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

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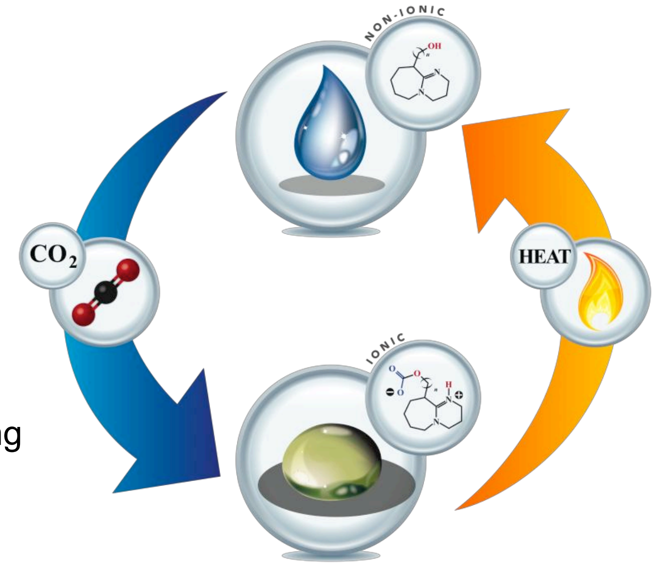

David J. Heldebrant

NETL CO_2 Capture Technology Meeting
Pittsburgh, PA
July 10, 2012

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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 to 5 through bench-scale testing

Image taken from www.separationsnow.com

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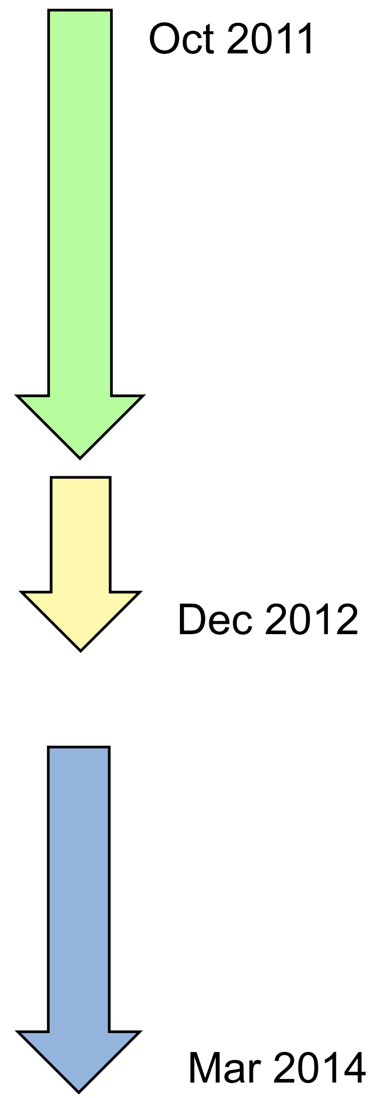
Project Schedule and Tasks

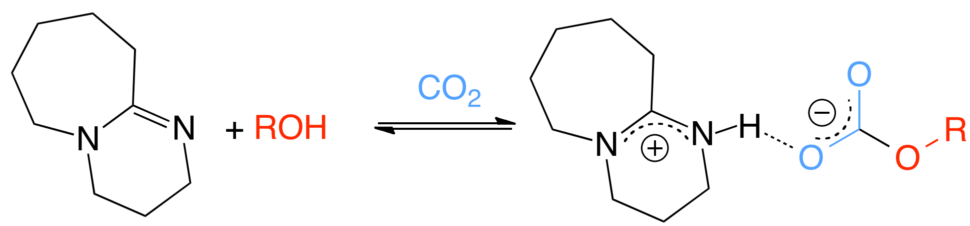
- **BP 1** (Oct 2011-Dec 2012)
  - 1. Project Management
  - 2. Initial techno-economic assessment
    - Full process description and analysis
    - Cost estimates
    - Measurement of missing data
    - Revise technology performance targets
  - 3. Bench-scale design and retrofits for PSAR
    - Solvent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

- **BP 2** (Jan 2013-Mar 2014)
  - 4. Bench-scale testing
    - Shakedown testing
    - Bench-scale testing on liquid PSAR and solid PSAR
  - 5. Full technology assessment



Our System: CO_2BOLs

Molecular liquid



Ionic liquid

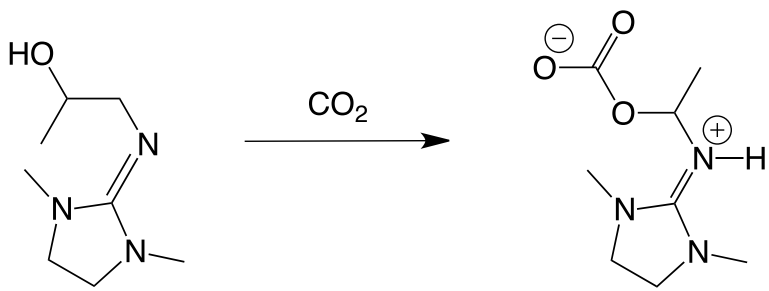
•Non-polar
•Non-conductive
•Non viscous
•Water immiscible
•0 wt % CO_2

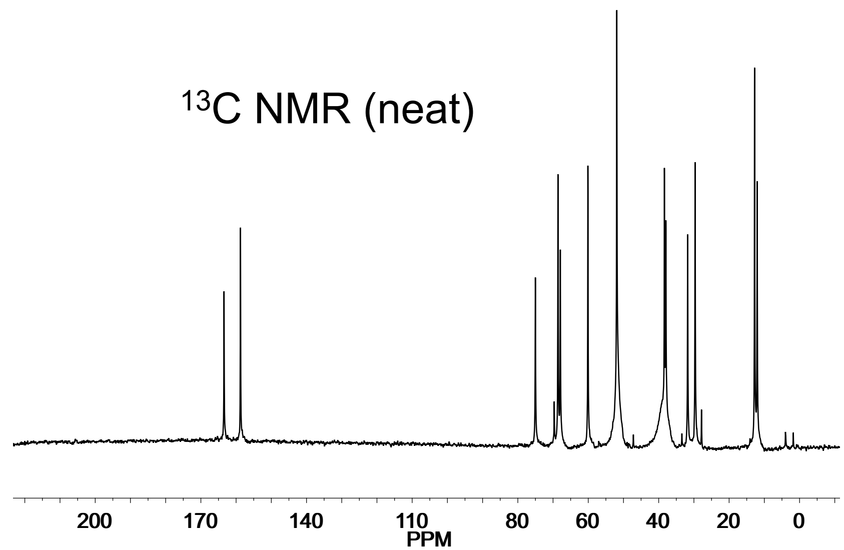
•Polar
•Conductive
•Viscous
•Water miscible
•15 wt % CO_2

- CO_2BOLs are a class of switchable ionic liquids discovered in 2004 with Professor Phillip Jessop (Queens University)*
- First switchable ionic liquid technology for gas separations

5 *Nature, (**2005**), 436, 1102; Ind. & Eng. Chem. Res. (**2008**); 47, 3, 539, Energy Environ. Sci.*, (**2008**), 1, 487

2nd Generation CO_2BOL: Alkanolguanidines



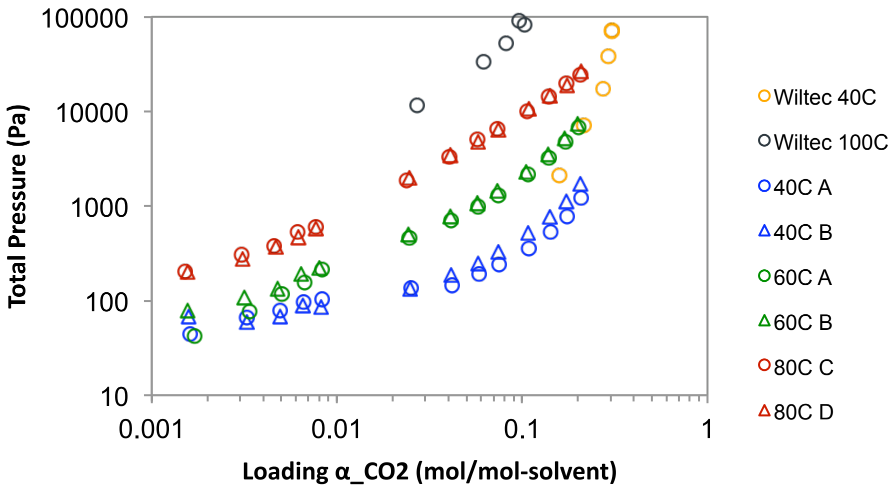


- Viscosity at 40 ˚C: 1 Cp (0 % CO_2) → 120 Cp (10 wt % CO_2)
- Moderate CO_2 uptake (10 wt % @ 40 ˚C, 1 ATM CO_2)
- Non-volatile
  - V.P. = 1.3 mm Hg @ 100 ˚C, B.P. = 262 ˚C, Decomposition > 200 ˚C
- Specific heat 1.9 $Jg^{-1}K^{-1}$ (30 ˚C)

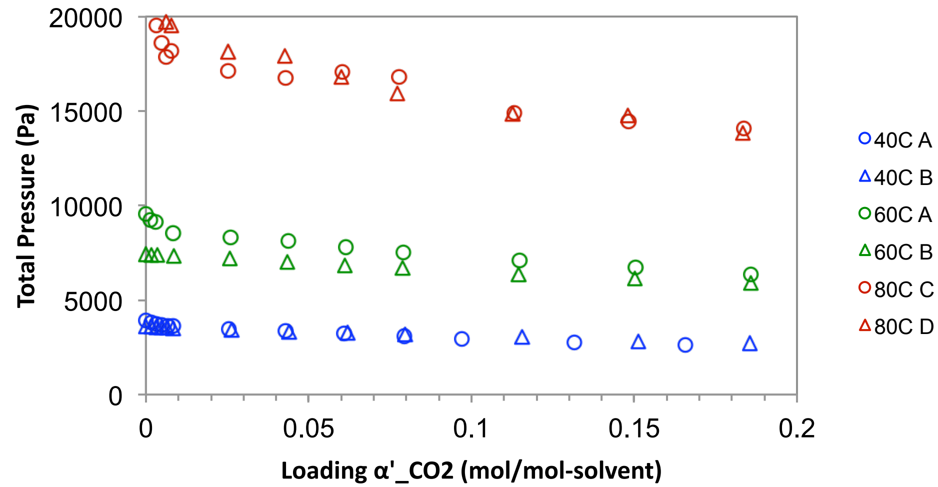
Koech *et al. Green Chem.* in Preparation

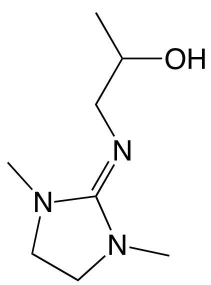
CO_2 Loading Profiles

Anhydrous



CO_2BOL + H_2O (1:1 by mol)





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- Measured by PTx method
- ~7 wt% CO_2 (40 ˚C, 0.1 ATM CO_2)
- Homogeneous liquid with 1:1:1 BOL, CO_2, H_2O
  - Enhanced CO_2 uptake with water (bicarbonate)
- Heat of solution with water -80-90 kJ/mol

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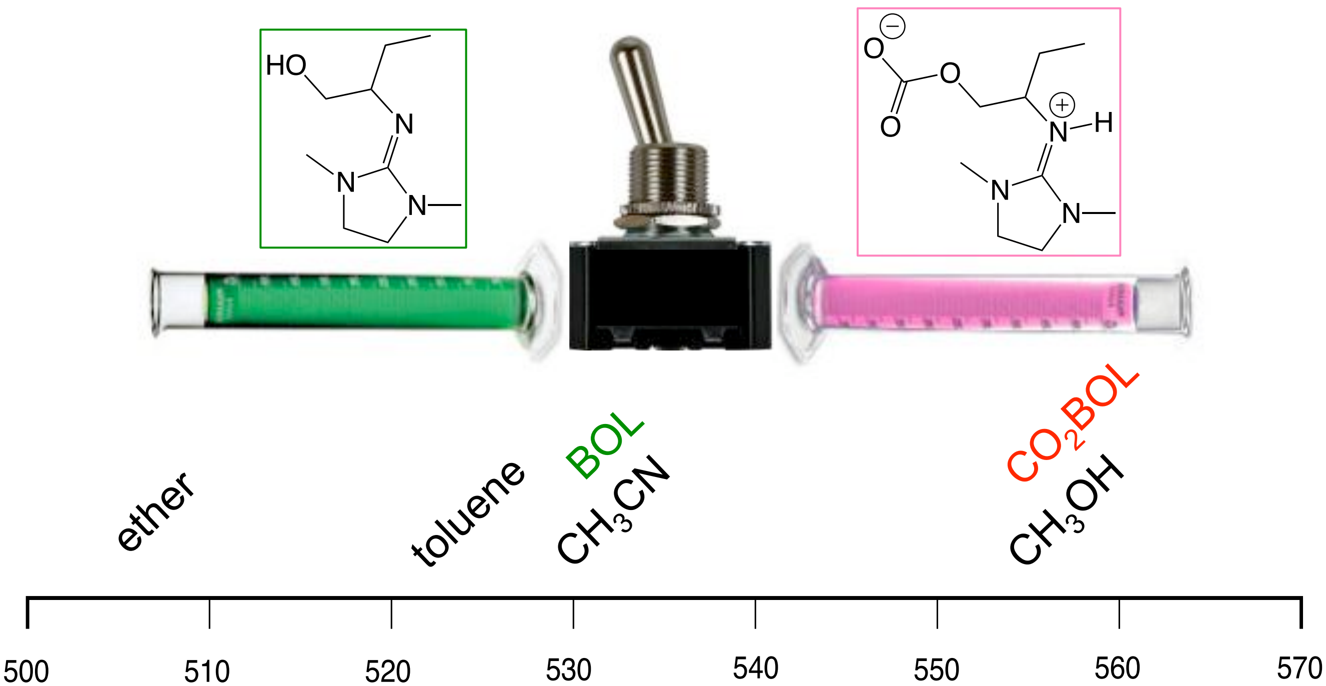
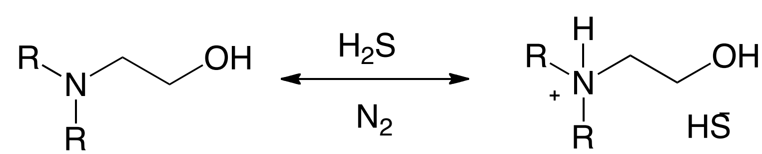
Polarity Swing Assisted Regeneration (PSAR)



hexanes + H_2SBOL

- Unique to switchable ionic liquid-like systems
- Anti-solvent addition favors CO_2-lean form



Energy. & Env. Sci. 4, **2011**, 1385-1390, Patent Pending

Anti-Solvent Changes Equilibrium Loading of CO_2

- Decreases the CO_2BOL's ability to hold CO_2 at a given temperature

Molar Ratios of Antisolvent (Heptane) : DBU : Propanol	Mass of Antisolvent (% of total DBU-Propanol mass)	CO2 Loading in BOL (wt%) at					
		25°C	45°C	60°C	75°C	90°C	120°C
0:1:1	0%	13.7%	12.7%	9.9%	8.6%	1.8%	0.0%
0.5:1:1	24%	13.7%	12.5%	8.1%	2.3%	0.6%	0.0%
1:1:1	47%	13.7%	10.8%	5.0%	0.5%	0.5%	0.0%
2:1:1	94%	13.7%	10.6%	4.1%	0.4%	0.0%	0.0%

- Full CO_2 release at 75 ˚C VS. 100 ˚C without antisolvent
  - Less thermal degradation and evaporative losses of sorbent
  - Optimal mole fraction of anti-solvent ~ 0.4

9 *Heldebrant et al. unpublished data 2011, Patent Pending*

Anti-Solvent Addition Enhances CO_2 Release Kinetics

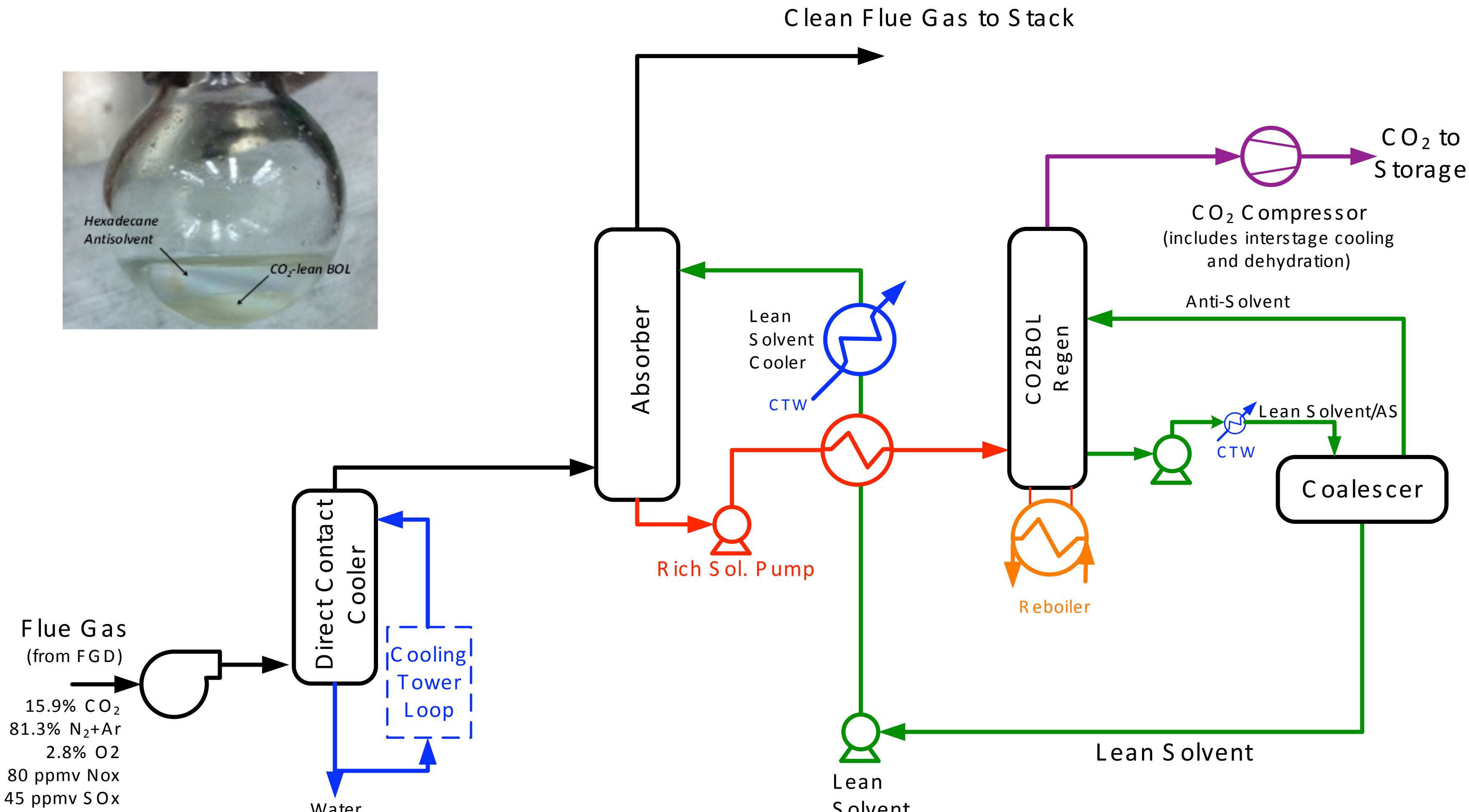
CO_2 release rates, with and without anti-solvent, from DBU-propanol initially loaded to 13.7 wt%. Reference measurement included for 30% MEA loaded at 7 wt% CO_2.[a]

Solvent (preloaded with CO_2)	Regeneration Temperature (˚C)	Maximum CO_2 Release Rate [mmol/min]
DBU-PrOH (1:1 on a molar basis), no antisolvent added at regeneration	60	0.6
	75	1.2
	90	2.0
DBU-PrOH (1:1 on a molar basis), 1:1 molar heptane (to DBU) antisolvent added at regeneration	60	0.9
	75	2.0
	90	20
MEA (30wt% solution)	120	1.0

- Faster release rates are estimated to allow smaller equipment sizing, thus lower capitol costs

10 *Heldebrant et al. unpublished data 2011, Patent Pending*

PSAR Conceptual Flow Diagram



Legend

AS	Anti-Solvent
CO2BOL	CO2 Binding Organic Liquid
CTW	Cooling Tower Water
FGD	Flue Gas Desulfurization (Unit)

11 *Heldebrant et al. unpublished data 2011, Patent Pending*

Initial Technology Assessment

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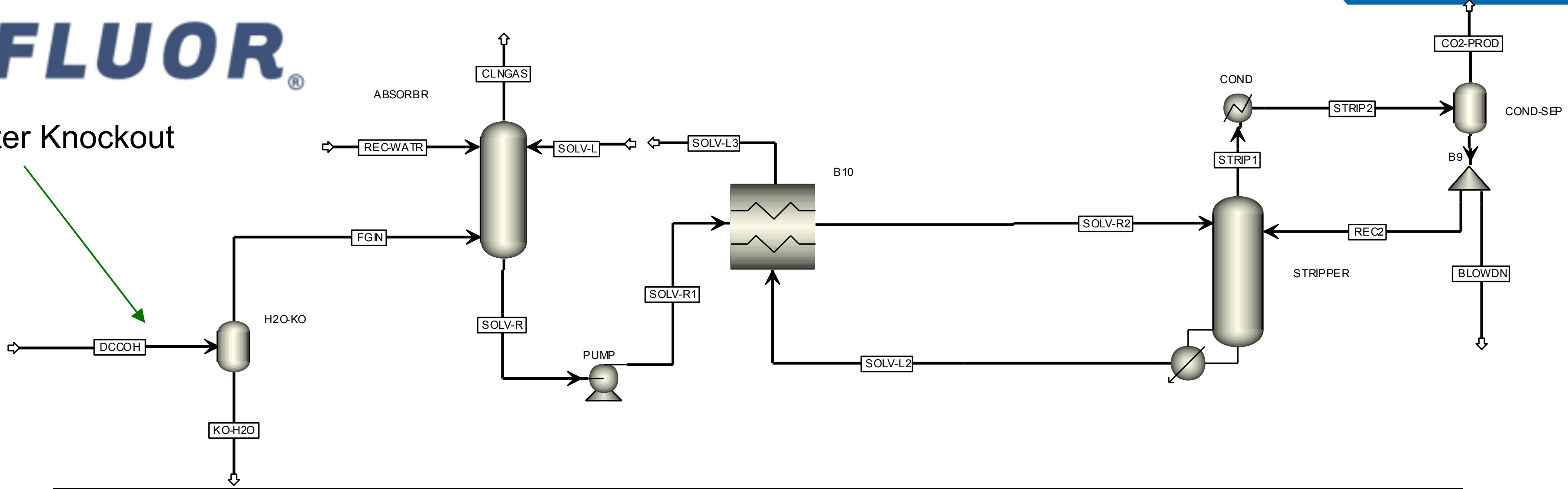
Water Knockout



	Recreated NETL Case 10	CO_2BOLs	CO_2BOLs/PSAR
CO_2 Recovery	90%	90%	90% (est)
Specific Steam Heat Rate, Btu/lb	1,575	970	?
Solvent Circulation Rate, lb/hr	1.02E+07	1.05E+07	?
Solvent:CO_2 Rate (moles/mole)	3.1	3.4	?
Absorber Feed Gas Temperature, °F	47	40	?
Absorber Feed Gas CO_2 Conc'n, %v/v	15.2%	15.3%	?
Reboiler Temperature, °C	120	140	?

- Results are **preliminary** on an equilibrium models, currently no kinetic input
- Water accumulation needs to be resolved
- CO_2BOL loss in absorber vent and blowdown needs to be addressed

PSAR Technical & Economic Advantages

- PSAR process enhances CO_2BOL release to as low as 75 ˚C
  - Lower evaporative losses and thermal degradation
  - Potential for reducing the pressure of the LP steam used for regeneration allowing more energy content to be used for producing power
- Heat integration engineering possibilities can have minimal impact to steam cycles
  - Retrofit options or greenfield with heat integration designs

PSAR Technical & Economic Challenges

- Time and efficiency of anti-solvent separation/carryover
- Impact of water on CO_2BOL/PSAR chemistry
- Costs of PSAR VS. thermal regeneration
- Is an MEA configuration correct?
- CO_2BOL material costs

Future Work

- Kinetics of absorption and desorption
  - Wetted wall testing
- Configuration of PSAR process
  - Optimization of anti-solvent/CO_2BOL blend
- Bench-scale testing of CO_2BOLs with and without PSAR
- Formal process simulations of PSAR using ASPEN+
- Toxicity of CO_2BOLs and potential degradation products
- Scale up and slipstream testing

Battelle's Wetted-Wall and Bench-Scale Testing Carts

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