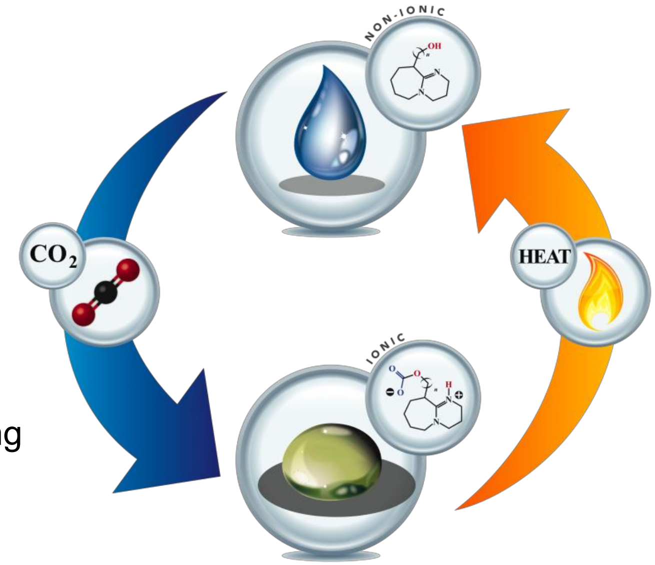
CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process With a Polarity-Swing-Assisted Regeneration



David J. Heldebrant

NETL CO_2 Capture Technology Meeting
Pittsburgh, PA
July 9, 2013

Battelle Memorial Institute

A leader in technology development and laboratory management

- World's largest non-profit R&D organization
- $4 billion total revenue
- 20,400 staff (including labs)
- 30+ scientific user facilities
- Battelle has managed PNNL since 1965 and retains ability to perform commercial business

Project Overview

- Project Team:
  - BPNWD; 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 from TRL 3 through 4 through bench-scale testing

Goals and Objectives

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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

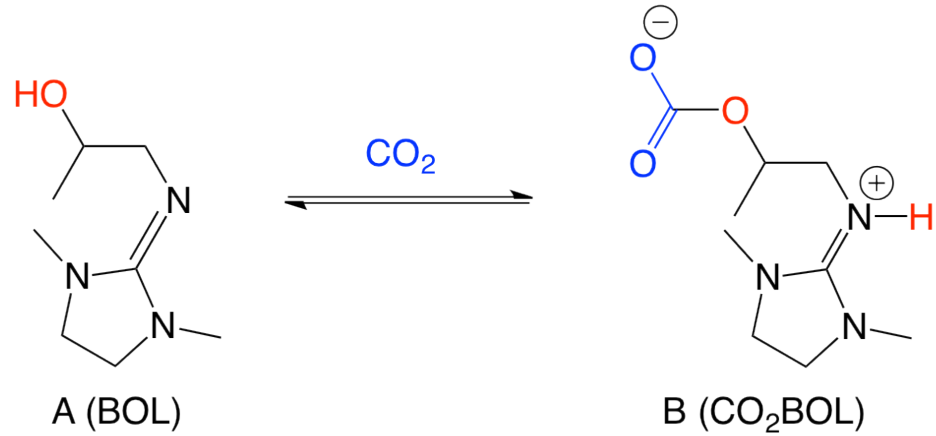
Oct 2011

Mar 2013

- **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

Jun 2014

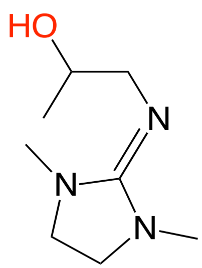
Our System: CO_2BOLs

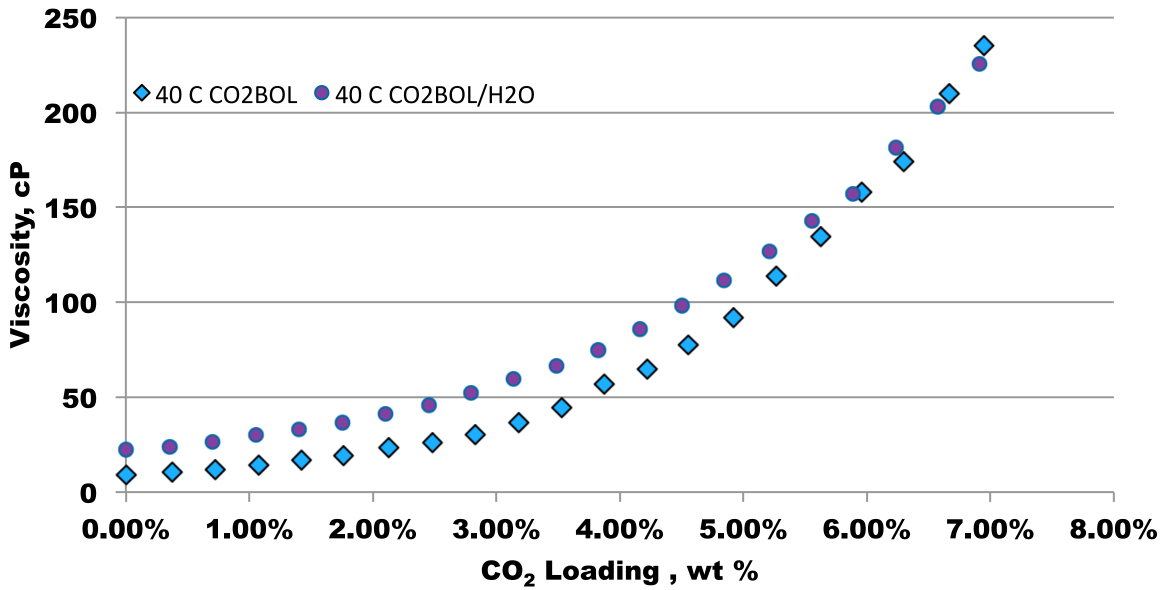


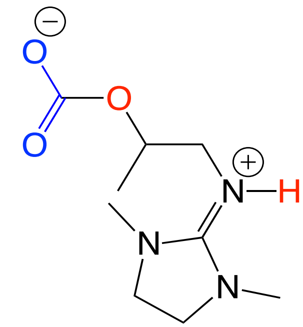
- "Water-lean" organic switchable ionic liquid solvent system
- Reduced heat duty from boiling and condensing less water
  - Water balance established
  - Optimal water level in circulating solvent estimated
    - (~5 wt. % water confirmed by simulation)
- Designed as a direct solvent replacement
- Heat of solution -80 kJ/mol

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

CO_2BOL Performance



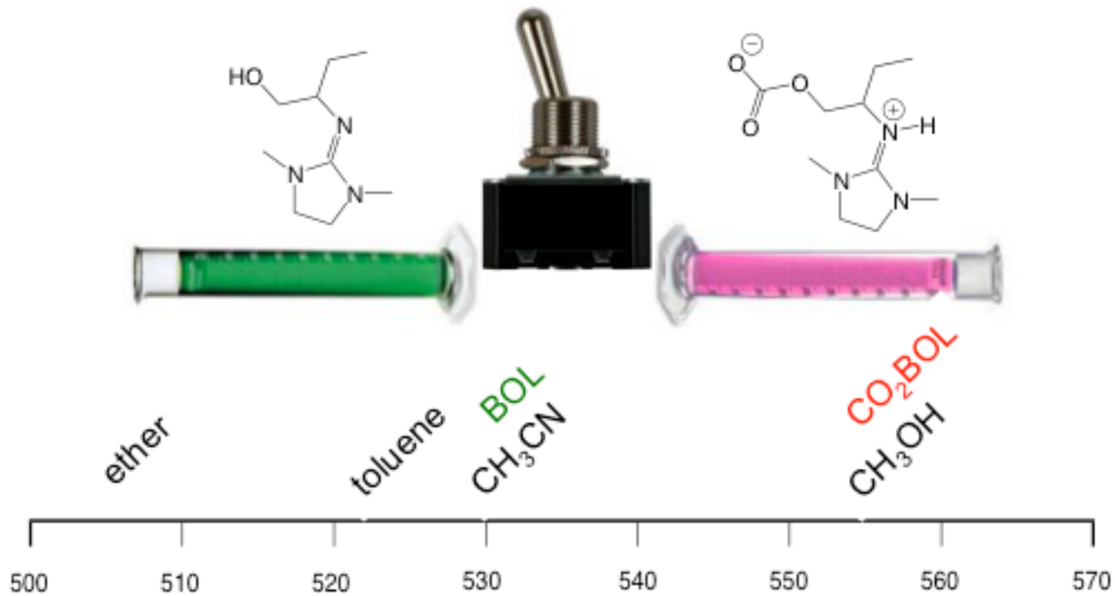




- Viscosity is two orders of magnitude less than previous 2nd Gen CO_2BOLs
- Water does not precipitate bicarbonate salts
- Viscosity with 10% water (worst case loading) has a minor impact
- Further reduction in viscosity needed (20 cP maximum operating viscosity targeted)
  - Molecular refinement underway
  - Diluents under investigation

This team recognizes water-free and water-lean solvents all face this challenge of viscosity

Polarity Swing Assisted Regeneration (PSAR) Concept

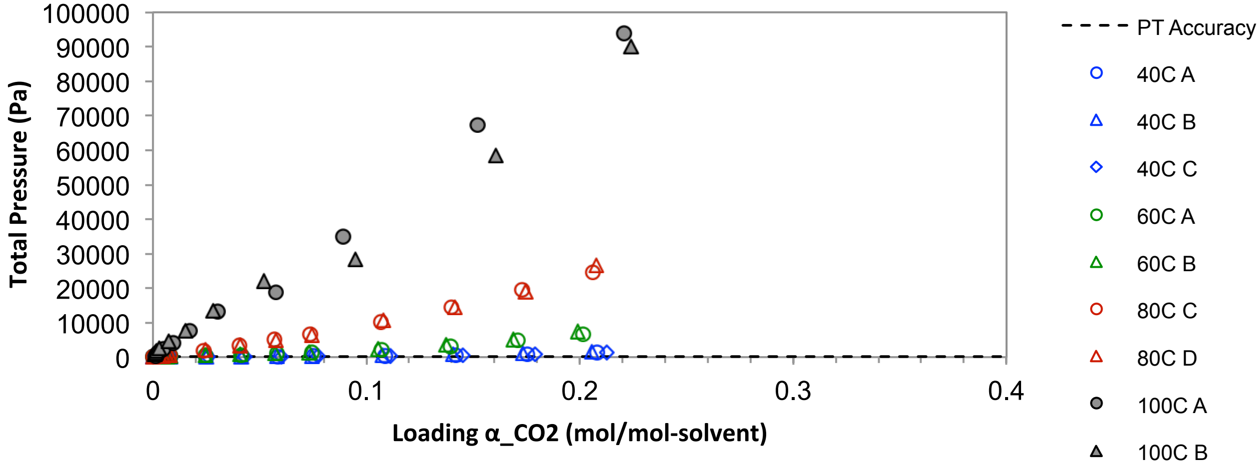


- Unique to switchable ionic liquid-like systems
  - PSAR inoperable for water-based or conventional IL systems
- Anti-solvent addition enables lower temperature stripping
  - Used in combination with thermal heating to release CO_2

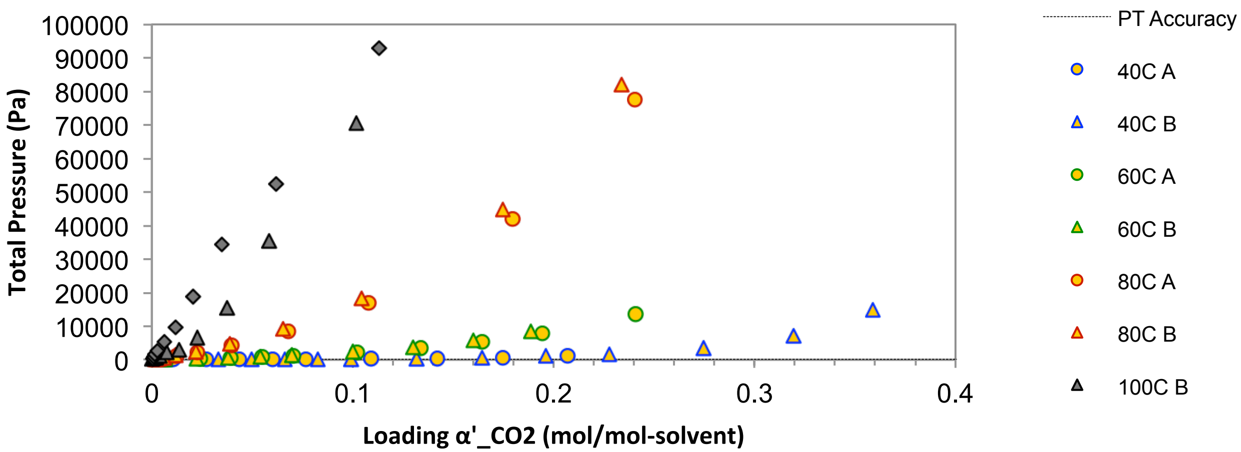
Energy. & Env. Sci. (***2013***), 6, 2233 - 2242, *Energy. & Env. Sci.*, (***2011***), 4, 1385-1390, Patent Pending

CO_2 Loading Profiles:
Addition of Anti-Solvent Changes Equilibrium Loading of CO_2

Anhydrous



With Antisolvent



- Antisolvent addition reduces CO_2 capacity at high temperatures
- No observed effect at 40 & 60 ˚C
- PSAR observed at 80 & 100 ˚C
- 0.11 mol fraction *less* CO_2 @ 100 ˚C

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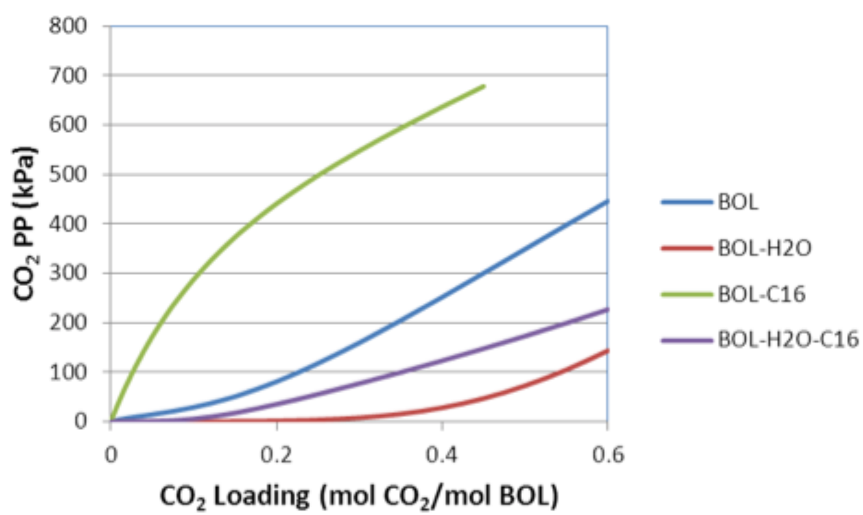
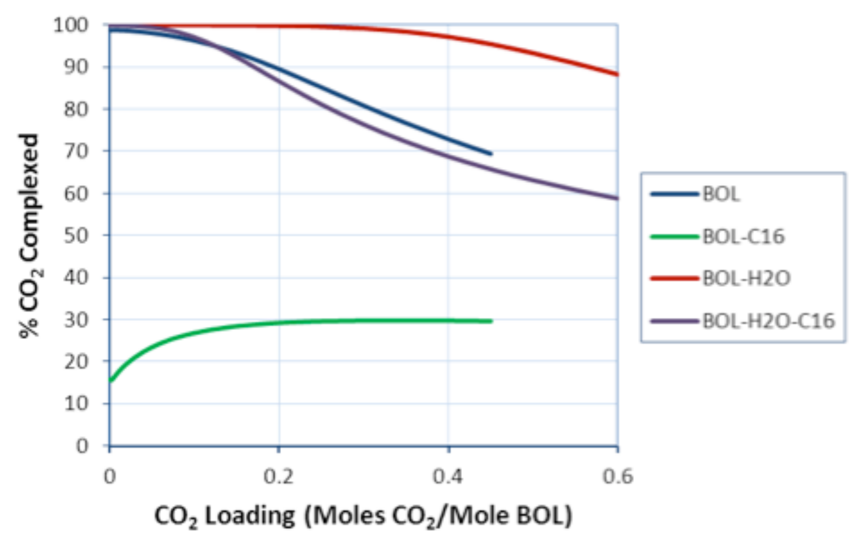
Thermodynamic Model

$$2\ CO_2 + 2\ BOL \leftrightarrow BOLCO_2^{+} + BOLCO_2^{-} \quad (1)$$
$$H_2O + BOL + CO_2 \leftrightarrow BOLH^{+} + HCO_3^{-} \quad (2)$$

- Separate charges needed for the zwitterionic CO_2BOL-CO_2 ionic species for Aspen Plus to enable the Born term
  - Accounts for the effect of the ionic strength and the solvent dielectric constant
  - Predicts the effect of the low-dielectric-constant AS to reduce the mixed solvent's complexation of CO_2
  - Model under continuous revision as new data becomes available





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Phase Behavior of CO_2BOL and Antisolvent

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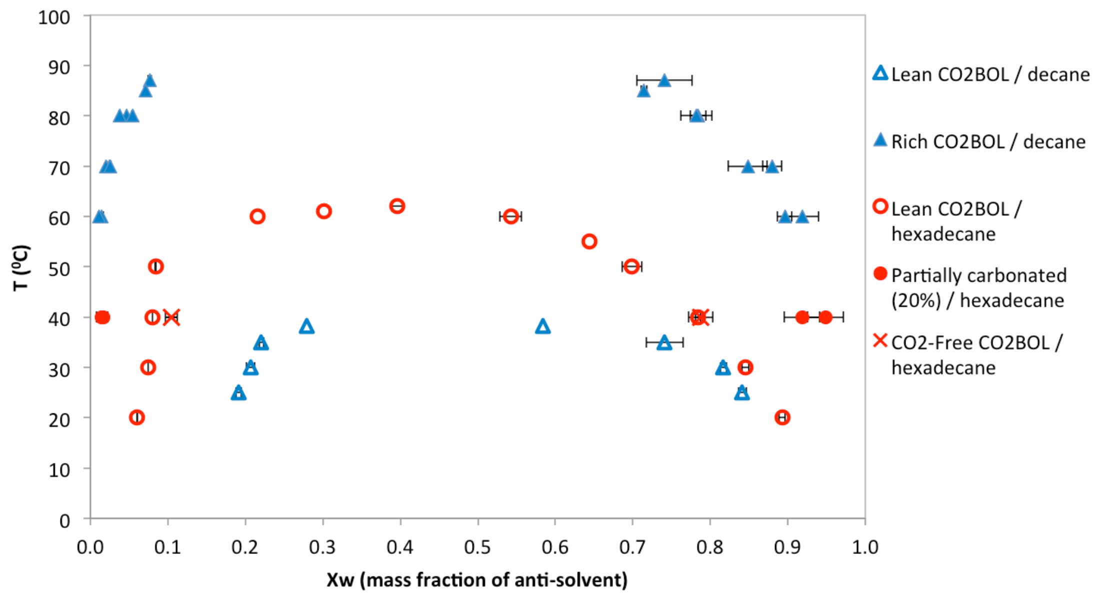
Queen's University



- Miscibility between either CO_2-lean BOL or CO_2-rich CO_2BOL with antisolvent
- Cooling below $T_{miscibility}$ promotes phase separation

Temperatures of miscibility for 50 mol% mixtures of various ASs in CO_2-lean (**A**)

Antisolvent	Chain Length	$T_{miscibility}$ (°C)
Heptane	7	> 30
Decane	10	38
Dodecane	12	39.3
Hexadecane	16	62

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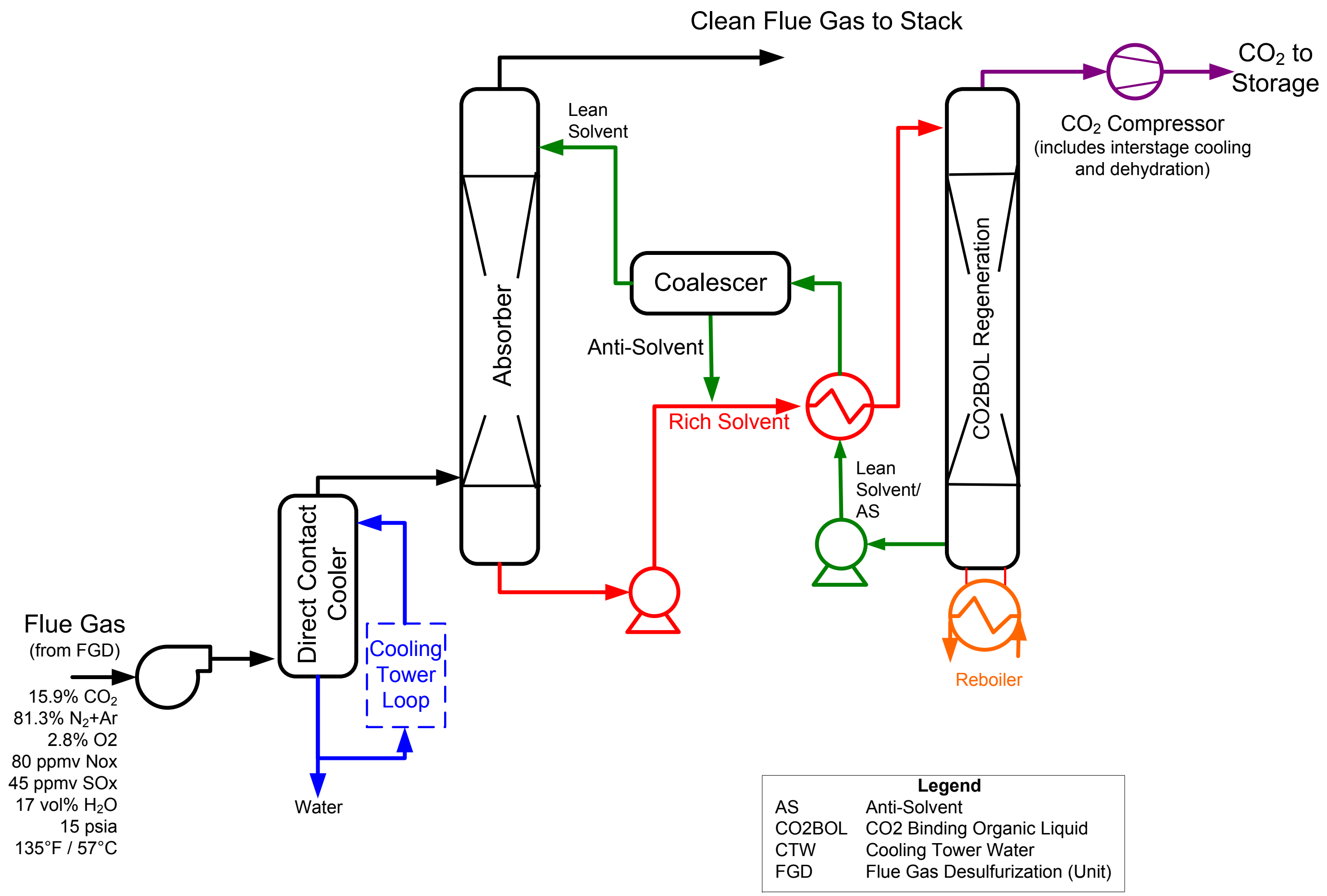
PSAR Conceptual Configuration



- Similar to aqueous amine systems albeit with coalescing tank and antisolvent loop

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

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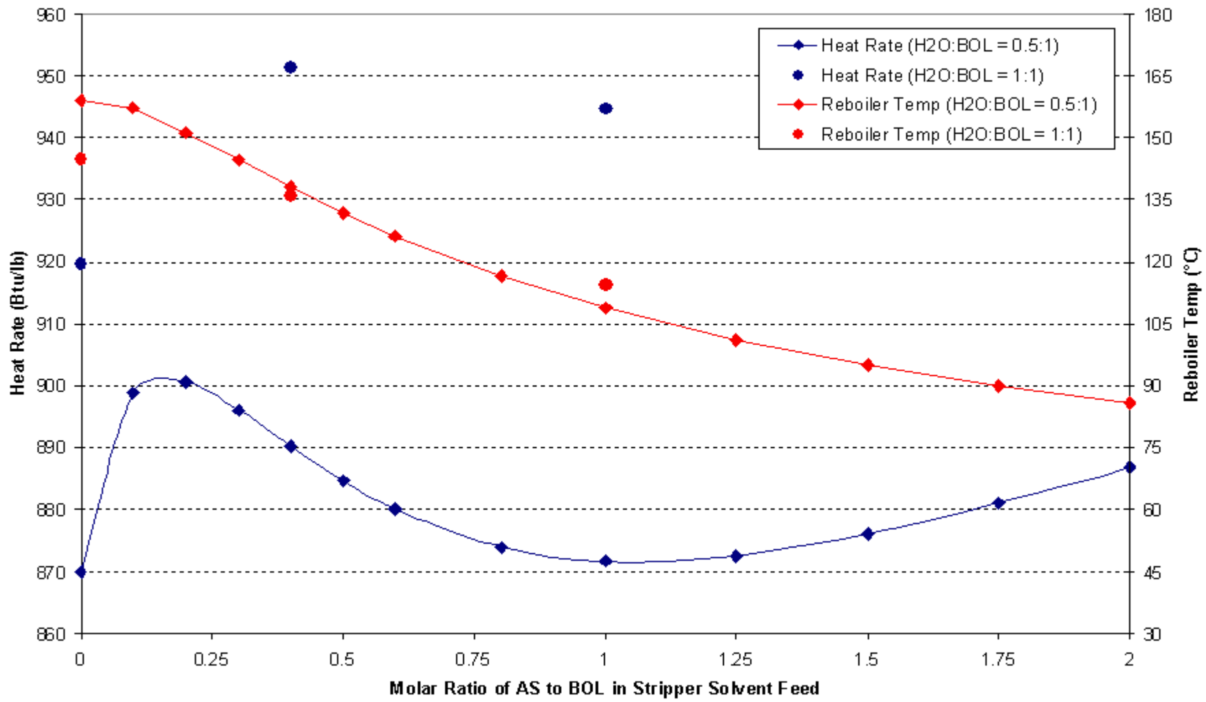

Heat rate and regeneration temperature as a function of antisolvent (hexadecane) loading

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

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PSAR May Increase Net Power Output Up to 102 MWe

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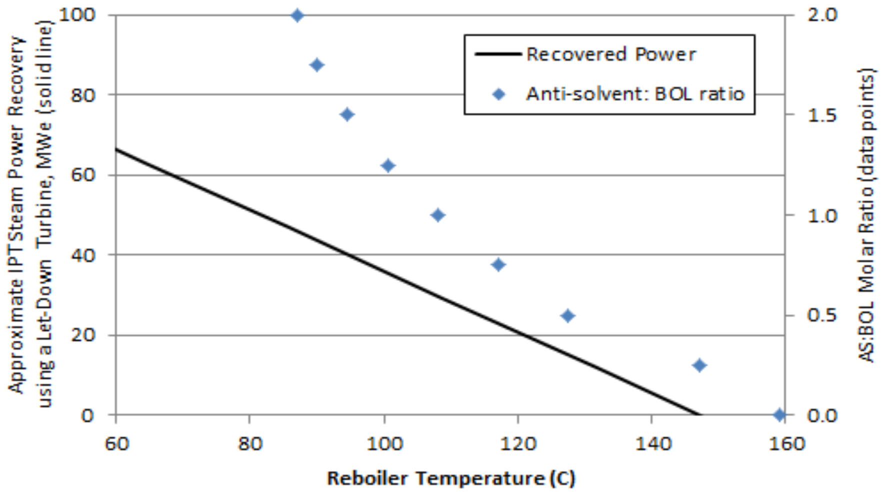
FLUOR



- 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

Key Findings To Date

- Water management for CO_2BOLs is not too costly
  - High water tolerance of the candidate CO_2BOL determined.
  - No precipitating bicarbonate salts at water loadings as high as 1 molar equivalent (9.5 wt %)
  - Full dehumidification not required (currently assuming a small, 7MWe, refrigeration unit)

- AspenPlus models of anhydrous solvents containing ions are sensitive to the Debeye Hückle term

- Separation of the CO_2BOL from the antisolvent is dependent on temperature & CO_2 loading
  - Enables antisolvent selection flexibility to tailor miscibility
  - Allows lower lean loadings of the CO_2BOL solvent and facile coalescing system design

- CO_2BOL/PSAR allows for a higher net power output than Case 10 by either:
  - Lower $T_{Regeneration}$ enabling a let-down turbine to produce more power
    - 45% lower parasitic power than Case 10 at current 86 ˚C regeneration temp forecast
    - As high as 51% lower parasitic power if 65˚C regeneration temp achieved
  - Or higher stripper pressure at a given $T_{regeneration}$ resulting in reduced CO_2 compression power
    - Analysis underway

Benefits of Technology to the Program*

- 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 Case 10
- At a given pressure, PSAR lowers the temperature at which CO_2 is released from the rich CO_2BOL (demonstrated 72 ˚C reduction)
  - Minimizes thermal degradation and evaporative losses of the CO_2BOL solvent
- PSAR decreases COE 17 points compared to the Case 10 baseline (68% versus 85%)
  - Potential for a 21-26 point decrease
- PSAR allows for novel heat integration strategies unavailable to other technologies
  - Retrofit or greenfield potential

* *All projections are based on an assumed loaded solvent viscosity at or below 20 cP.*

Project Technical & Economic Challenges

- Refined CO_2BOL formulation needed to keep viscosity below 20 cP max operating limit
  - Molecular refinement desired
  - Diluents may be applicable, but may impact PSAR performance
  - Separate/ follow-on programmatic work will likely be necessary
- CO_2BOL material costs are too high ($35-70/kg)
  - Alternate synthesis strategies need to be developed
- Bench-scale validation of process needed for mass transfer coefficients, solvent lifetime
- Validation/optimization of PSAR process under continuous flow conditions
  - Time and efficiency of anti-solvent separation/carryover
  - Antisolvent impacts on absorber performance
  - Cheap, “green” antisolvent alternatives desired

Project Performance and Future Work

Overall Accomplishments

- All Milestones and deliverables have been completed within budget
- All risks have been addressed and mitigated to date
- Completed an initial feasibility study of the CO_2BOL/PSAR process and confirmed economic viability

Future Plans

- Bench-scale testing of the current best-case CO_2BOL solvent and PSAR antisolvent.
- EH&S study of CO_2BOL and degradation products
- Synthesis of less viscous CO_2BOL molecules already identified (as funding permits)
- Development of cheaper synthesis of CO_2BOL solvent
- Final technology feasibility study-facilitated by bench scale results

Beyond BP 2

- Testing at slipstream scale

BPNWD's Testing Facilities

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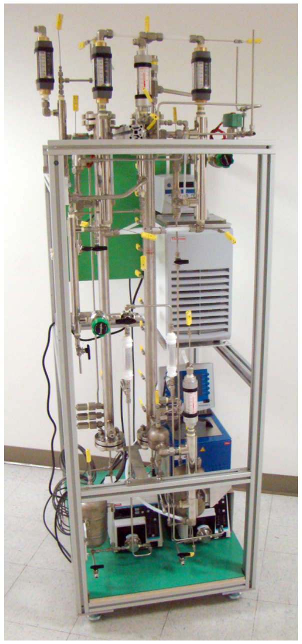
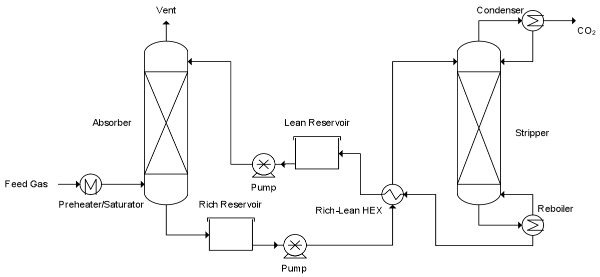
- BPNWD's Carbon Capture Laboratory Completed in 2012
- $2,000,000 in internal investments
- Facilities include wetted wall column, PTx cells & Mobile Bench-Cart, viscometers, 5L synthesis reactor

Specifications:	
Column diameter:	1.26 cm
Column height:	9.1 cm
Gas flow rate:	1-5 slpm
Solvent flow rate:	300 ml/min
Absorption temperature:	25 – 60 ^oC
Absorption pressure:	1 to 5 bar
Gas/Liquid interface area:	37.3 cm^2
Reservoir capacity:	2 liters
Gas analysis:	Mass spectrometer

Wetted Wall

5-L Synthesis Reactor





Bench-scale solvent cart specifications:	
Max. gas flow rate:	30 slpm
Solvent flow rate:	250-300 ml/min
Max. temperature:	200 ^oC
Operating pressure:	1 to 5 bar
Structured packing:	Sulzer EX
Packing height (absorb/strip):	83 cm / 55 cm
Packing diameter:	3.2 cm
Bed height:	108 cm
Reservoir capacity:	2 liters
Gas analysis:	Mass spectrometer

Bench-Scale Portable Cart

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