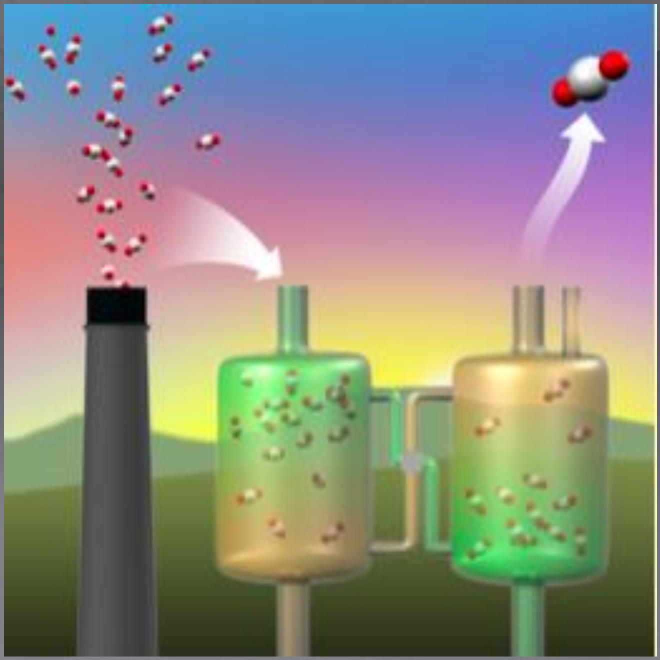

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# Low-Viscosity, Water-Lean $CO_2$BOLs with Polarity-Swing Assisted Regeneration (FWP-70924)

DAVID J. HELDEBRANT

NETL $CO_2$ CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
AUGUST 13, 2018

U.S. DEPARTMENT OF ENERGY

DOE/NETL Federal Project Manager: Sai Gollakota

# Acknowledgment



"This material is based upon work supported by the U.S. Department of Energy under Field Work Proposal FWP-70924."

# Project Objectives

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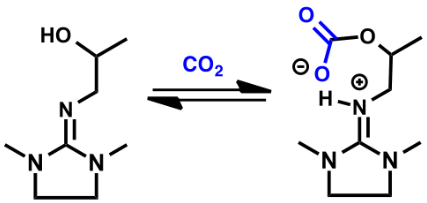
- Rapidly scale-up and demonstrate a promising 3rd Generation CO2BOL solvent candidate from prior solvent development work (1-BEIPADIP-2-BOL)
  - Retains water-lean functionality (only 5-10% water in circulated solvent)
  - Retains shift in polarity upon loading with $CO_2$ (i.e. still leverages polarity swing)
  - Is a single-constituent solvent (not a blend)
  - Developed to overcome past viscosity challenges (<50cp when fully loaded)
- Leverage the capabilities in the Carbon Capture Simulation for Industry Impact ($CCSI^2$) program.
- Engage industry – recently formed a team with RTI, EPRI, and Fluor Corporation

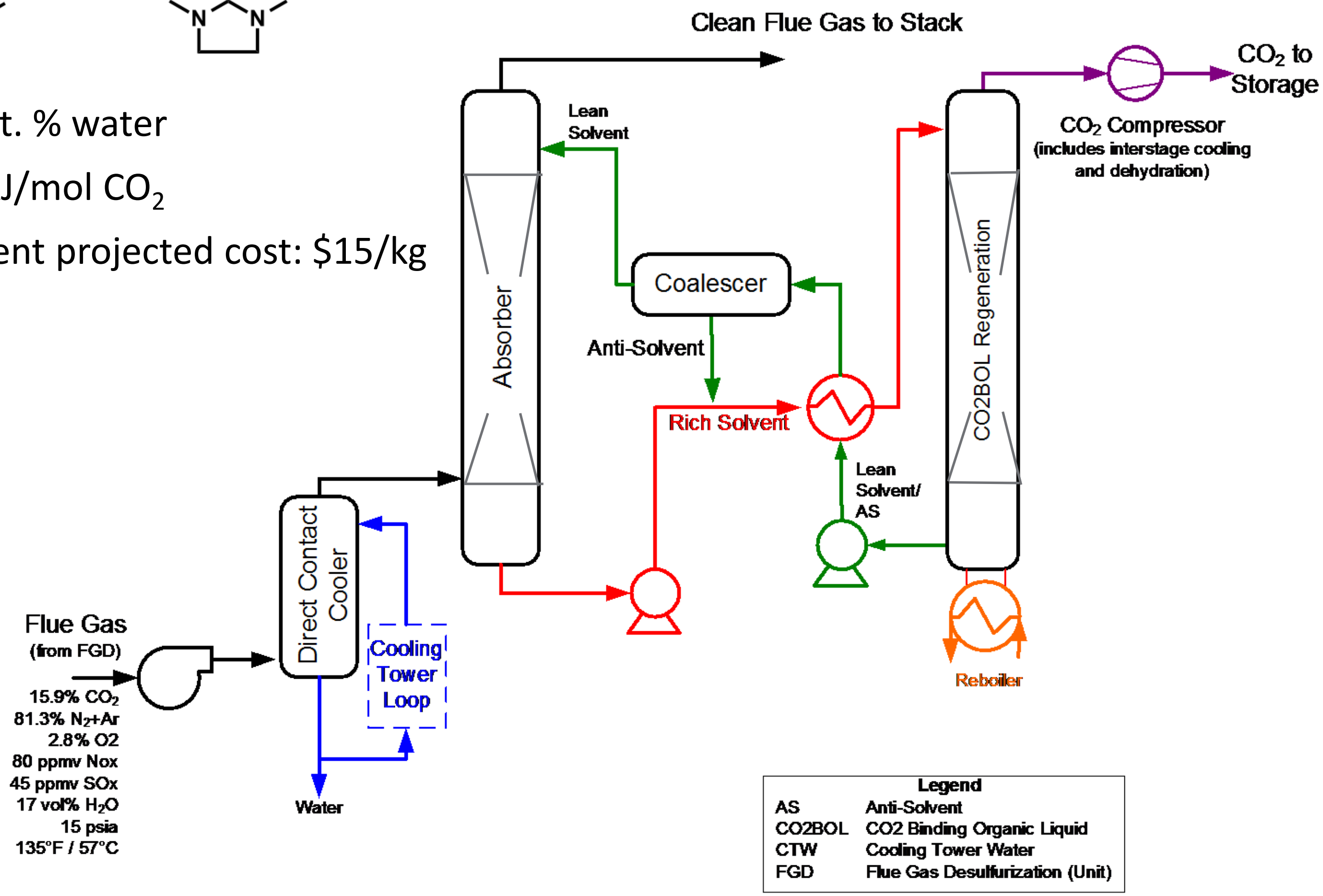
# $CO_2$-Binding Organic Liquids ($CO_2$BOLs)

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






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




*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;

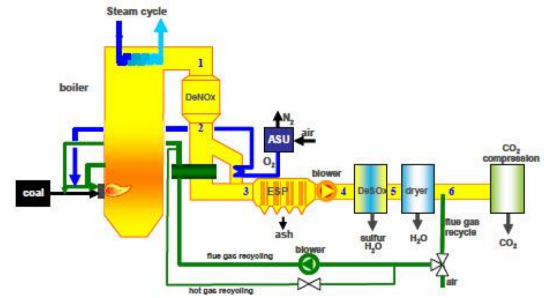
# Project Funding & Tasks



**Funding: $2,792,000 / 36 months**

Solvent Scale-up

Parametric testing: $O_2$, $SO_x$, $NO_x$, $H_2O$



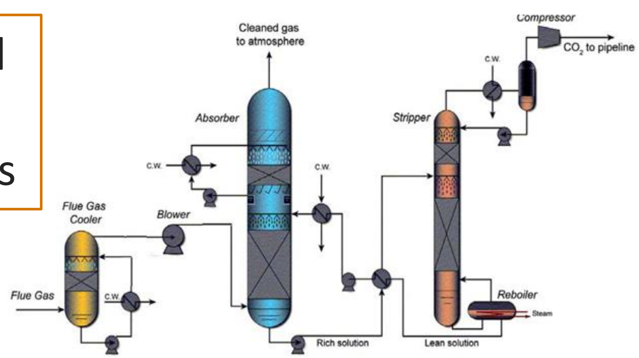

Kinetic Testing

Techno-economic Assessment

CCSI$^2$ Carbon Capture Simulation for Industry Impact

aspentech

Absorber and Stripper Configurations




Industry Handoff

# Project Funding & Tasks

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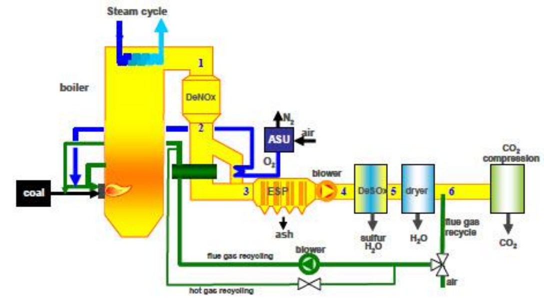
**Funding: $2,792,000 / 36 months**

Solvent Scale-up

**2L synthesized**

Parametric testing: $O_2$, $SO_x$, $NO_x$, $H_2O$

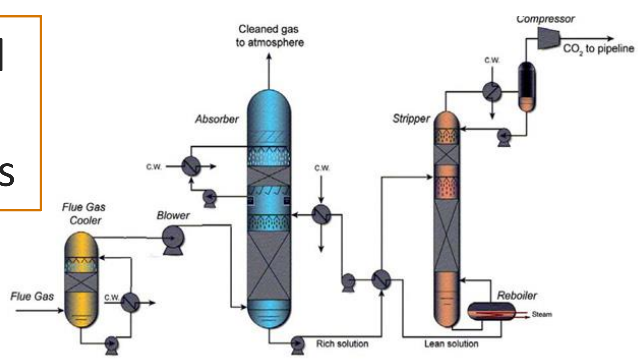



Kinetic Testing

Techno-economic Assessment

**Preliminary TEA In Progress**

Absorber and Stripper Configurations




Industry Handoff

**Industrial Extension Started**

# Project Plan

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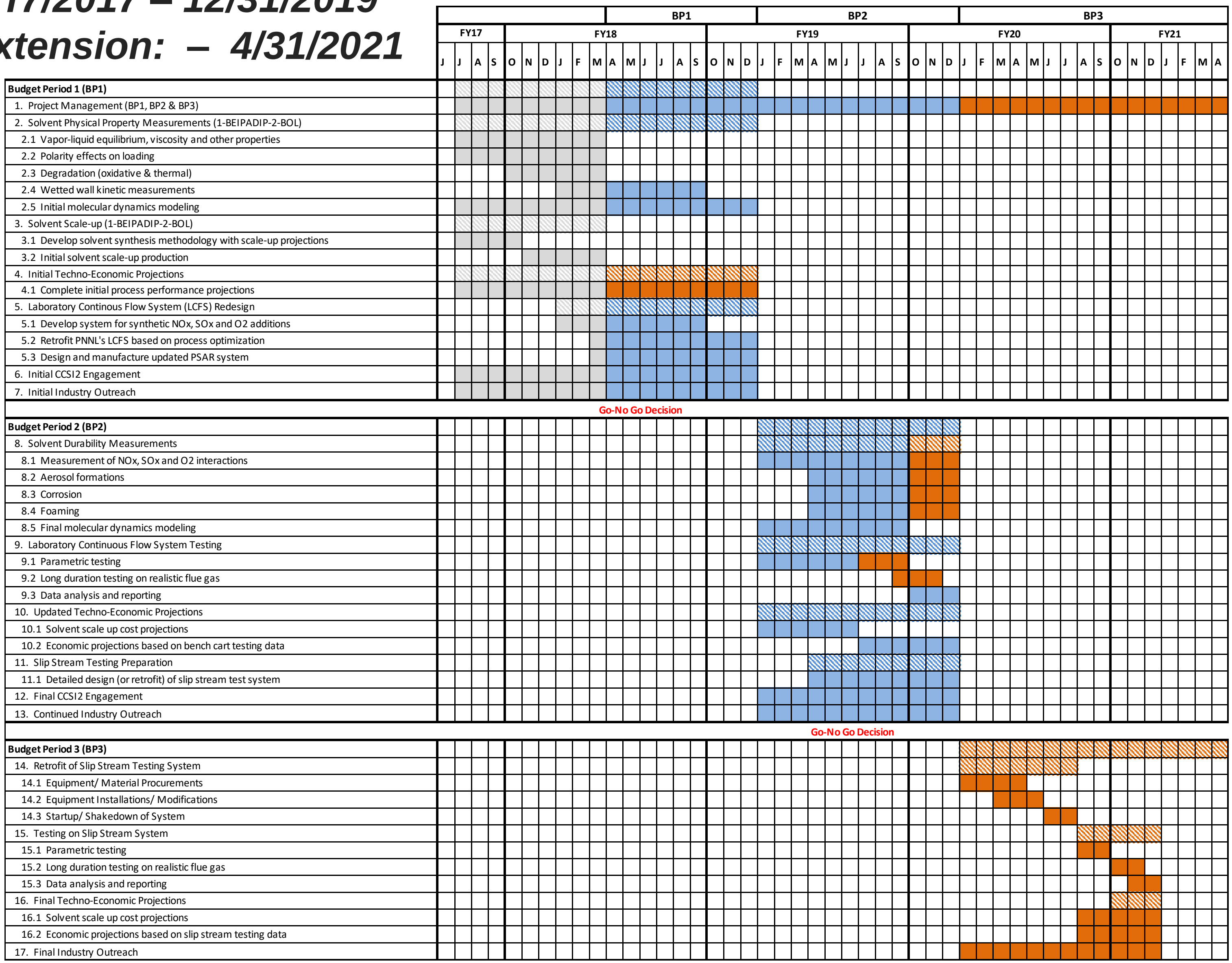
## *7/17/2017 – 12/31/2019*
## *Extension:  –  4/31/2021*



# $CO_2$BOL Evolution

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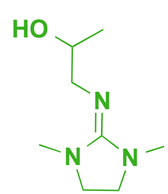
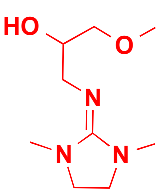
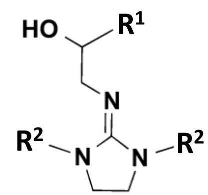
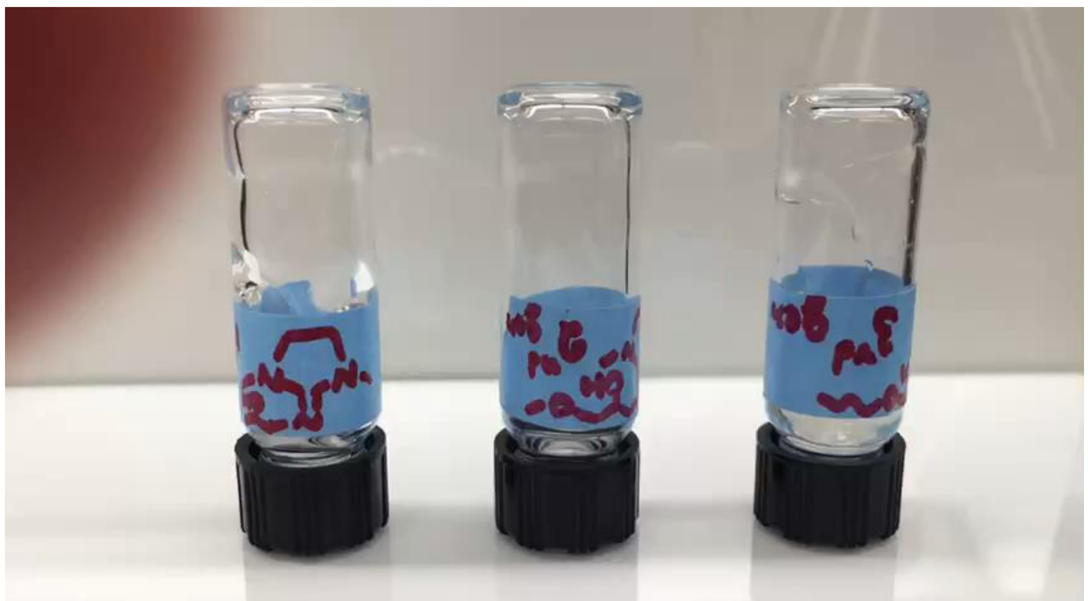
## ***3rd Generation derivatives are 98% lower in viscosity.***







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

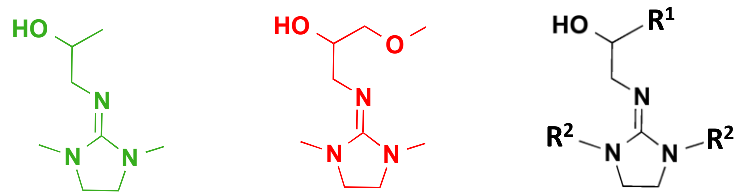


**$CO_2$BOL Generations**

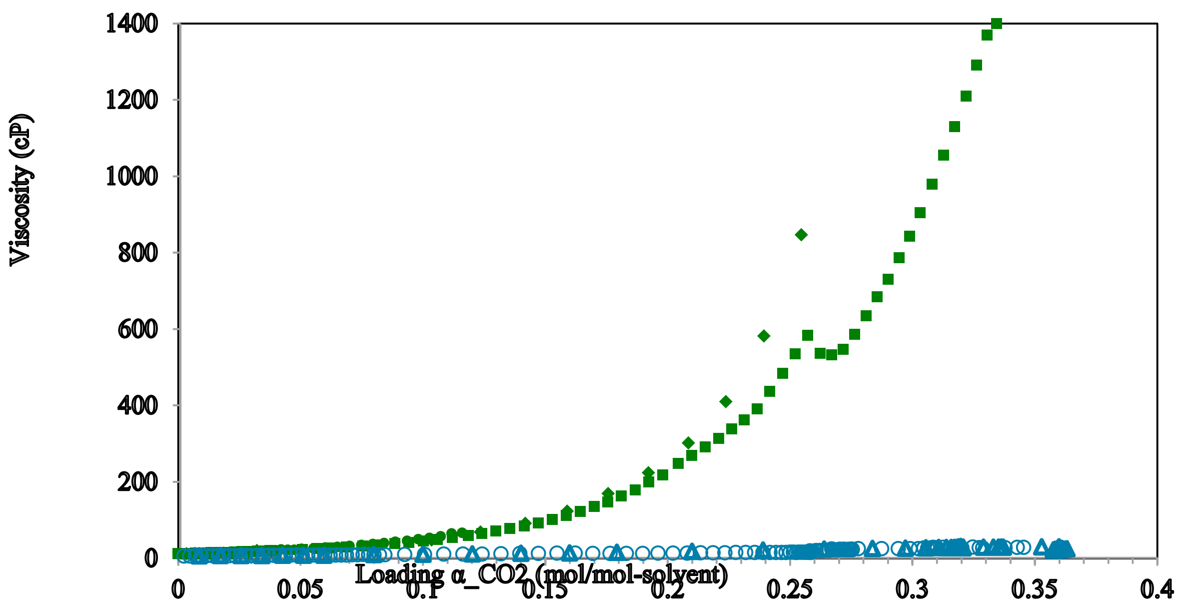
Malhotra *et al., Manuscript In Preparation.*

# $CO_2$BOL Evolution

***3rd Generation 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% $CO_2$

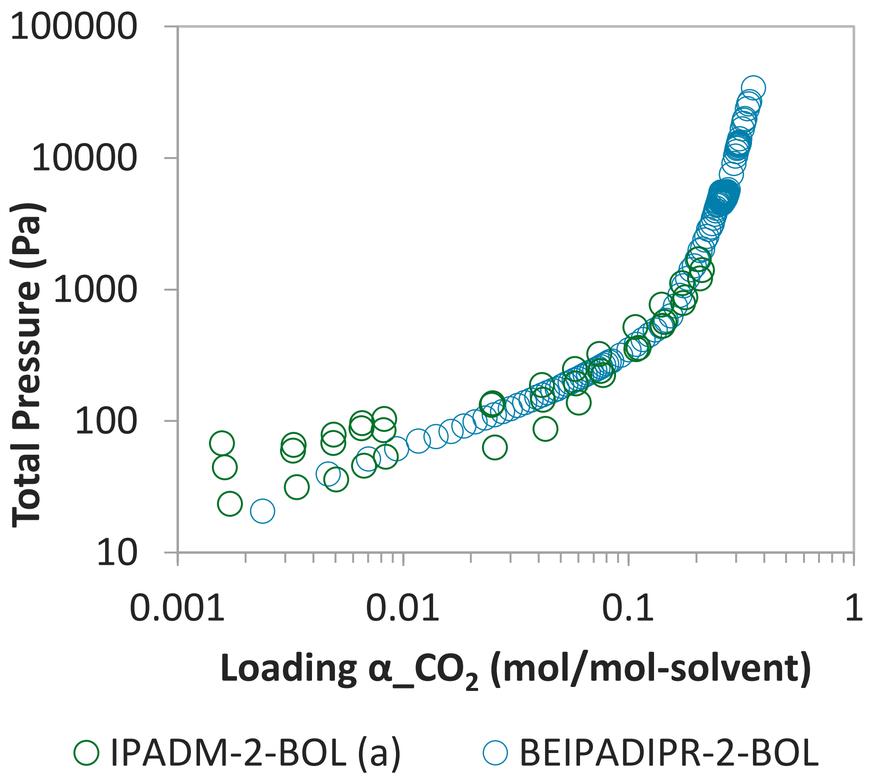



**$CO_2$BOL Generations**

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

# 3rd Generation Derivative Properties

***PVT testing shows physical and thermodynamic properties were retained.***




Malhotra *et al., Manuscript In Preparation.*

# 3rd Generation Derivative Properties

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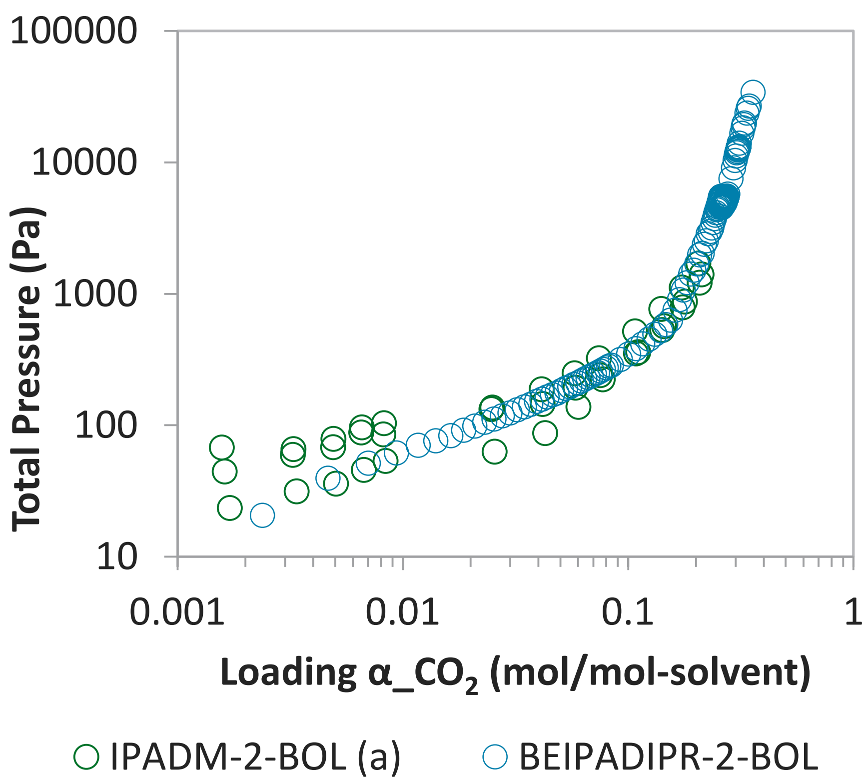
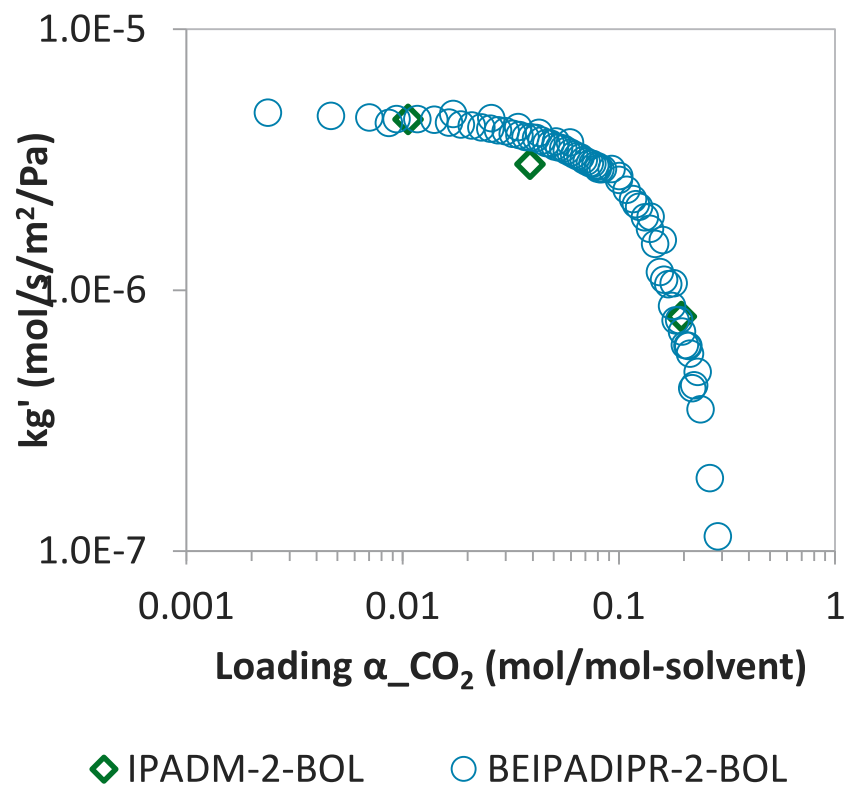
***PVT testing shows physical and thermodynamic properties were retained.***




- 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.*

# 3rd Generation Derivative Properties

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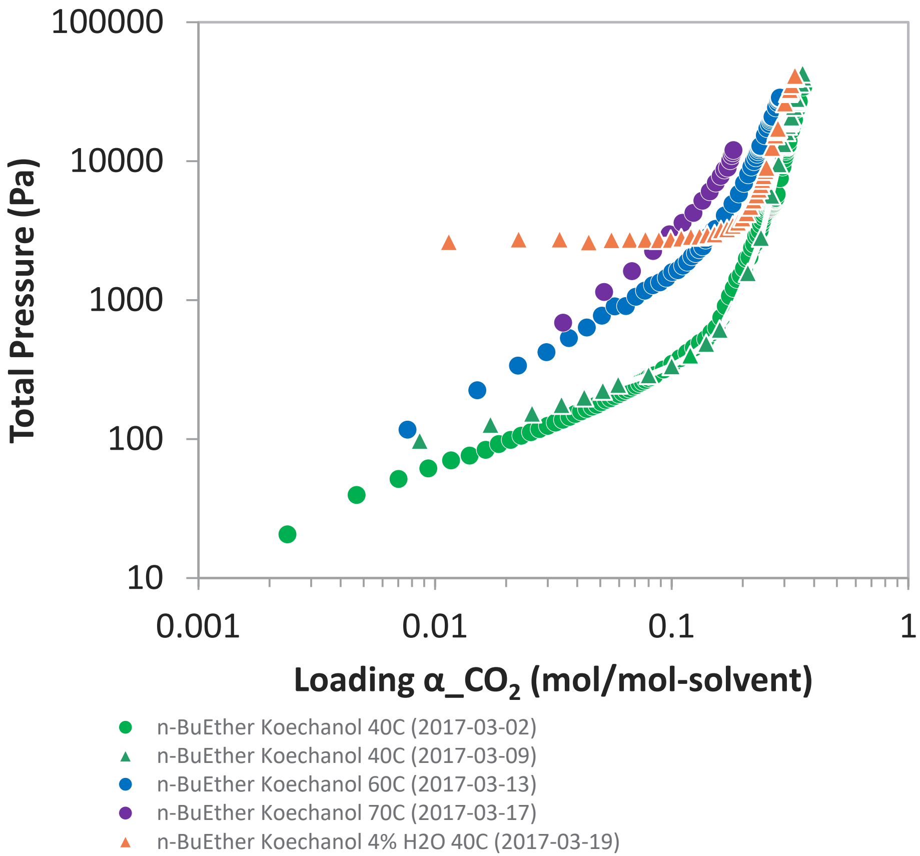
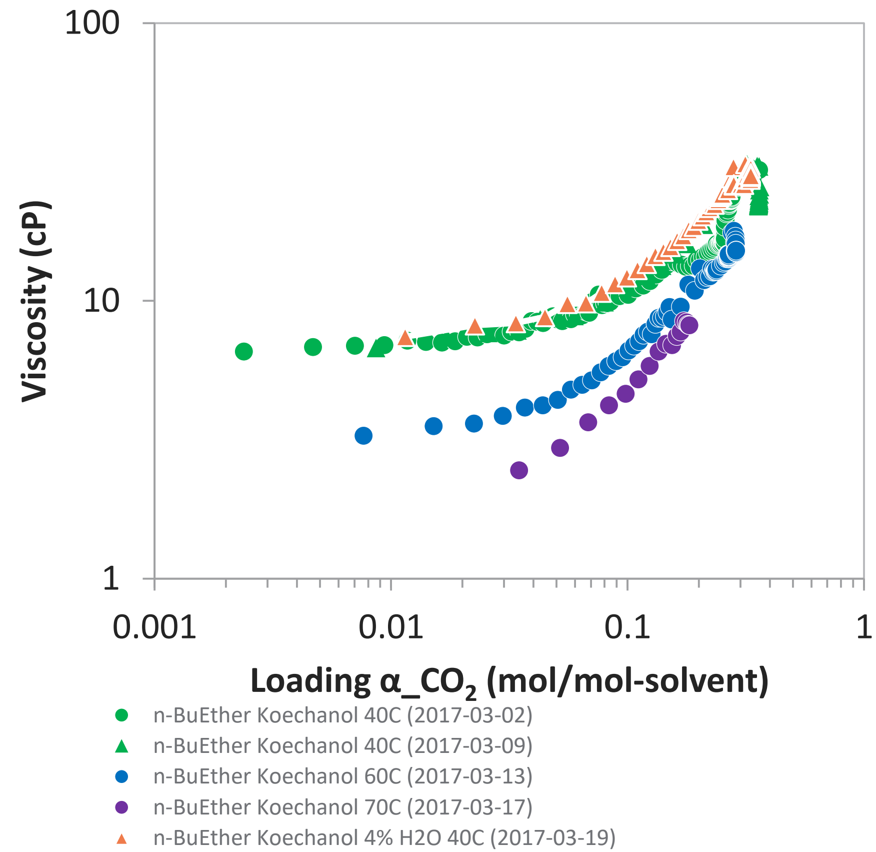
***PVT testing shows reasonable VLE, viscosity, kg'***




- Minimal impact of water on viscosity
- 2.5 and 7.5 wt% isotherms needed to fully quantify VLE with water



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

# 3rd Generation Derivative Properties

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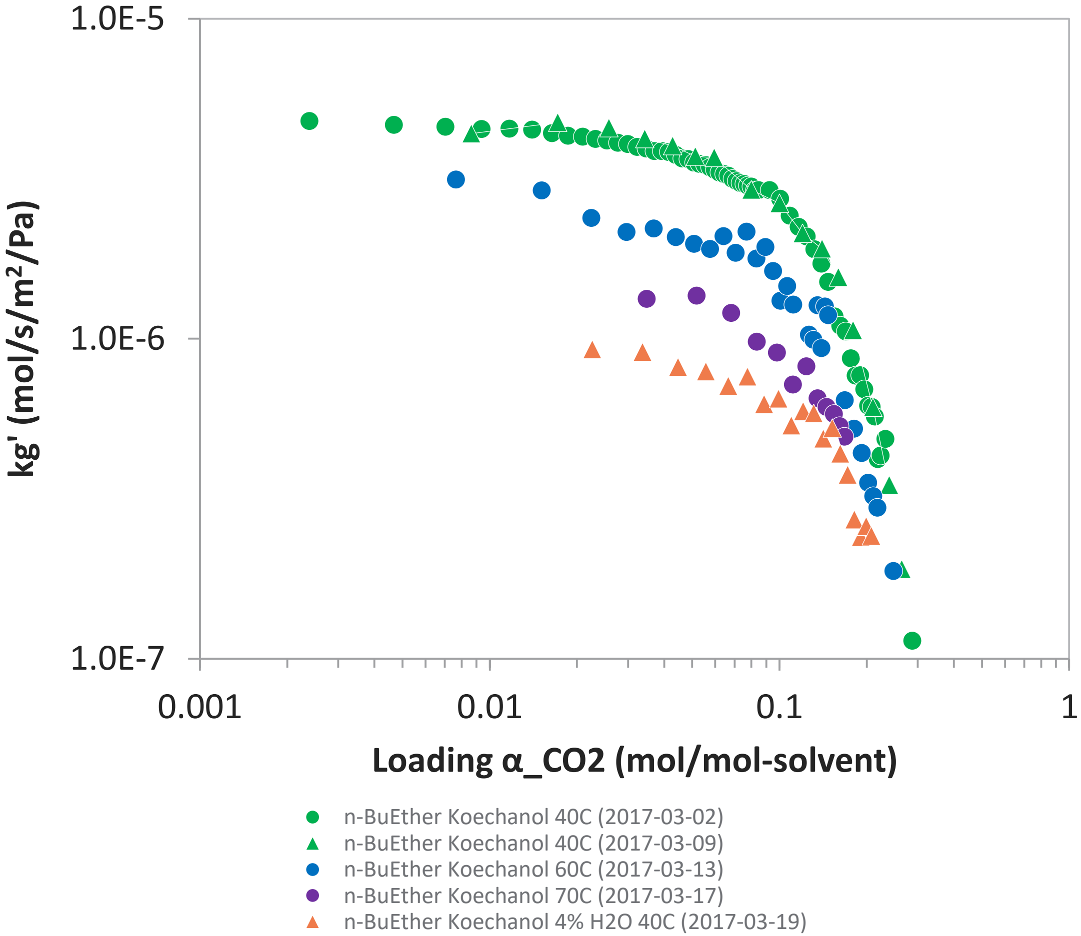
***PVT testing shows rapid kg' for $CO_2$.***




- Comparable (*kg'*) of $CO_2$ compared to piperazine and MEA



Malhotra *et al., Manuscript In Preparation.*

# 3rd Generation Derivative Properties

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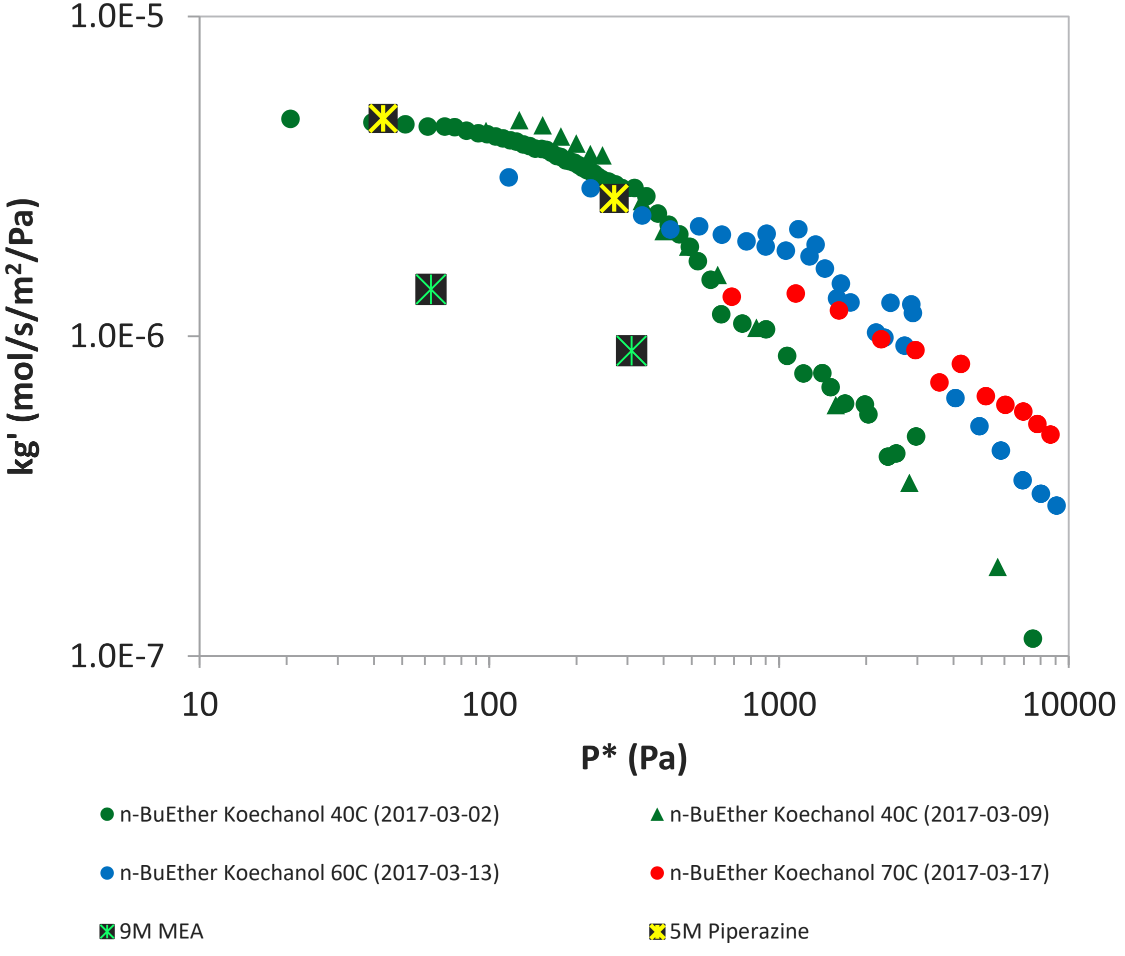
***PVT testing shows comparable (kg') of $CO_2$ compared to piperazine, higher than MEA as a function of driving force.***






5M PZ and 9M MEA data from UT Austin

# 3rd Generation Derivative Scale-Up Synthesis

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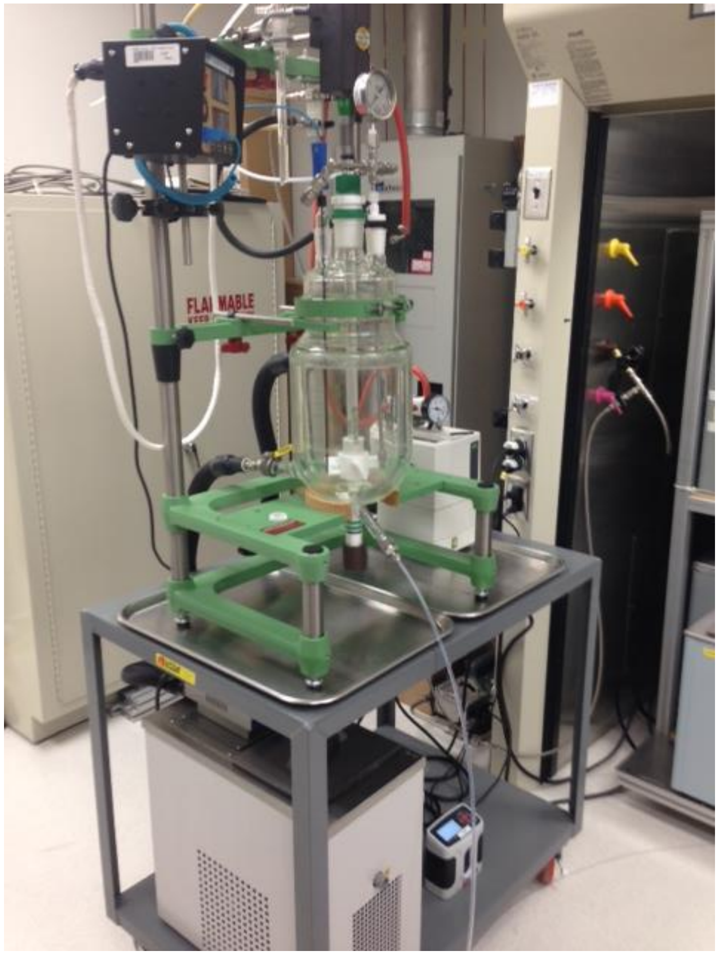
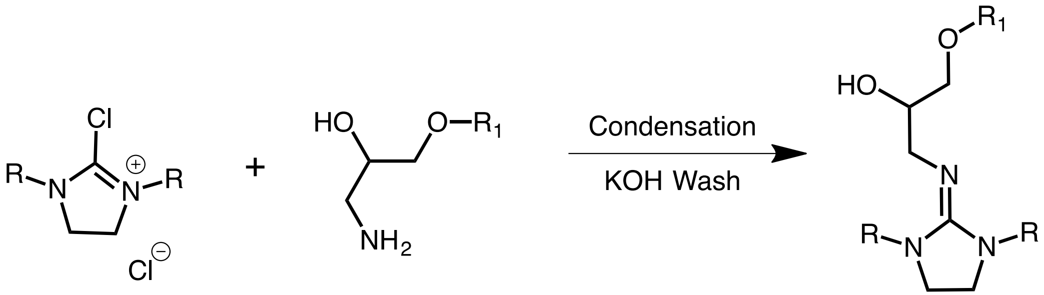
***Synthesis of 2L of solvent for property testing***




- All reagents made in-house
  - Previous scales: 10-50g
  - Current batch size: 100-300g

# 3rd Generation Derivative Properties

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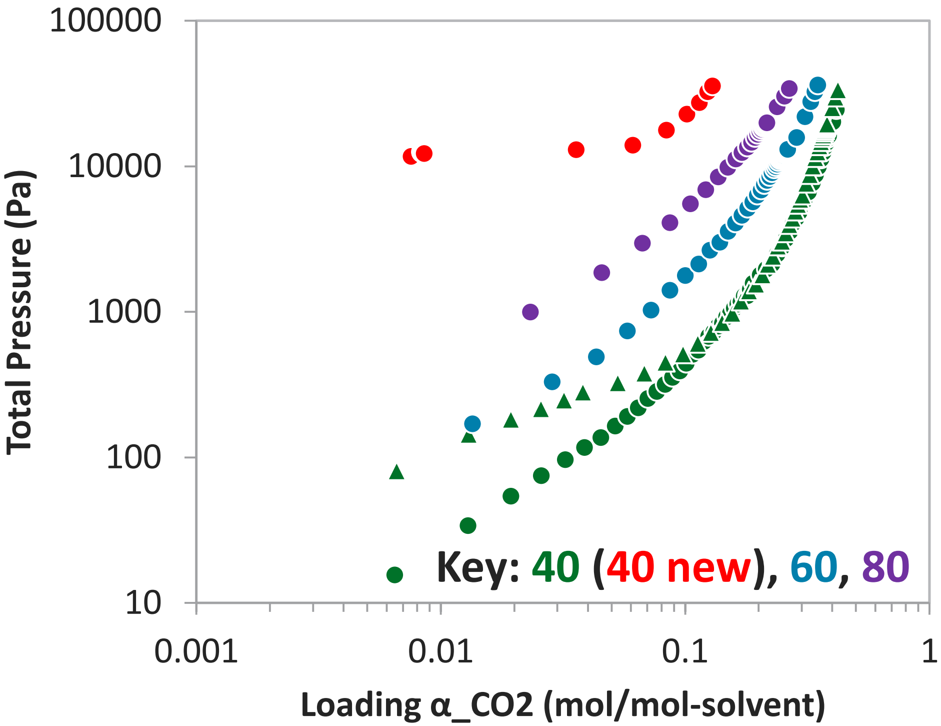
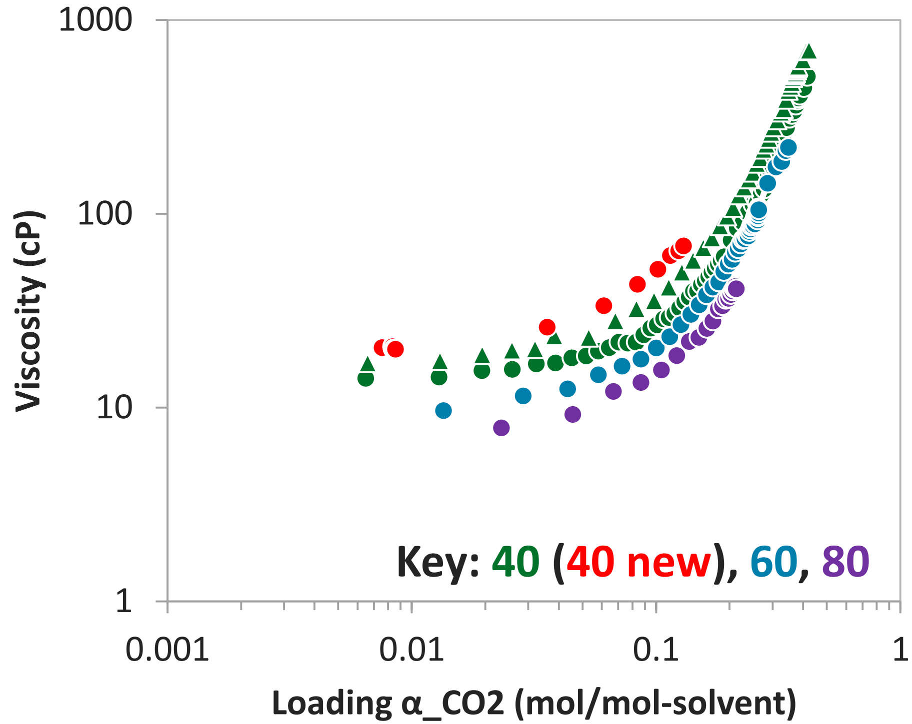
***PVT testing of scaled-up (2 L) compound is showing different properties than small-scale batches.***



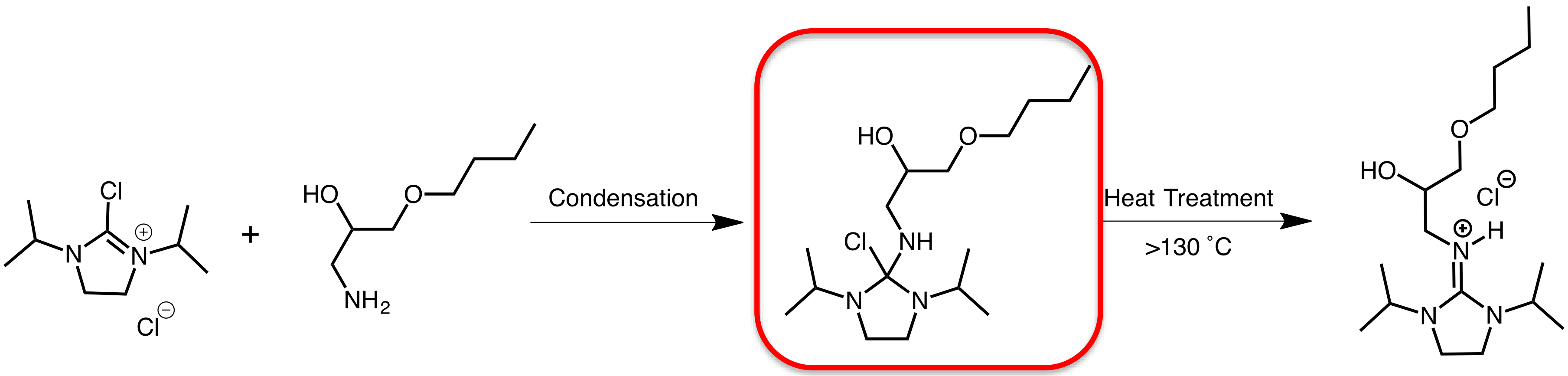

- Sample binds and releases $CO_2$ but has different VLE *and* viscosity
- Suggests a different compound



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

# 3rd Generation Derivative Characterization

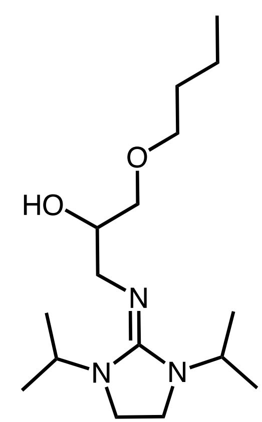
***$^{1}H$ and $^{13}C$ NMR, IR & Mass Spec data all indicate the same compound,***




BP= 130 ˚C @ 11mm hg

BP= N/A

- Ether based amino alcohol condensed with Vilsmeier salt
- Chloro-intermediate condenses losing HCl, producing 1-BEIPADIP-2-BOL

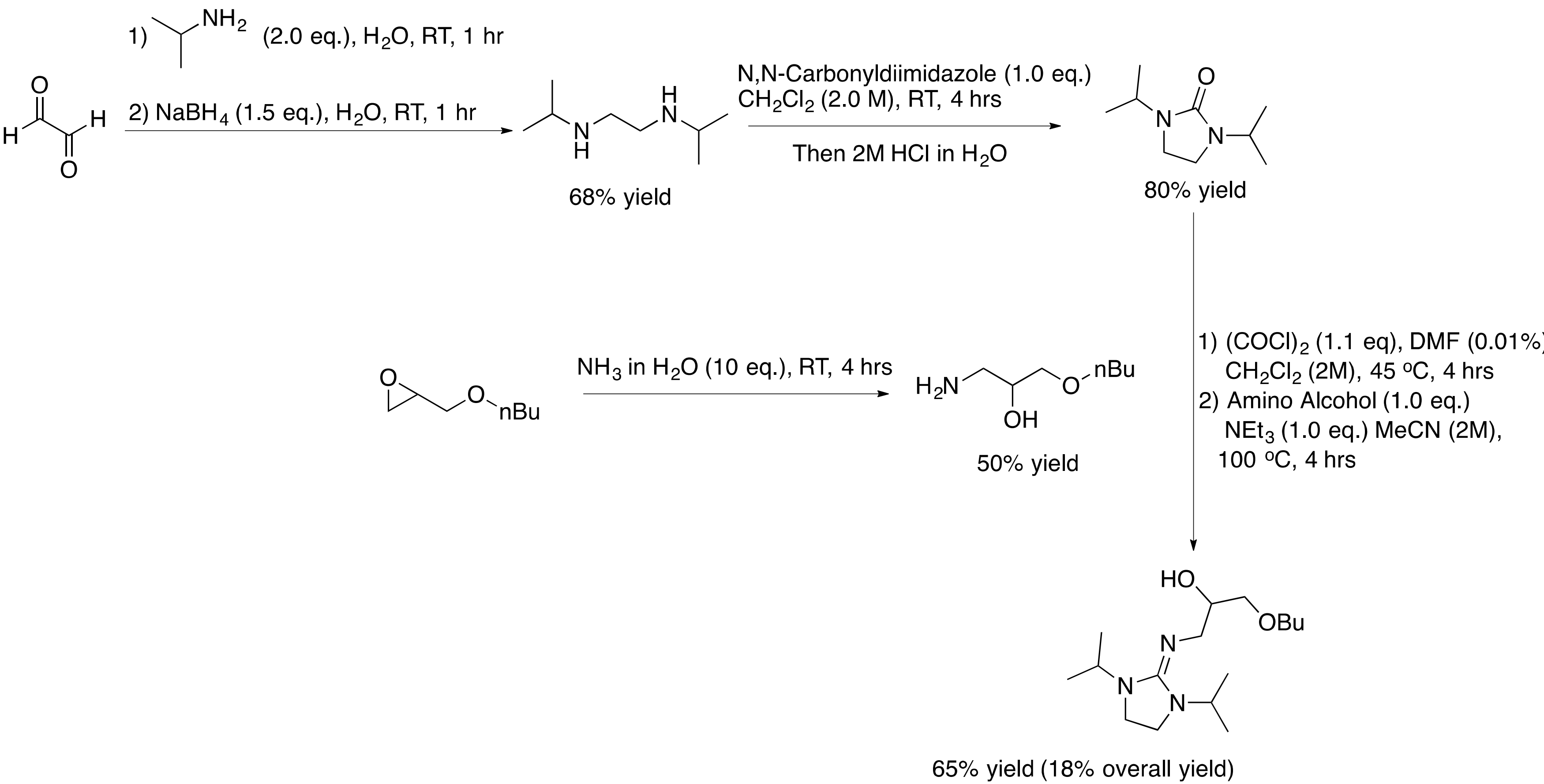



BP= 150 ˚C @ 11mm hg

****Scale-up of custom solvents is not trivial and due diligence must be used.***

# Alternative 3rd Generation Derivative Scale-Up

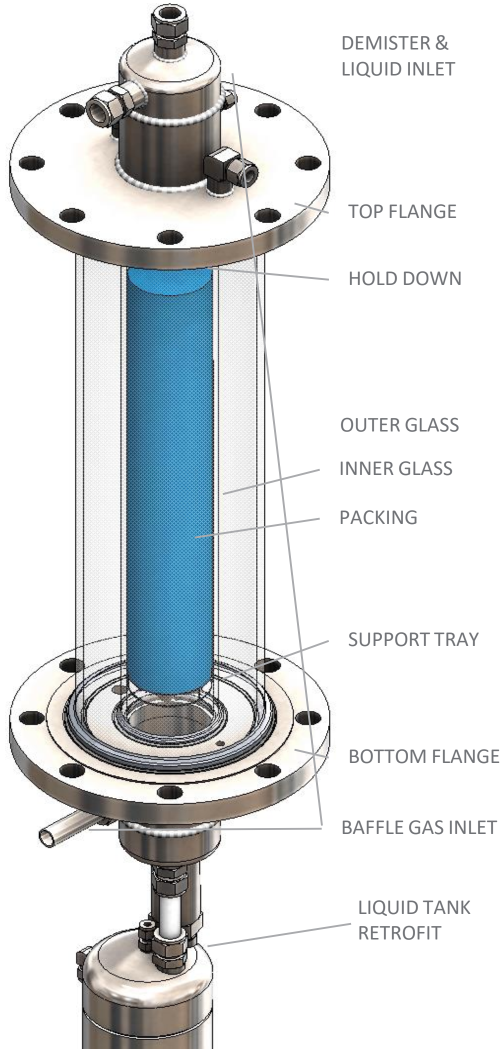
***Currently working on alternative methods of synthesis to bypass intermediates and achieve ($10/kg) cost targets.***




- Revised synthesis increased yields and potential for 50% reduced costs

# Continuous Flow Cart Upgrade, Retrofit & Shakedown

***Using CCSI² toolset to redesign PNNL's testing cart for optimal data collection. Shakedown on 1st gen solvent late August***




- All infrastructure has been sized and ordered
  - Columns
    - Glass for assessment of flow and phase behavi
    - Jacketed stainless for formal measurements
  - Sampling valves (liquid and gas on absorber/stripper/coalescer)

# $CO_2$BOL/PSAR Optimal Process Configurations

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***Optimal process configurations are solvent-specific.***

Preliminary assessment of solvent regeneration configurations for 1-BEIPADIP-2-BOL-1

| Solvent | MEA | BOL | | BOL | | BOL | | BOL | |
|---|---|---|---|---|---|---|---|---|---|
| Configuration | SS | SS | | TSF | | IHC | | LVC | |
| AS/BOL (mol/mol) | | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| Reg. Temp (°C) | 116 | 130 | 108 | 130 | 105 | 130 | 108 | 129 | 104 |
| Reg. Pressure (bar) | 1.62 | 1.81 | 1.81 | 1.81 | 1.81 | 1.81 | 1.81 | 1.81 | 1.81 |
| Pressure ratio | | | | 1.75 | 1.75 | | | 1.8 | 1.8 |
| Heat rate (GJ/tonne $CO_2$) | 3.67 | 2.11 | 2.10 | 2.48 | 2.28 | 1.98 | 1.97 | 1.91 | 1.90 |
| Plant $\eta$ (%, HHV) | 25.4 | 28.7 | 29.3 | 28.1 | 29.1 | 28.9 | 29.5 | 28.6 | 28.9 |

Increasing antisolvent loading in PSAR has minimal effect
Lowest Heat Rate= LVC
Lowest $W_{eq}$= IHC



*All calculations performed using ASPEN Plus.

# Thermodynamic Efficiency of the $CO_2$BOL/PSAR Configurations

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***Calculated equivalent work consumption (kJ/mol $CO_2$) for varied stripper configurations using ASPEN Plus.***

| Solvent | MEA | BOL | BOL | BOL | BOL | BOL |
|---|---|---|---|---|---|---|
| Configuration | SS | SS | TSF | IHC | AFS | LVC |
| Reboiler/heater[(b)] | 36.7 | 21.0 | 24.8 | 19.8 | 23.1 | 19.2 |
| Cooling | 2.4 | 1.3 | 1.4 | 1.1 | 1.2 | 1.1 |
| Refrigeration[(c)] | | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 |
| Pump | 0.04 | 0.14 | 0.14 | 0.14 | 0.14 | 0.14 |
| Compressor | 13.2 | 12.8 | 11.9 | 12.8 | 12.8 | 14.7[(d)] |
| Total | 52.4 | 37.3 | 40.3 | 35.9 | 39.3 | 37.2 |

(a) None of the above scenarios is optimized.
(b) A Carnot efficiency ($\eta\_(stm-tb)$) of 0.9 is used.
(c) The inlet flue gas is chilled by R-134A refrigeration cycle.
(d) This value includes the work of both $CO_2$ compressor and lean vapor compressor

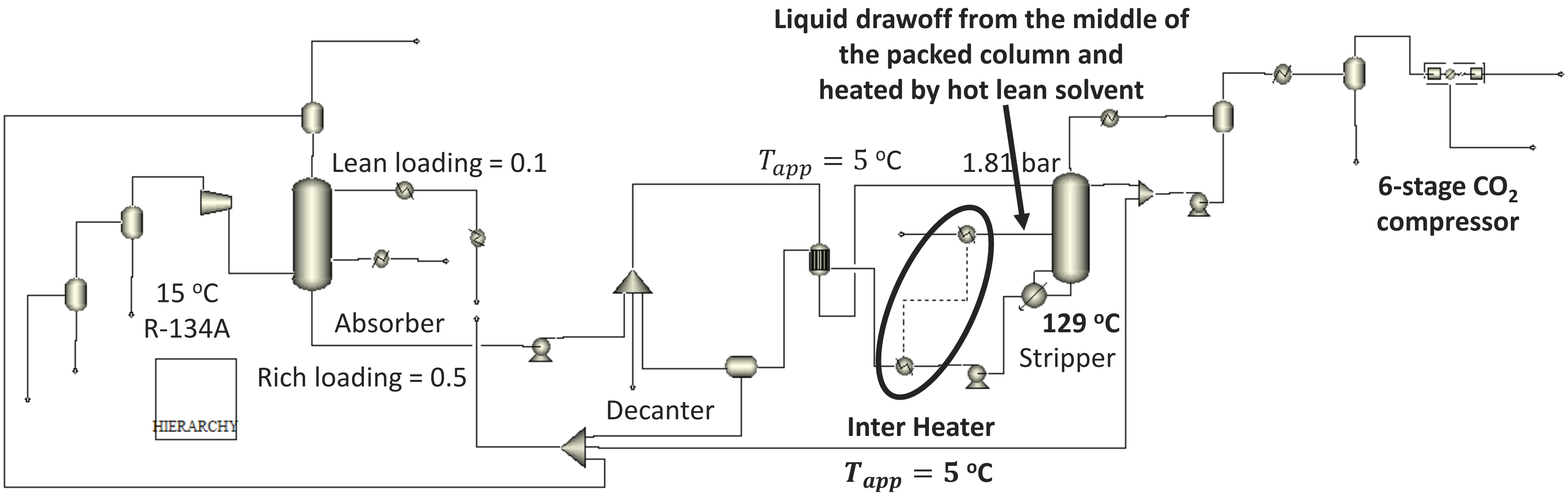
*Modeling of LLE is empirical at this stage
**Identified LLE data needs for more comprehensive analysis



SS= simple stripper, TSF= two stage flash, IHC= inter-heated column, AFS= advanced flash, LVC= lean vapor compressor

# Optimal Stripper Configuration for 1-BEIPADM-2-BOL/PSAR

*Interheated Column (IHC) had the lowest total equivalent work and was used to the preliminary TEA.*




**Advantages**: strip out $CO_2$ more efficiently – prevent rich feed from substantial flashing at the top of stripper

**Disadvantages**: additional plant complexity

# Initial TEA of 1-BEIPADM-2-BOL/PSAR

***Preliminary sizing and cost analysis indicates BEIPADM-2-BOL CAPEX is ~35% higher than MEA, but half of that of IPADM-2-BOL.***

| | No Capture | MEA | IPADM-2-BOL/PSAR | BEIPADM-2-BOL/PSAR (AS:BOL=2:1) | |
|---|---|---|---|---|---|
| | NETL Case 9 | NETL Case 10* | (356 cP) | SS | IHC |
| Fuel Cost | 1.52 | 2.20 | 2.03 | 1.91 | 1.90 |
| Capital Cost | 3.12 | 5.95 | 7.88 | 5.91 | 5.89 |
| Variable Cost | 0.51 | 1.02 | 1.03 | 0.97 | 0.96 |
| Fixed Operating Cost | 0.78 | 1.33 | 1.24 | 1.17 | 1.16 |
| Tran., Seq., Mon. | ------ | 0.59 | 0.56 | 0.53 | 0.52 |
| Total ¢/kWh | 5.94 | 11.09 | 12.75 | 10.48 | 10.44 |
| Increase VS No Capture | ------ | 86.7% | 115% | 76% | 76% |

*Recreated Case 10

**$CO_2$BOL processes are unoptimized, values subject to change.

***CAPEX is currently limited by heat exchanger size and solvent cost.

*COE calculation methodology from Energy & Fuels 30 (2), 1192-1203.

# Preliminary TEA

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***Preliminary sizing and cost analysis indicates BEIPADM-2-BOL Is making progress towards DOE's $30/tonne target.***

| | NETL Case 10* – MEA | $CO_2$BOL/PSAR IPADM-2-BOL | $CO_2$BOL/PSAR BEIPADIP-2-BOL-SS | $CO_2$BOL/PSAR BEIPADIP-2-BOL-IHC |
|---|---|---|---|---|
| Rich solvent viscosity (40 ˚C) | 10 | >353 | 36 | 36 |
| Estimated Reboiler Duty (GJ/tonne $CO_2$) | 3.67 | 2.67 | 2.11 | 1.97 |
| Net Plant Efficiency (HHV) | 25.4% | 27.5% | 29.3% | 29.5% |
| Capital Cost (M USD) | 423.5 | 1103.3 | 599.7 | 608.1 |
| ¢/kWh | 11.09 | 12.75 | 10.48 | 10.44 |

*Recreated Case 10
**$CO_2$BOL processes are unoptimized, values subject to change.

# Conclusions

- Solvent scale-up challenges are not insignificant
- BEIPADM-2-BOL has comparable mass transfer to 5M PZ
- Total equivalent work calculated by Aspen Plus is 35.9 kJ/mol $CO_2$
  - Includes all units of operation
  - Currently unoptimized
- BEIPADM-2-BOL reboiler duties as low as 1.9 GJ/tonne $CO_2$
- Modeling of LLE is highly empirical at this stage
  - Identified LLE data needs for more comprehensive analysis
- No one size fits all configuration, optimal process configurations appear to be solvent-specific
- BEIPADM-2-BOL projects 50% lower CAPEX than IPADM-2-BOL, 35% higher than MEA
  - Costs still limited by heat exchanger and solvent cost

# Acknowledgements

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

DOE/NETL PM: Sai Gollakota

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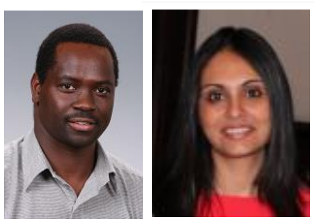
## PNNL Team

Solvent Design
Chemical Durability
Synthesis & Scaleup

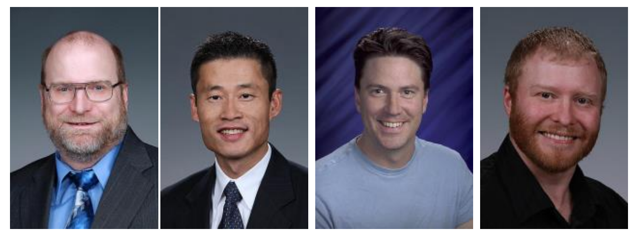


Dr. Phillip Koech
Dr. Deepika Malhotra

Advisory Computational Modeling

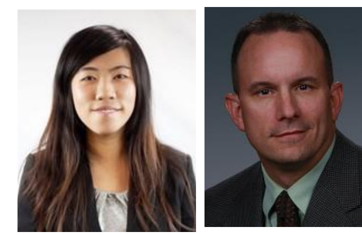
Dr. Vanda Glezakou
Dr. Roger Rousseau

Parametric Materials Testing & Analysis



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

Process
Modeling
Performance
Projections



Dr. Yuan Jiang
Charles Freeman

## Collaborators

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Dr. Josh Stolaroff

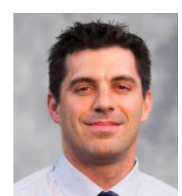
RTI INTERNATIONAL

Dr. Marty Lail

EPRI

Abhoyjit Bhown

CCSI[2] Carbon Capture Simulation for Industry Impact



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FLUOR®

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