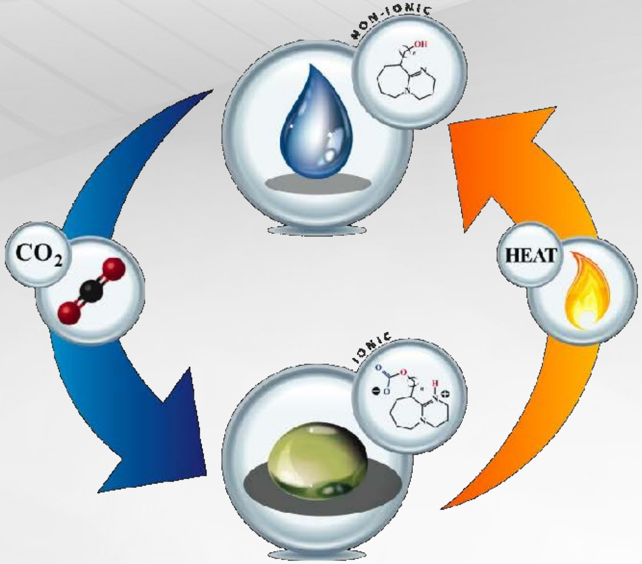


CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process With a Polarity-Swing-Assisted Regeneration

DAVID J. HELDEBRANT

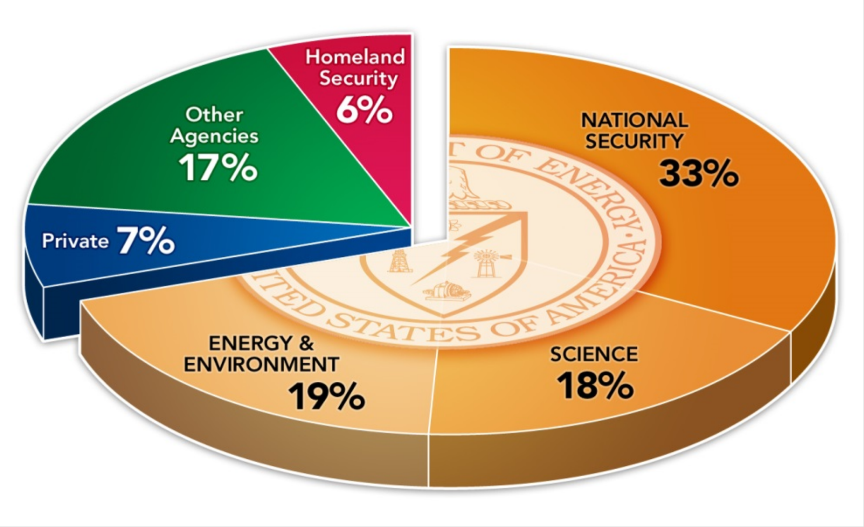
NETL CO_2 CAPTURE TECHNOLOGY MEETING
PITTSBURGH, PA
JULY 30, 2014

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 5 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.

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

Limitations:

- Some advanced solvents have not yet demonstrated water tolerance
- Full dehydration impractical
- Cost challenges with a custom solvent

Unknowns:

- Unknown compatibility with existing infrastructure
  - Absorber, stripper
  - Cross exchanger
- Viscosity increase as a function of CO_2 loading

Image taken from www.separatinosnow.com

Project Overview

- Project Team:
  - PNNL; project lead, materials development, testing
  - Fluor Corporation; process engineering, technology assessment
  - Queens University; PSAR testing, EH&S

- Project Award:
  - DOE funding:1.99 million/ 30 months
  - Cost share (Fluor): 500k
  - Sub contract (Queens) 130k
  - Project start Oct 1, 2011

- Project Scope:
  - To advance CO_2BOLs/PSAR from TRL 3 through 4 through bench-scale testing

Goals and Objectives

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Goals

- Further develop and verify the performance of the process combining CO_2 binding organic liquids (CO_2BOLS) with newly discovered polarity-swing-assisted regeneration (PSAR) process.

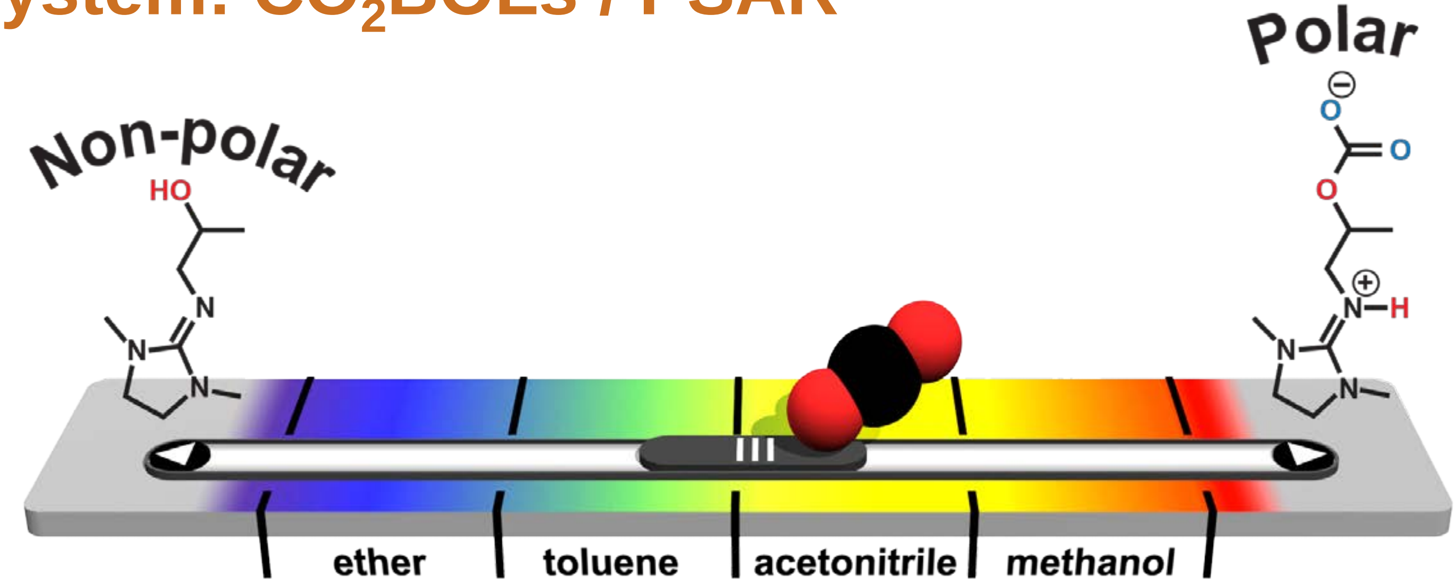
Objectives

- Develop the CO_2BOLs/ PSAR solvent and process configuration against DOE's carbon capture goals of 90% CO_2 capture and a Levelized-Cost of Electricity (LCOE) increase of <35%.
- Collect necessary additional thermodynamic and kinetic information to develop an optimized process configuration for the CO_2BOLs/ PSAR concept that can be demonstrated at bench scale.
- Conduct a bench-scale demonstration of the technology that includes extended testing for quantifying solvent makeup requirements, by-product formation, and equipment corrosion.
- Use bench-scale testing data to make robust energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system.
- Quantify large-scale EH&S impacts for the technology.

Project Schedule and Tasks

- **BP 1** (Oct 2011-Dec 2012)
  - 1. Project Management
  - 2. Initial techno-economic assessment
    - Full process description and analysis
    - Cost estimates
    - Measurement of missing data
    - Revise technology performance targets
  - 3. Bench-scale design and retrofits for PSAR
    - Solvent scale up of two candidate BOLs
    - Retrofit equipment for PSAR
- **BP 2** (Mar 2013-Jun 2014)
  - 4. Bench-scale testing
    - Shakedown testing
    - Bench-scale testing on liquid PSAR and solid PSAR
  - 5. Full technology assessment

Our System: 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.

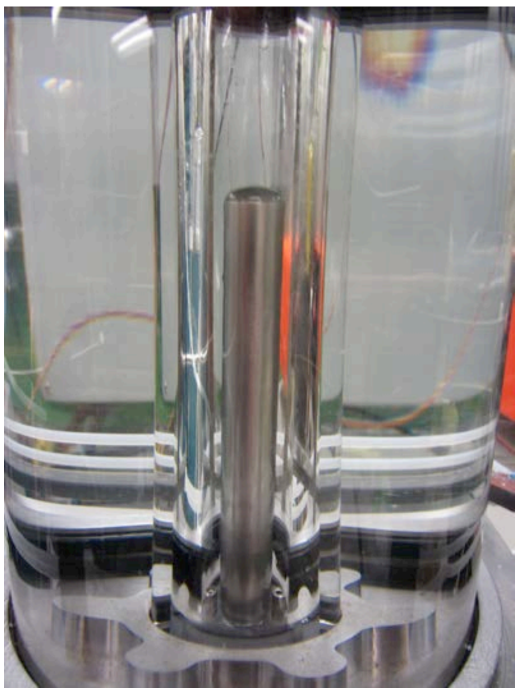
Nature, (**2005**), 436, 1102; *Ind. & Eng. Chem. Res.* (**2008**); 47, 3, 539, *Energy Environ. Sci.*, (**2008**), 1, 487
Koech *et al. RSC Adv.*, (**2012**), 3, 566-572, *Energy. & Env. Sci.* (**2013**), 6, 2233 - 2242

PNNL's Testing Equipment Facilities

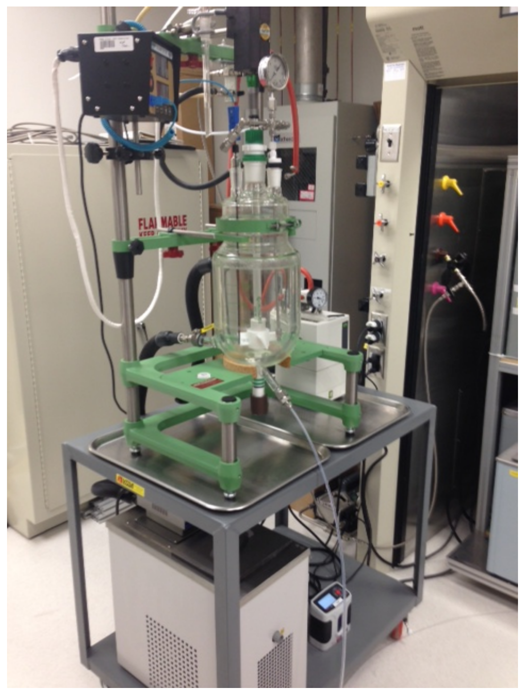
Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- PNNL's Carbon Capture Laboratory Completed in 2012
- $2,000,000 in internal investments
- Facilities include wetted wall column, PTx cells & Mobile Bench-Cart, viscometers, 5L synthesis reactor
- Over four months of continuous testing on a single batch of solvent

Wetted Wall



5-L Synthesis Reactor

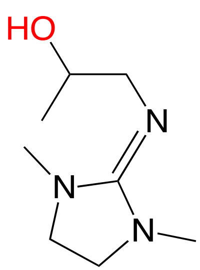


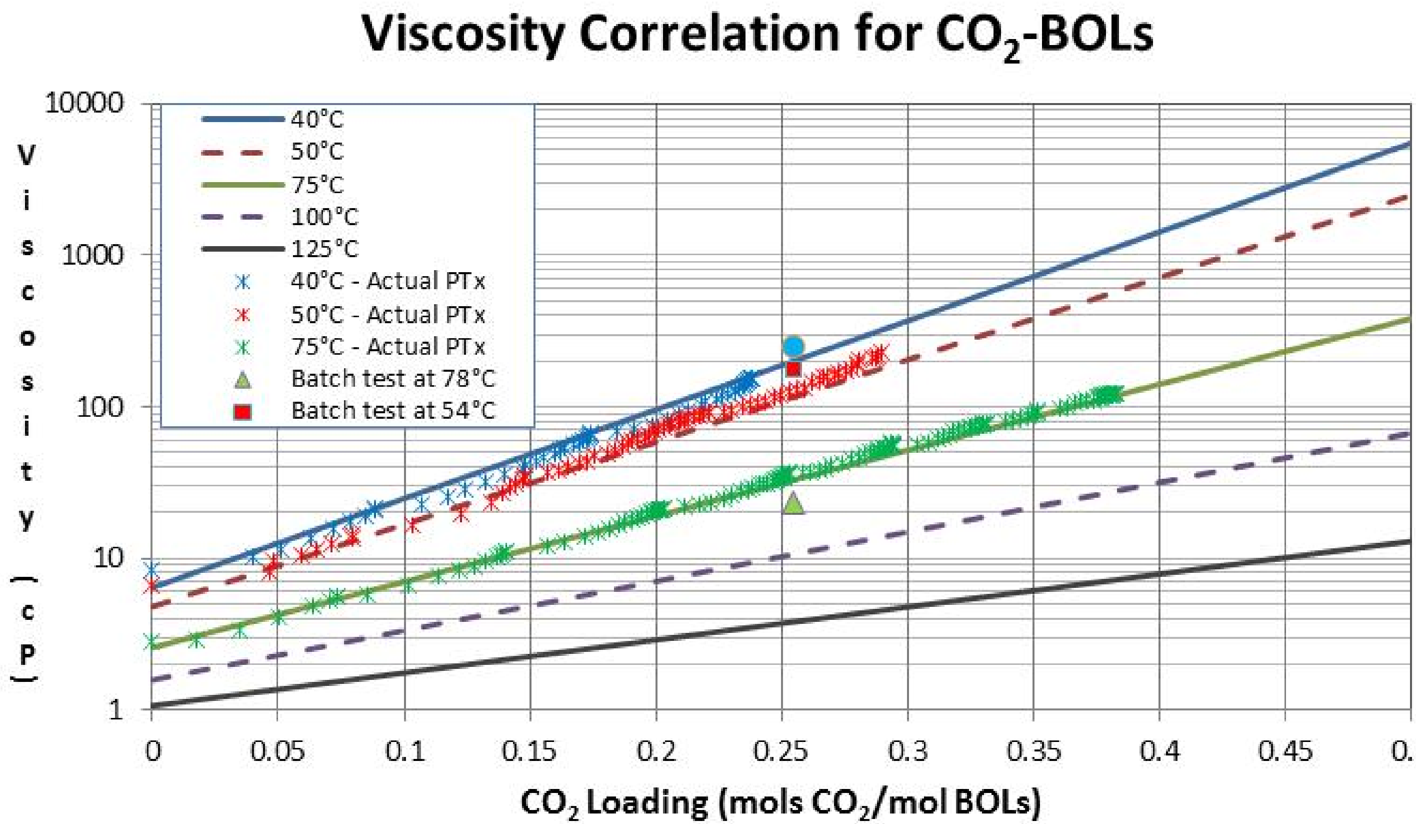
Bench-Scale Portable Cart

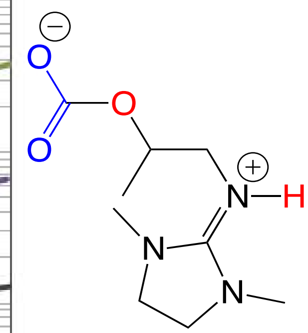
CO_2BOL Viscosity

FLUOR®

Pacific Northwest
NATIONAL LABORATORY
Battelle Since 1965







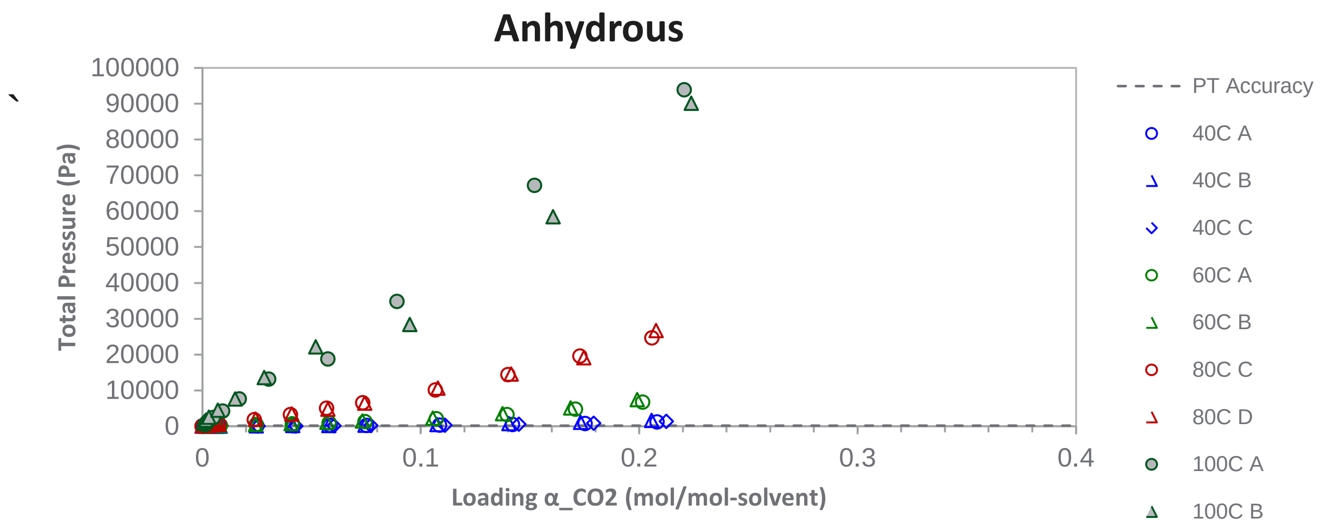
- Points are measured data and lines are model fits
- Water does not precipitate bicarbonate salts
- Viscosity with 10% water (worst case loading) has a minor impact
- Equilibrium model projections of current formulation (0.25 LEAN -0.5 RICH) would be 200-3,000 cP

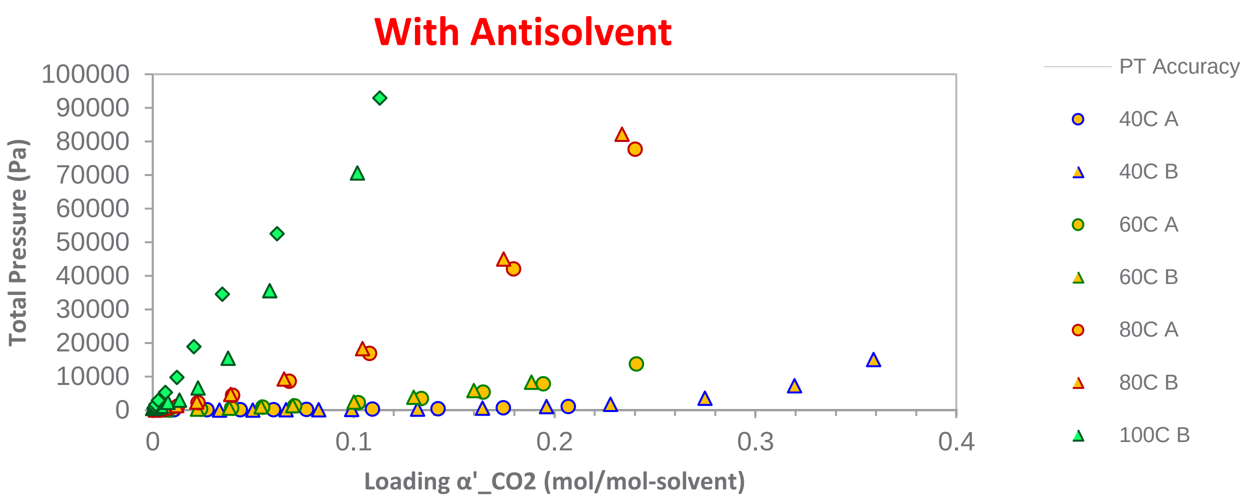
Koech *et al. RSC Adv.*, (***2012***), 3, 566-572

CO_2 Loading Profiles:

Addition of Anti-Solvent Changes Equilibrium Loading of CO_2

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

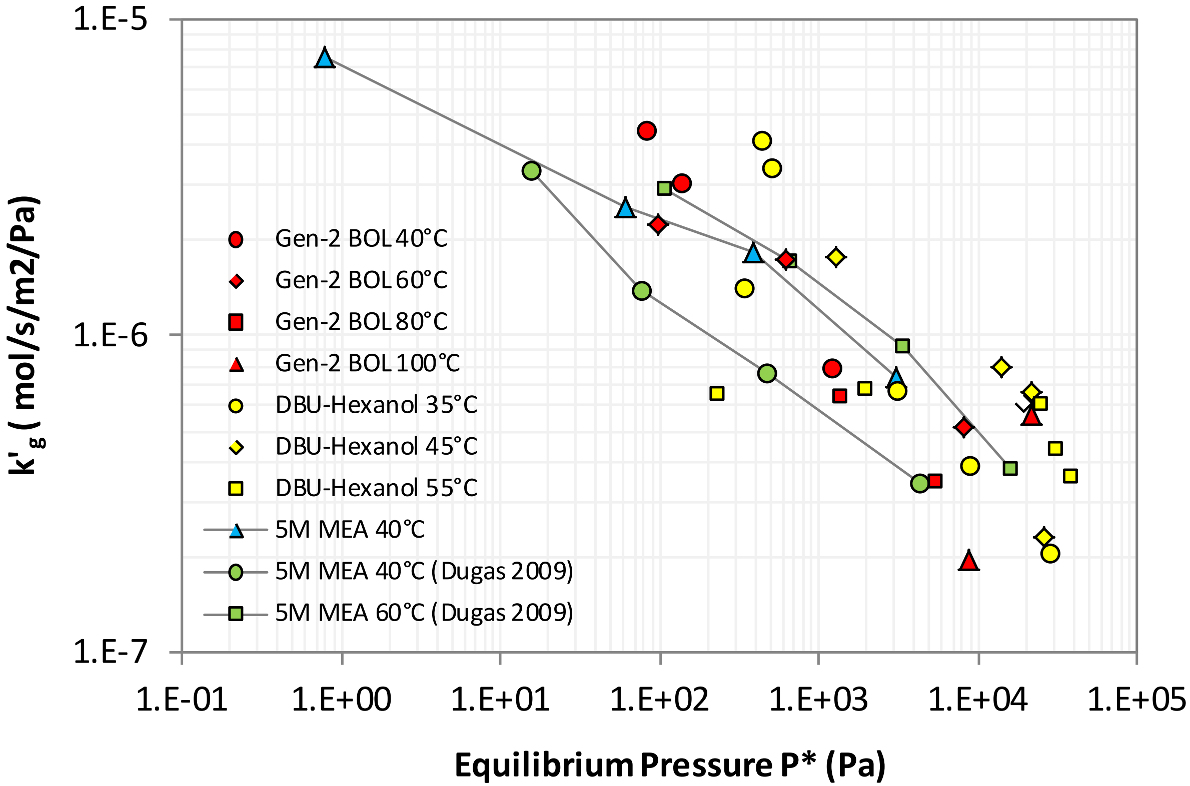




- Antisolvent addition reduces CO_2 capacity at high temperatures
- PSAR not observed in absorber conditions (~40 ˚C)
- PSAR effect observed under stripping conditions (> 62 ˚C)
- Enables CO_2 release at lower temperatures than thermal regeneration alone

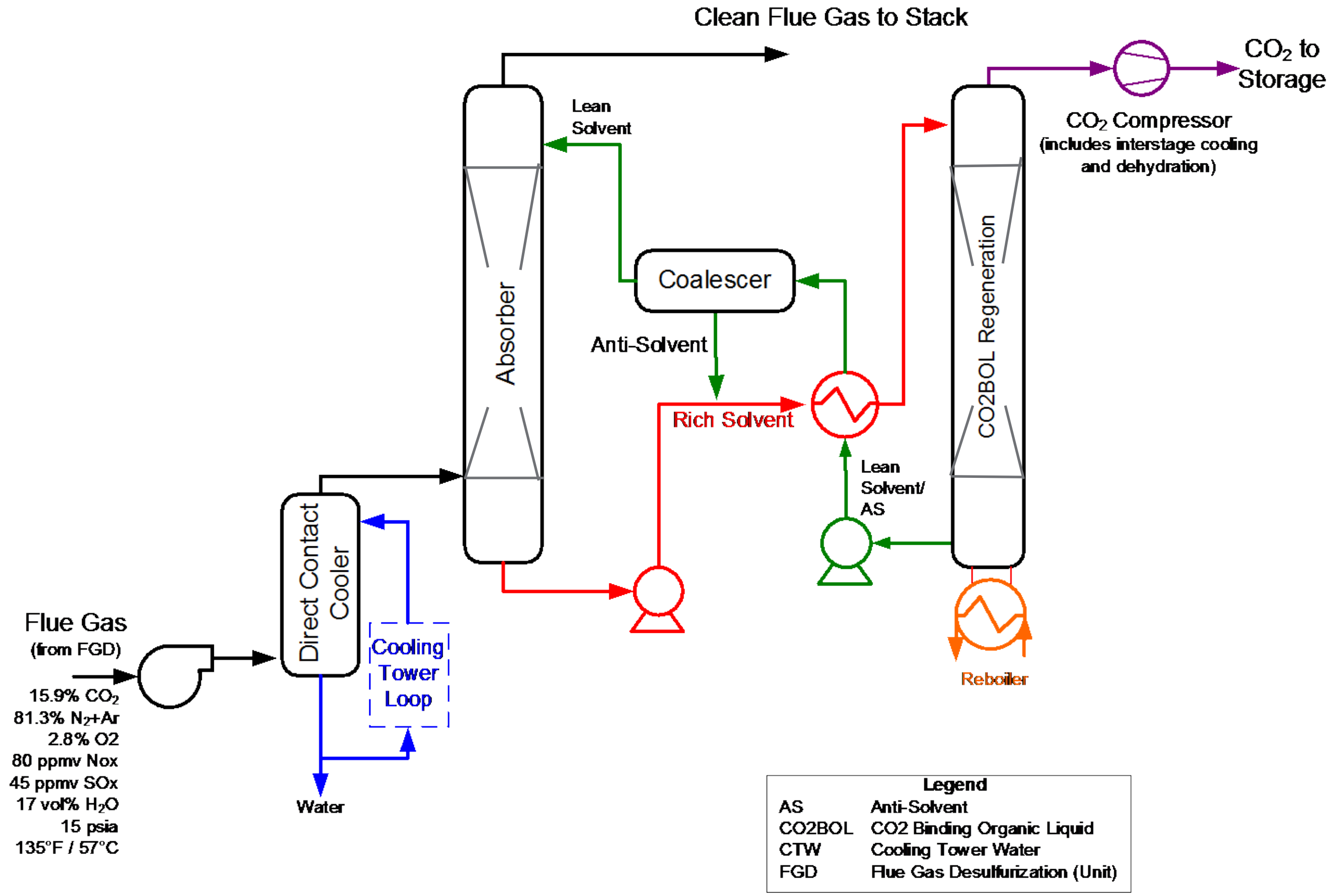
Energy. & Env. Sci. (***2013***)**,** 6, 2233 - 2242

Liquid Film MTC vs. P* of Different CO_2 Solvents



- Mass transfer of CO_2 in CO_2BOLs is comparable to MEA and Piperazine under similar driving force
- Viscosity's impact of CO_2 mass transfer is less than anticipated
  - Attributed to high CO_2 solubility in organic/ionic forms
  - Similar effect projected for other non-aqueous technologies

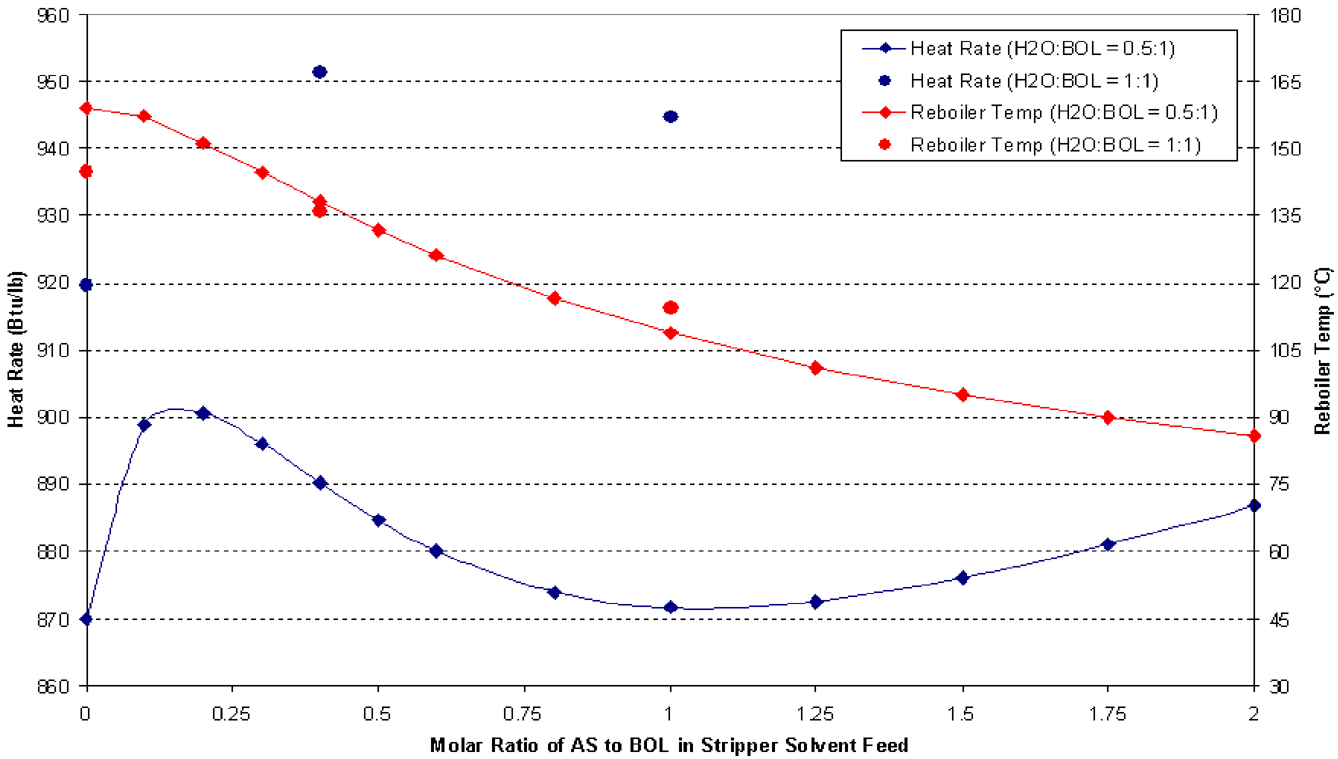
CO_2BOL/PSAR Conceptual Configuration



- Similar to aqueous amine systems albeit with coalescing tank, antisolvent loop, and water management equipment
- Commercially available equipment and infrastructure

Energy. & Env. Sci. ***(2013)*, **6, 2233 - 2242

PSAR Impacts On CO_2BOL Reboiler Heat Duty & T_{Regen}

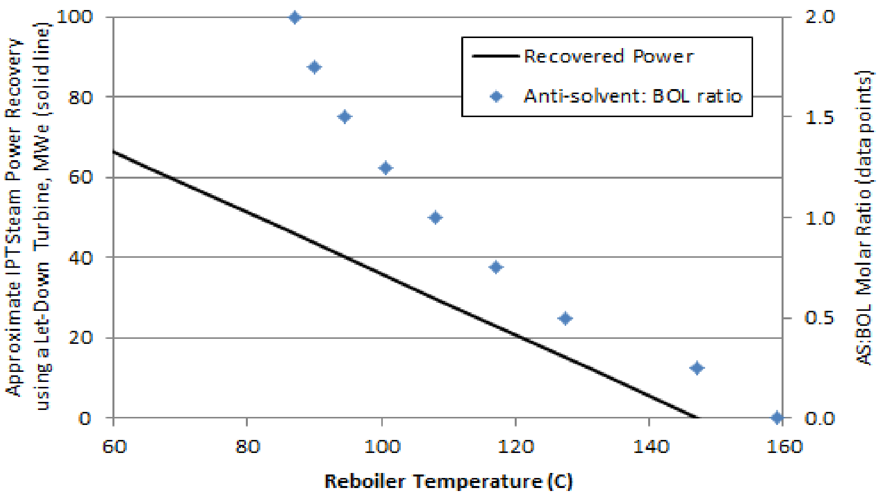


Heat rate and regeneration temperature as a function of antisolvent (hexadecane) loading

- T_{regen} drops with increased loadings of antisolvent (72 ˚C drop at 2 molar equivalents)
- Reboiler heat duty remains unchanged
- Sensitive to water

Energy. & Env. Sci. (***2013***)***,*** 6, 2233 - 2242

PSAR May Increase Net Power Output Up to 102 MWe



- For reboiler temperatures that do not require the IP steam temperatures 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.

Projected net electric power output for CO_2BOL-PSAR as a function of AS (C16) loading

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. & Env. Sci. (***2013***), 6, 2233 - 2242

Bench Scale Testing of CO_2BOL/PSAR

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

Testing Conditions:

Four months of continuous testing on a single batch of solvent

Anhydrous Thermal:

- 15% CO_2, 85 % N_2 gas inlet
- Absorption at 40 ˚C
- Stripping at 80 ˚C with N_2

PSAR Addition:

- Addition of coalescer tank, static mixer, antisolvent circulation pump
- 5-L Decane antisolvent delivered at 60 cc/min circulation rate

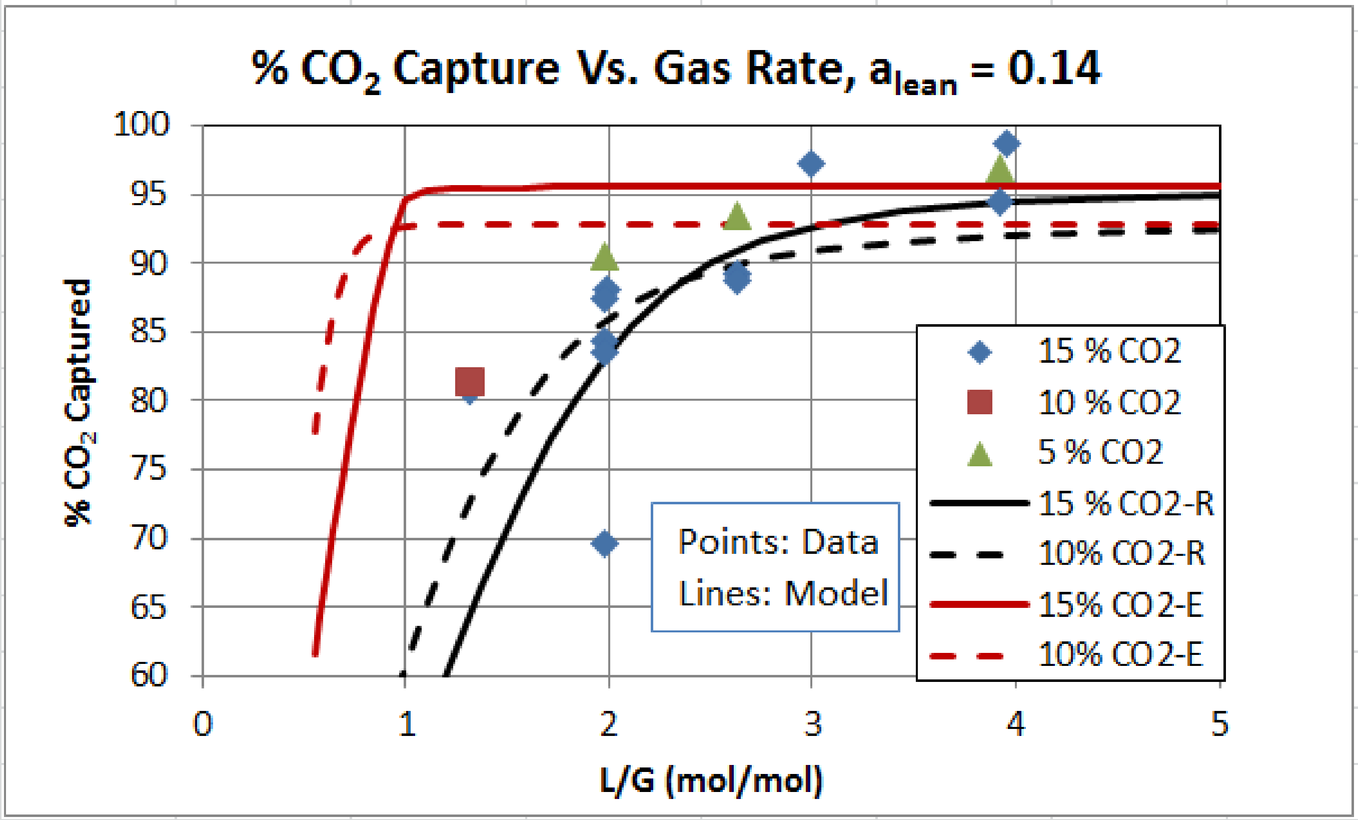
PSAR + Water Addition:

- 5 wt% water loaded to BOL
- 15% CO_2, 85 % N_2 gas inlet saturated with water

CO_2BOL/PSAR Bench Scale Data

FLUOR®

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



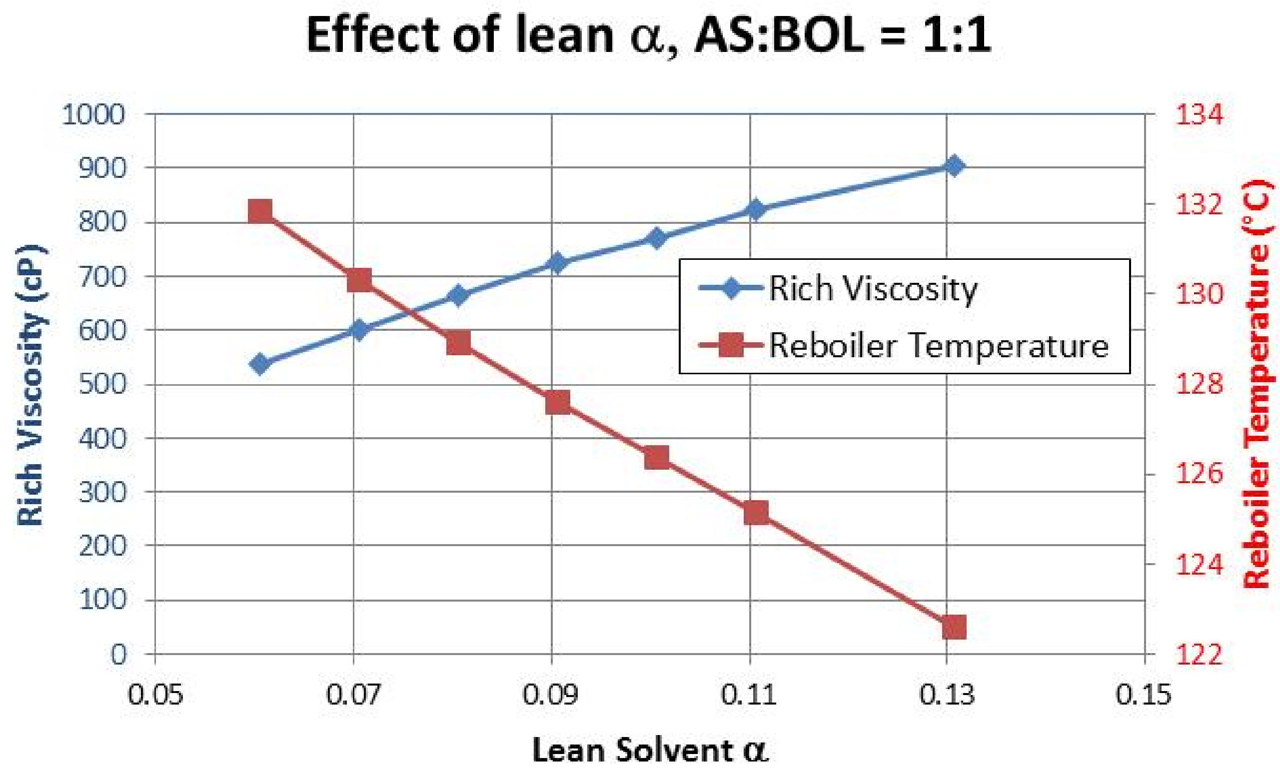
- Four L/G ratios tested at three different CO_2 concentrations (5, 10, 15%)
- Up to 56 hours steady state with no loss in capture efficiency
- PSAR effect on stripper validated
- Minimal PSAR effect on absorber performance

•Absorption at 40 ˚C, stripping at 80 ˚C with N_2

•Decane antisolvent

Manuscript In Preparation

Viscosity Implications On Process Performance



- Rich viscosity is limiting reboiler temperature and process performance
- Initial equilibrium model performance projections (assuming 20 cP target) may be realized
- Reduced viscosity allows higher α, which reduces $T_{reboiler}$ and reduces circulation rate
- Power plant efficiency benefit becomes significant when $T_{reboiler} < 100$ ˚C

Manuscript In Preparation

ASPEN Simulations of CO_2BOL/PSAR Cases

		Case 2	Case 4	20 cP Target
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

- Case 2 is moderate OPEX, high CAPEX
- Case 4 is improved OPEX with expected higher CAPEX
- 20 cP Target projects improved OPEX, CAPEX TBD

- Formal cost projections of Case 2 are currently underway

** Equilibrium projections based on assumed loaded solvent viscosity at or below 20 cP.*

Manuscript In Preparation

Expected Program Findings

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- PSAR favorably reduced stripper duties with little/no impact to absorption
- >90% CO_2 capture achievable at reasonable L/G's
- High viscosities greatly impact CAPEX (specifically absorber and cross exchanger)
- High viscosities greatly impact OPEX (specifically lower lean loadings required)
- Measured low evaporative losses of BOL
- No evidence of foaming during bench scale testing
- Comparable ecotoxicity (Water Daphnia) to MEA
  - CO_2BOL: 169.47 mg/L
  - Monoethanolamine: 103.63 mg/L

Unexpected Program Findings

- A steady state 5 wt.% water is achievable with nominal 13 MW refrigeration unit and properly configured reboiler
- Mass transfer of CO_2BOLs not greatly impeded by viscosity
- Bench system able to operate with loaded solvent viscosities up to 700 centipoise (cP)
- Facile separation of antisolvent from lean CO_2BOL
- No measurable solvent degradation over 4 months of testing – even with 5 wt% water present
- No evidence of bi-phasic liquid impacts to absorber

Benefits of Technology to the Program

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

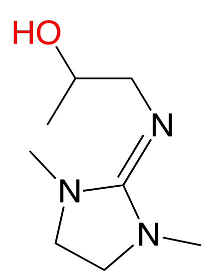
- Comprehensive study of a water-lean solvent platform, applicable to other transformational solvent platforms
  - Thermodynamic performance validated
    - Electrolyte Aspen Plus™ models are sensitive to the Born term
  - CO_2 mass transfer for BOLs (at higher viscosities) is comparable to MEA and Piperazine under similar driving force
  - Viscosity impacts to CAPEX and OPEX quantified
  - Non-aqueous solvents can use existing infrastructure and hardware

- If viscosity is comparable to aqueous technologies*
  - The reboiler heat duty for the CO_2BOL process is 57% of NETL Case 10
  - PSAR may add an estimated 20% increase in net electric power output over NETL Case 10
  - CO_2BOL/PSAR may reduce parasitic loads of NETL Case 10 by 19% at an equivalent coal feed rate

* *Equilibrium projections based on assumed loaded solvent viscosity at or below 20 cP.*

Conclusions And Recommendations for this Specific Formulation of CO_2BOLs

- **Current derivative is energetically feasible but capital cost impractical**
  - CO_2BOL energetics project reduced reboiler duty and higher net power output
    - Potential for greater reductions in reboiler duty and increased net power output with less viscous derivative
  - CAPEX projections indicate this derivative is too costly for commercialization
    - Projected reductions in CAPEX with less viscous derivative
- Viscosity reduction is a critical need to reach CO_2BOL performance projections
- Recommended continued studies of CO_2BOL solvent platform to improve process performance
  - Thousands of potential derivatives

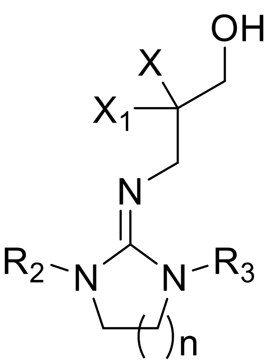


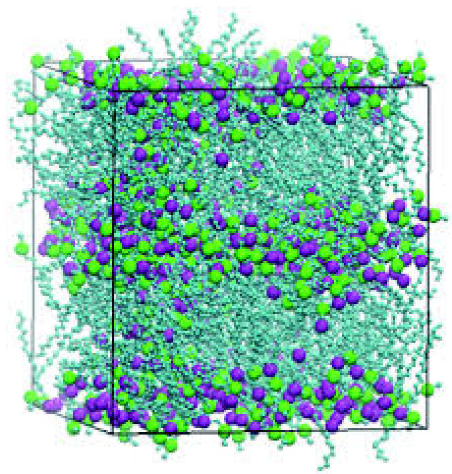
Current/Future Work

New program "Accelerating the Development of "Transformational" Solvents for CO_2 Separations"

- Aiding DOE's transformational solvent portfolio address the grand challenge of viscosity
  - Molecular design and computational modeling to develop tools for viscosity prediction
  - Advanced solvent design for reducing viscosity of water-lean solvent systems
  - Test materials performance at PNNL's Carbon Capture Lab and model process energetics

Model Validation
Refinement of Design





Molecular Design of Molecules

Molecular Modeling & Property prediction

Synthesis & Characterization

Experimental Measurements

Acknowledgements

- Funding:
  - US Department of Energy Office of Fossil Energy DE-FC-FE0007466
  - NETL PM: Andy Aurelio

- PNNL:
  - Phillip Koech
  - Charlie Freeman
  - Mark Bearden
  - Feng Zheng
  - Igor Kutnyakov
  - Andy Zwoster

The Fluor Corporation
- Paul Mathias
- Kash Afshar
- Arnie Smith
- Mukund Bhakta

Queens University:
- Philip Jessop
- Tamer Andrea