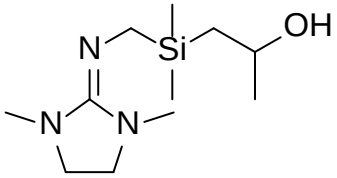
R=Pr, i-Pr, Bu, t-Bu
R_1=Me, Et, i-Pr
with n=1, 2, 3

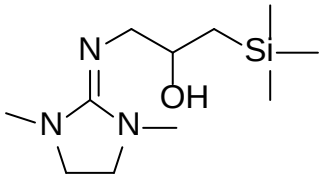
Electronic Effects



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

Charge Solvation (Silane-Based)



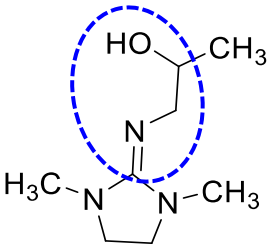


Integrating Molecular Modeling and Design Towards Liquids for CO_2 Capture

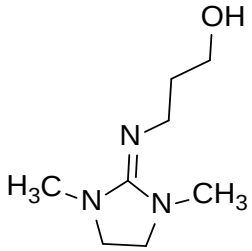
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Model validation through testing of known compounds
  - Evaluate inter- *vs* intra-molecular hydrogen bonding effects on viscosity
  - 3-D steric interactions
  - Reduced intermolecular interactions
- Simulate pure liquids and mixtures at 15%, 25%, and 50% CO_2, determine viscosity from analysis of trajectories

Control Molecules & Complexes

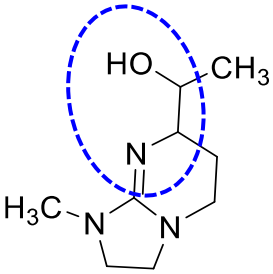


Current best-performing BOL
Viscosity ~ 200cP at 0.25 mol %CO_2

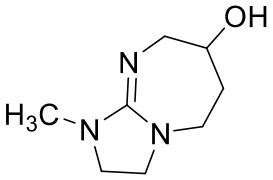


Poor performing BOL
Viscosity >>1,000 cP at 0.25 mol %CO_2

Trial Molecules & Complexes



-Preserves weights and functional groups of Current BOL (2nd amine and alcohol-i.e. similar CO_2 adsorption energy)
-Partially restrict mobility of aliphatic side chain w. 2nd ring.
-Favors internal H-Bond.
-May be a more readily synthesizable target.

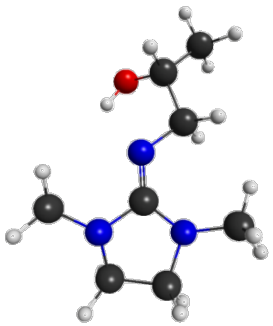


-Preserves weights and functional groups of Current BOL (2nd amine and alcohol, i.e. similar CO_2 adsorption energy)
-Restrict mobility of aliphatic side chain w. 2nd ring.
-Hinders internal H-Bond.

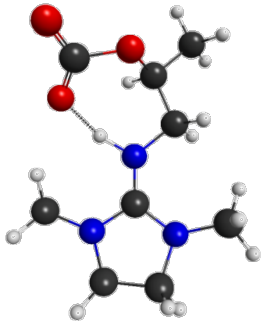
Computational Materials Design

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- *Ab Initio* Electronic Structure for Molecular Properties (~10^2-10^3 atoms)
  - Accurate description of molecular properties
  - Atomic charges and intermolecular contacts
  - Reaction energetics: H-bonding, CO_2 absorption energy
  - Spectroscopic properties: IR, Raman, NMR

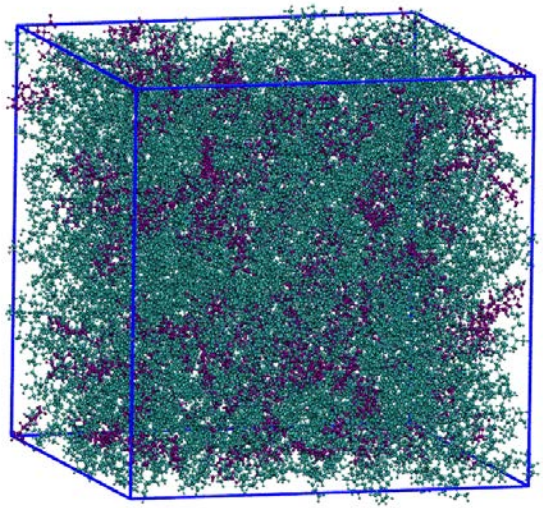


IPADM-2-BOL



CO_2-loaded IPADM-2-BOL

- Classical Molecular Dynamics (~10^4-10^5 atoms)
  - Accurate description of molecular liquid structure
  - Universal OPLS with *ab initio* charges
  - Transport properties: diffusion and viscosity
  - Viscosity can be directly computed from long simulations (1μs) Codes, Software: GROMACS (www.gromacs.org)



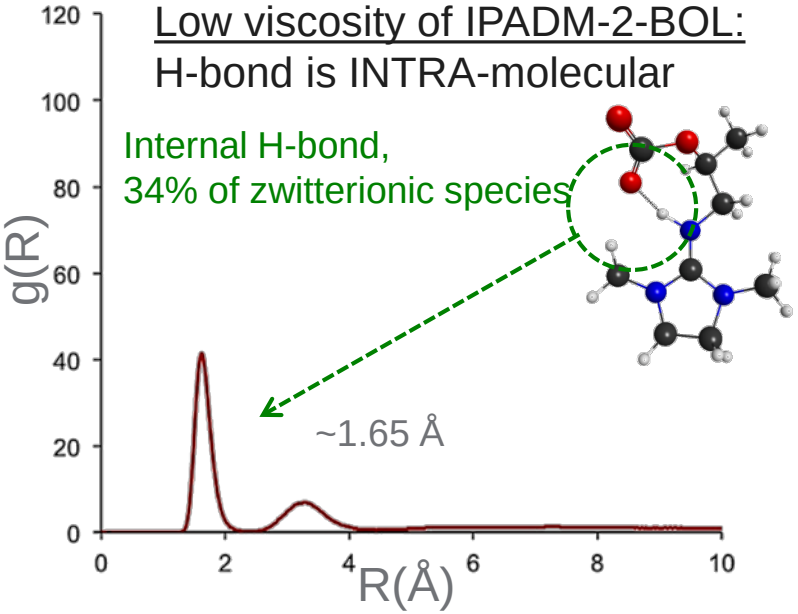
- Reduced ordered model capabilities
  - Shift through many candidates in short time (few days)

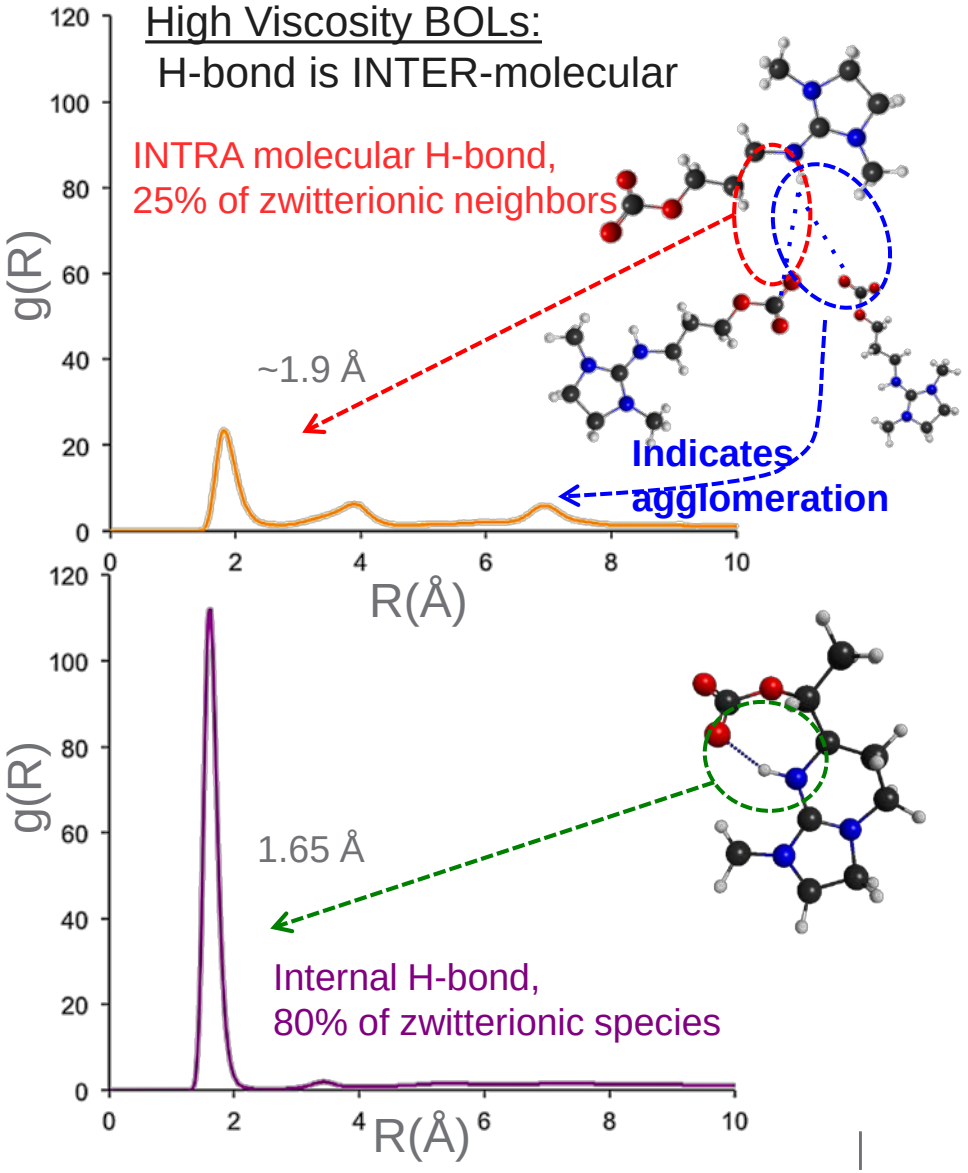
- Codes, Software:
  - CP2K (www.cp2k.org),
  - NWChem (www.nwchem.org)

Molecular-Level Interactions: The Hydrogen Bond

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965





Advanced molecular design:

Locking in an INTRA-molecular H-bond (~80%)

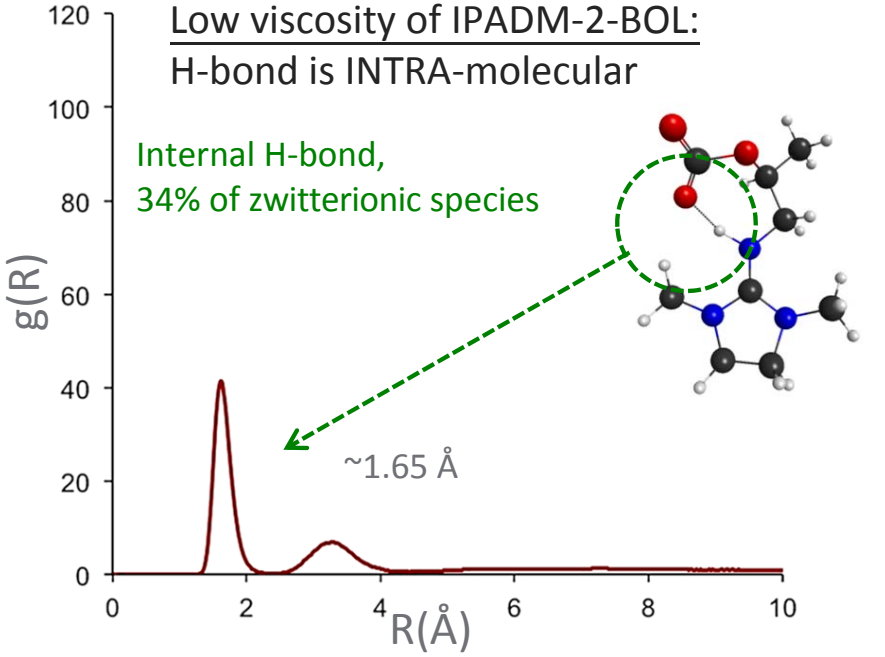
Lower projected cP at all CO_2 loadings

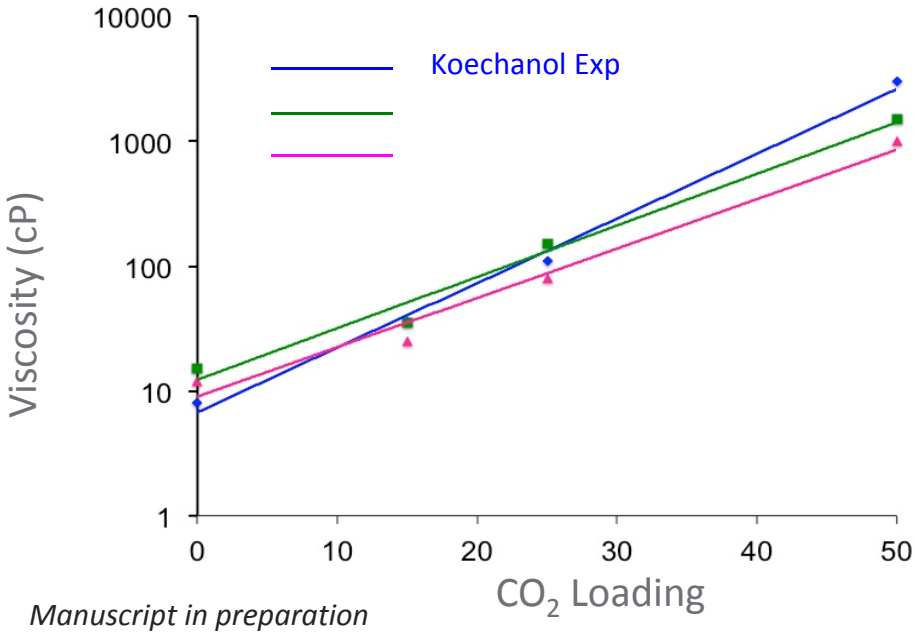
Manuscript in preparation

Molecular-Level Interactions: The Hydrogen Bond

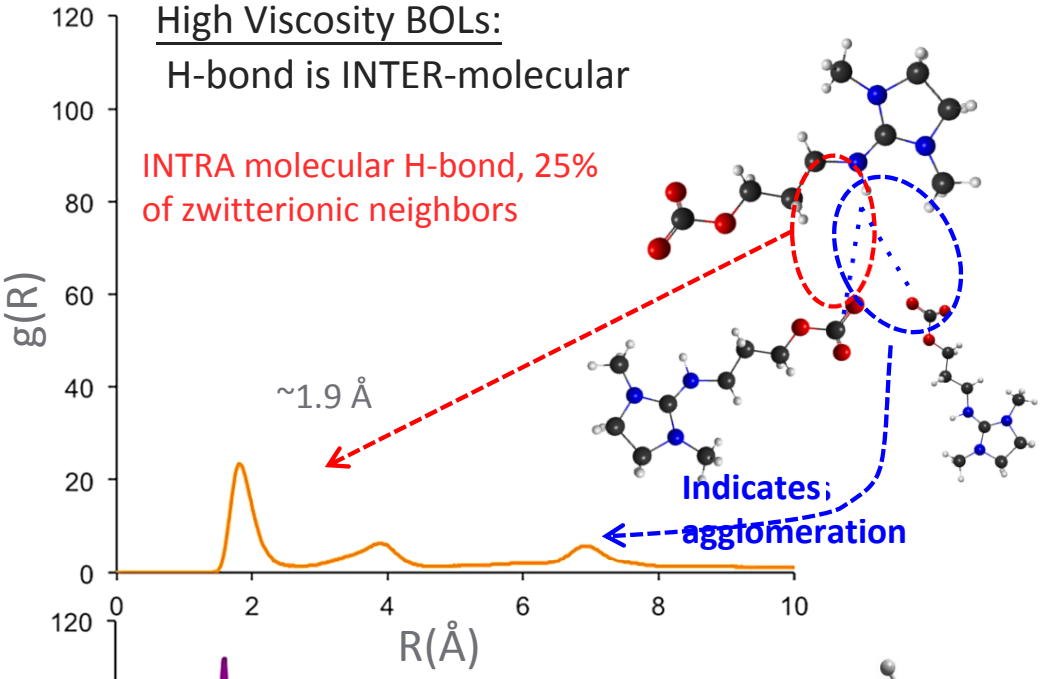
Pacific Northwest NATIONAL LABORATORY

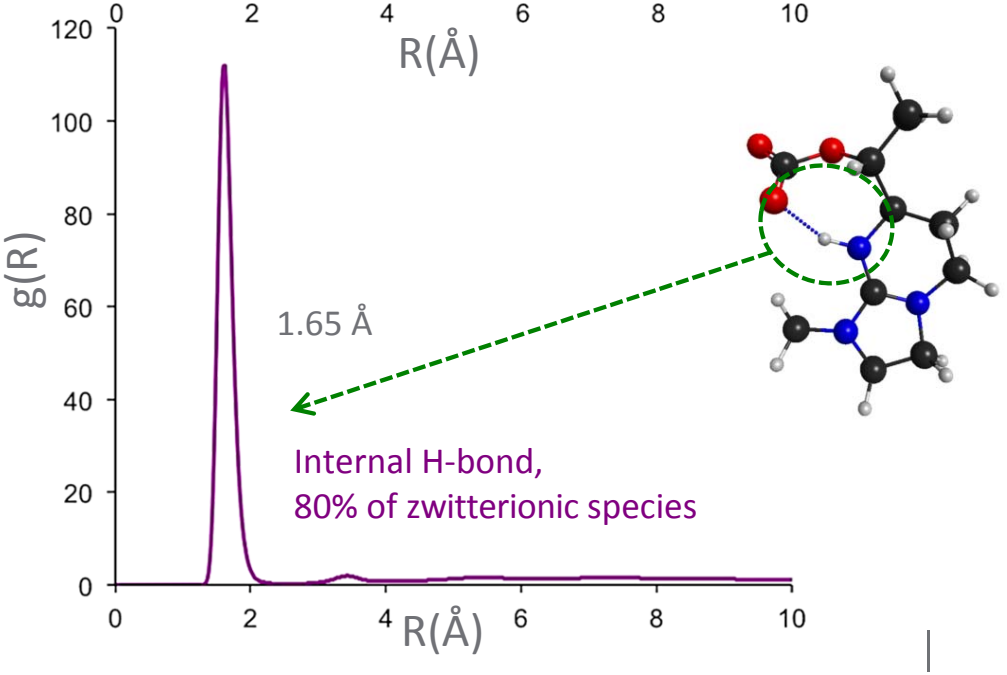
Proudly Operated by Battelle Since 1965





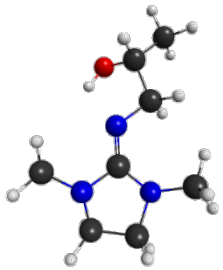
Manuscript in preparation





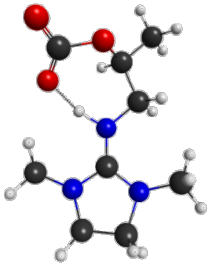
Validation of the Model With Experimental Data is Critical

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



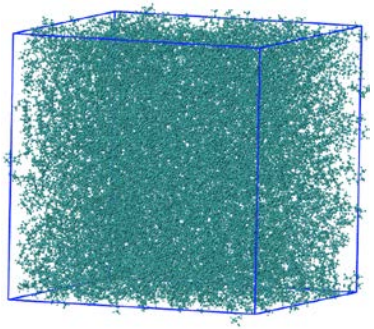
IPADM-2-BOL

System (IPADM-2-BOL)	Experimental viscosities (cP)	Calculated viscosities from MD (cP)
0% mol CO_2	8	15
15%mol CO_2	36	35
25%mol CO_2	110	150
50%mol CO_2	~3000	>1000

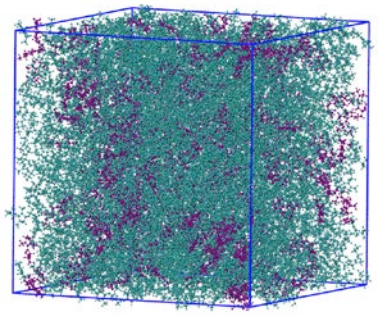


CO_2-loaded IPADM-2-BOL

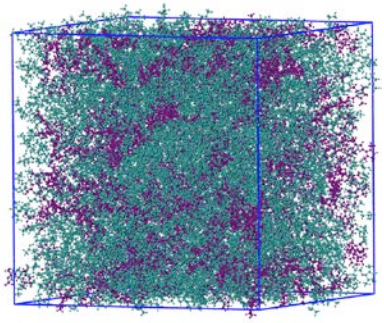
IPADM-2-BOL (0% CO_2)



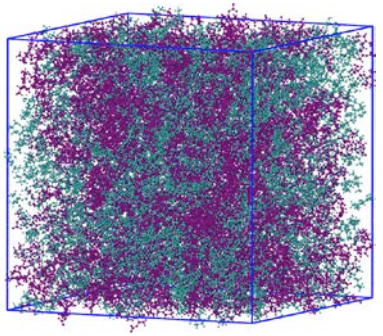
IPADM-2-BOL (15% CO_2)



IPADM-2-BOL (25% CO_2)



IPADM-2-BOL (50% CO_2)



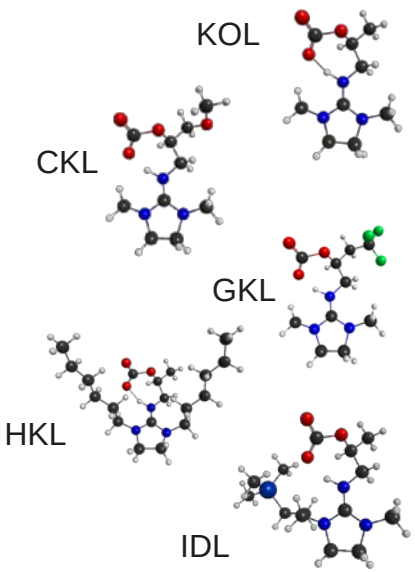
Energy Procedia 2015

Integration of Molecular Modeling and Molecular Design

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

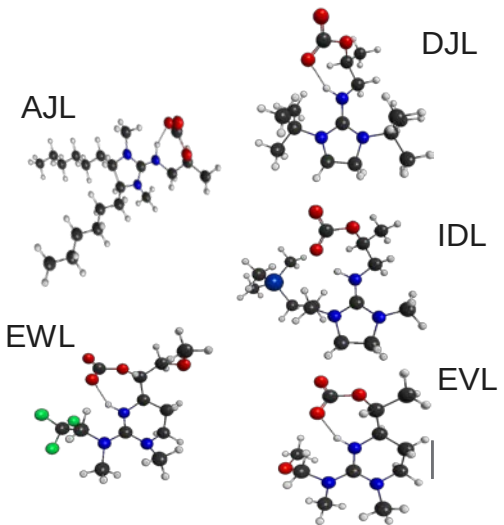
Validation of model performance with experimental data



Compound	Pint * (Model predicted)	ΔΔE (kJ/mol) (CO_2 BE)	η MD	(cP) (25%) Reduced	Exp
KOL	41% (34% MD calculated)	0.0	150	110	110
CKL	40% (52% MD calculated)	8.3	100	113	≦KOL
GKL	43% (34% MD calculated)	-5.6	100	104	N/A
HKL	15% (6% MD calculated)	21.9	250	234	N/A
IDL	75%	11.7	N/A	35	< KOL

Promising targets from validated reduced Model

Compound	Pint * (Model predicted)	ΔΔE (kJ/mol) (CO_2 BE)	(cP)(25%) Reduced model
DJL	87%	0.8	18
AJL	79%	16.2	30
IDL	75%	11.7	35
EWL	75%	-8.2	37
EVL	69%	-4.1	46



Manuscript in preparation

(*Pint = % of internal H-bond)

Current Work: Experimental Validation

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Comprehensive data collection equipment for liquid systems

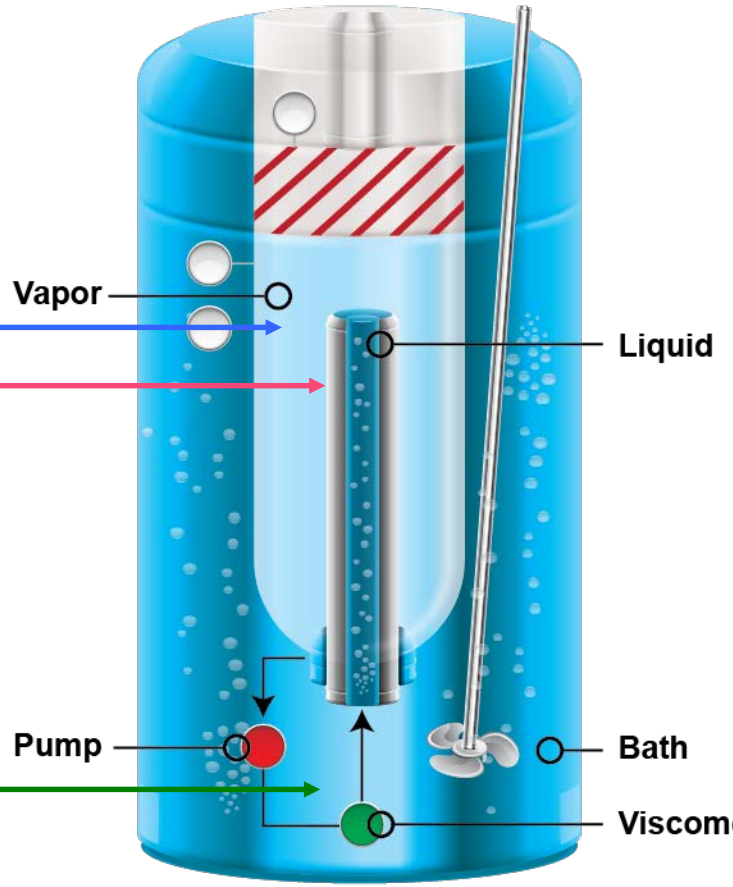
- Scale-up 5-L synthesis reactor
- PTx cells (equilibria data)
- Wetted-wall column (kinetics)
- Viscometer (transport data)
- Continuous-flow liquid and sorbent carts (mobile capability for flue gas evaluations)

5-L Synthesis Reactor

Wetted-Wall

Continuous Flow Cart

Custom ΔPVT Cell

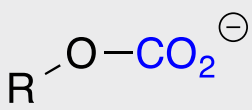
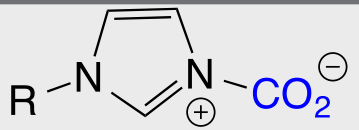


Enables equilibrium, kinetic and viscosity measurements on only 20 mL of sample

Benefits of Technology to the Program

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- An approach that can impact a broad set of materials (solvents)
- Rapid modeling and testing of all CO_2 binding mechanisms
- Detailed understanding of molecular level interactions and how it impacts process performance

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

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

Acknowledgements

- **Funding: US Department of Energy Office of Fossil Energy**
  - **FWP 65872, PM Andy Aurelio**

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

PNNL team:


Dr. Phillip Koech

Dr. Roger Rousseau
Dr. Vanda Glezakou

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


Mr. Charles Freeman


Mr. Mark Bearden

Collaboration:

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

EPRI ELECTRIC POWER RESEARCH INSTITUTE
Mr. Abhoyjit Bhown

Lawrence Livermore National Laboratory
Dr. Josh Stohlaroff,
Dr. John Vericella

THE UNIVERSITY OF CALIFORNIA IRVINE
Prof. Aaron Esser-Kahn