Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture

Project NT43091

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July 2012

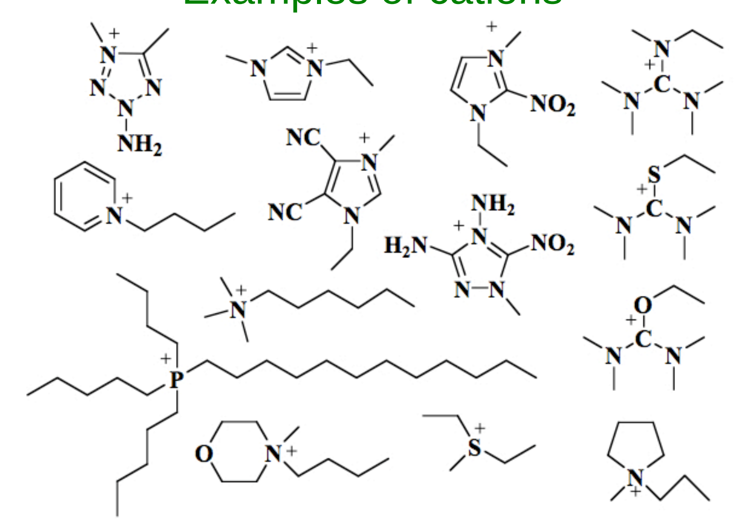
Project Overview

- Project funding:
  - DOE Share: $2,741,784
  - Non-DOE share: $1,411,264
- Performance dates:
  - March 1, 2007- September 30, 2012
- Project participants:
  - University of Notre Dame (lead)
  - Babcock and Wilcox
  - DTE Energy
  - EMD Chemicals / Merck (no longer on project)
  - Air Products (no longer on project)
  - Koei Chemical
  - Trimeric Inc.
  - MATRIC
- Project objectives:
  - Develop ionic liquid solvents that can be used as a cost effective post-combustion CO_2 capture solvent

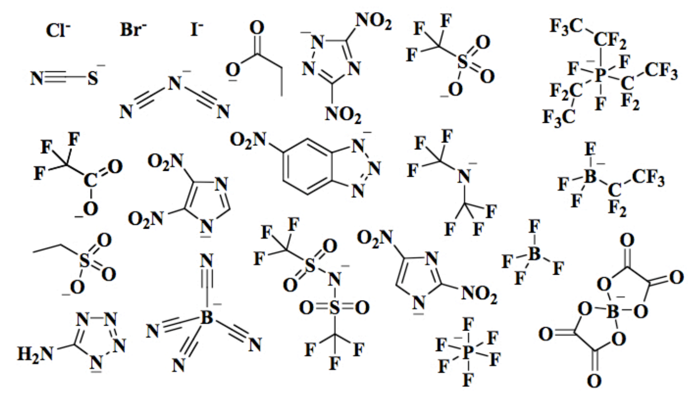
Technology Fundamentals

- Ionic liquids are pure salts that are liquid around ambient temperature
  - Not simple salts like alkali halides
- Many favorable properties
  - Nonvolatile
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity
  - High intrinsic CO_2 solubility and selectivity

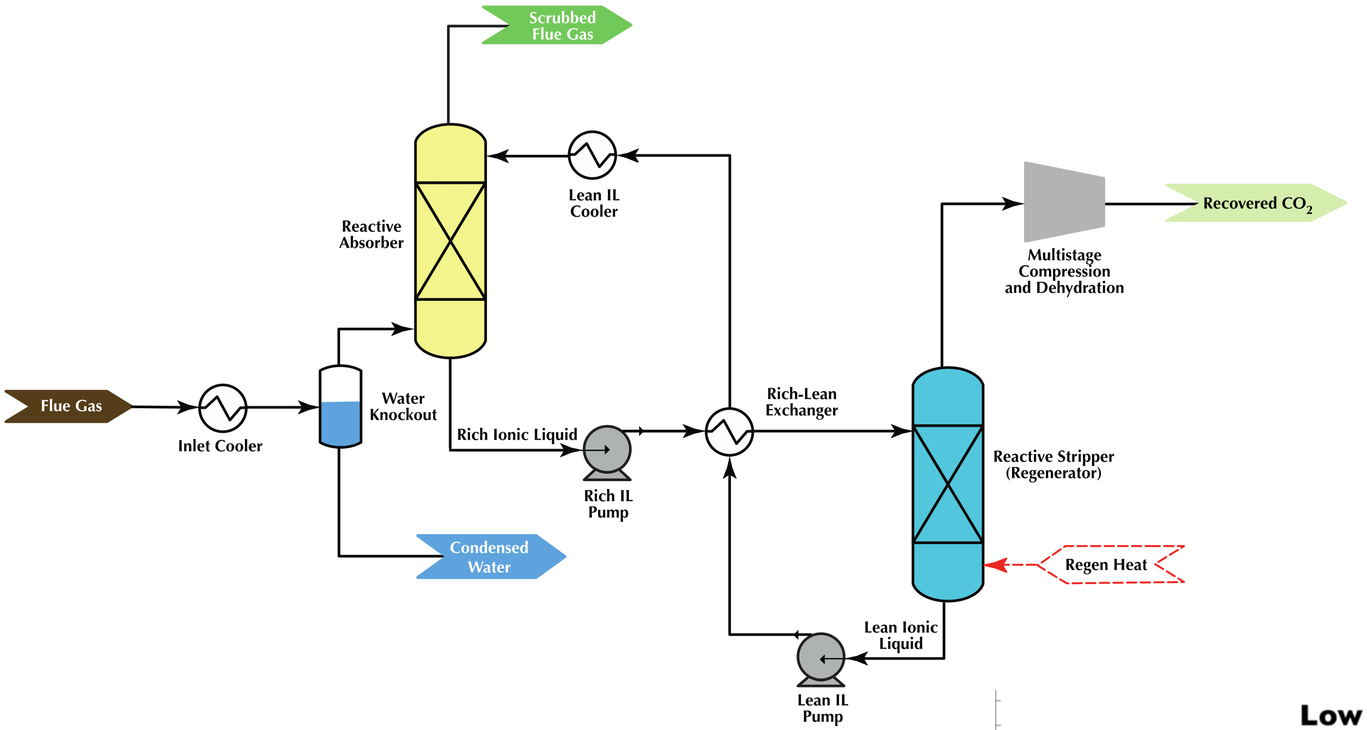
Examples of cations

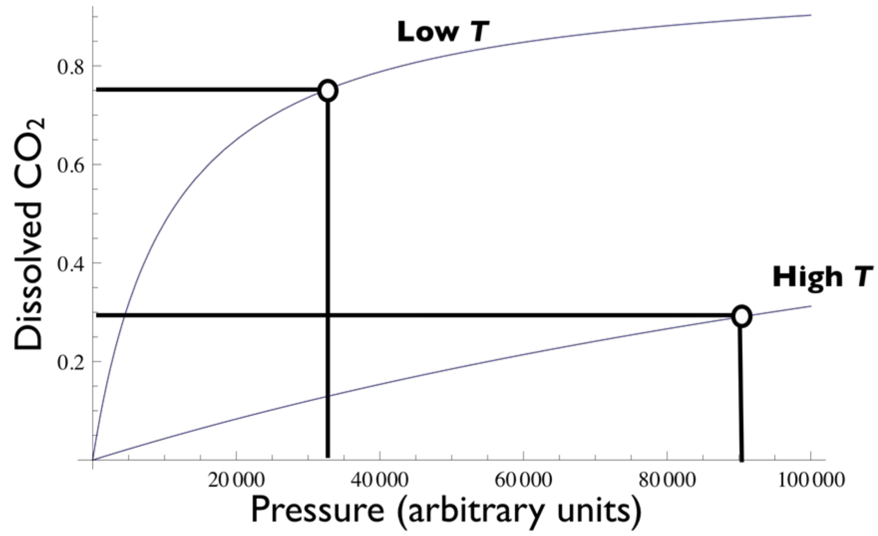


Examples of anions



Process Configuration





Preferred operating conditions

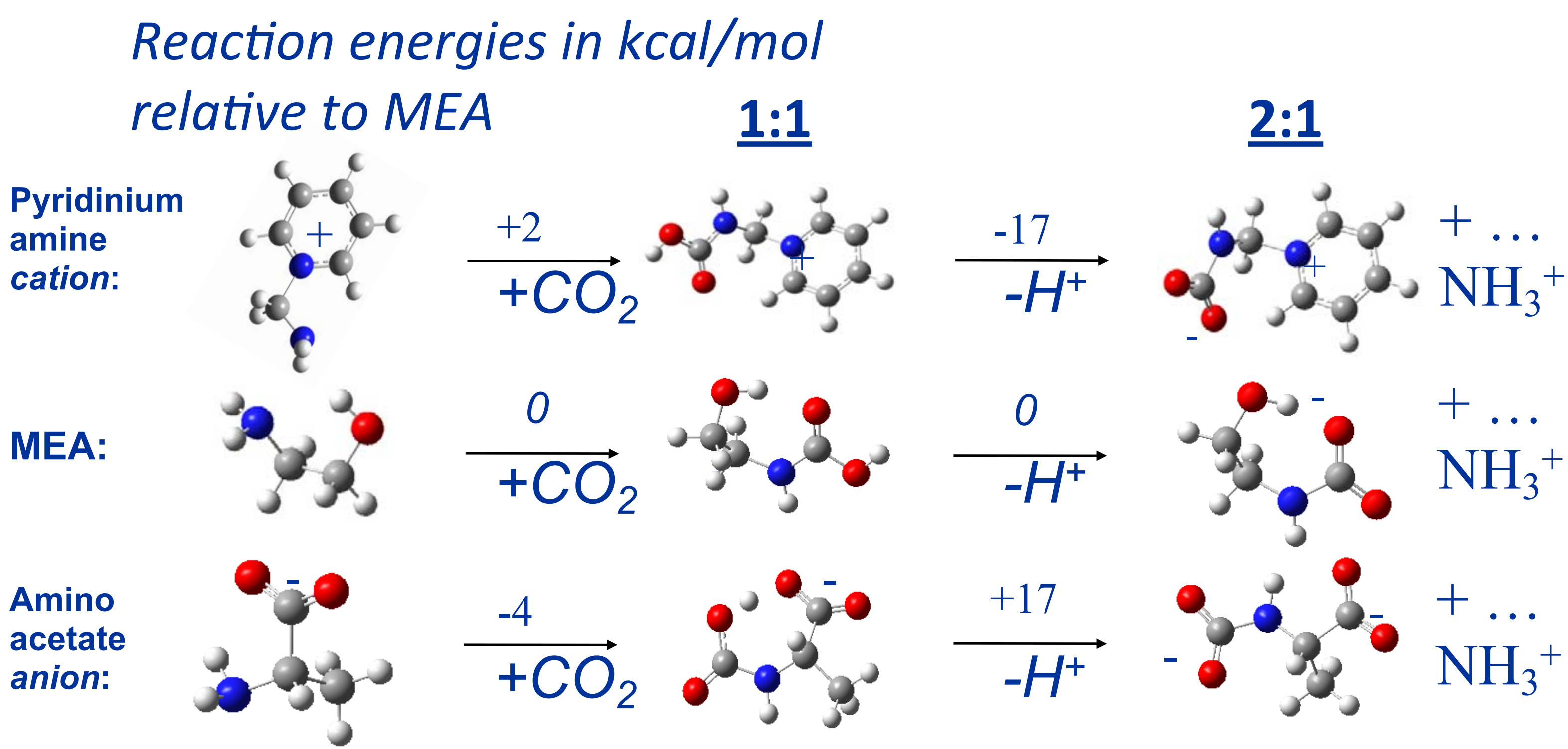
- Absorber: T~40 ^oC, P~1 atm
- Stripper: T ~ 140 ^oC, P >1atm

ILs vs. Aqueous Amines

- **Benefits of ILs**
  - **Better oxidative stability**
  - **Better thermal stability**
  - **No added water so reduce energy needed in regenerator for evaporation of water**
  - **Non-volatile**
- **Challenges we are addressing**
  - **Capacity**
  - **Viscosity**
  - **Enthalpy**
  - **Water stability**
  - **Operability**
  - **Cost**

Progress and Current Status: Capacity

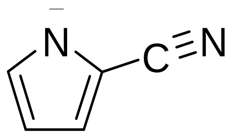
- **Showed how to double capacity**
  - **Add chemical functionality to cation – 2 IL : 1 CO_2**
  - **Add chemical functionality to anion – 1 IL : 1 CO_2**

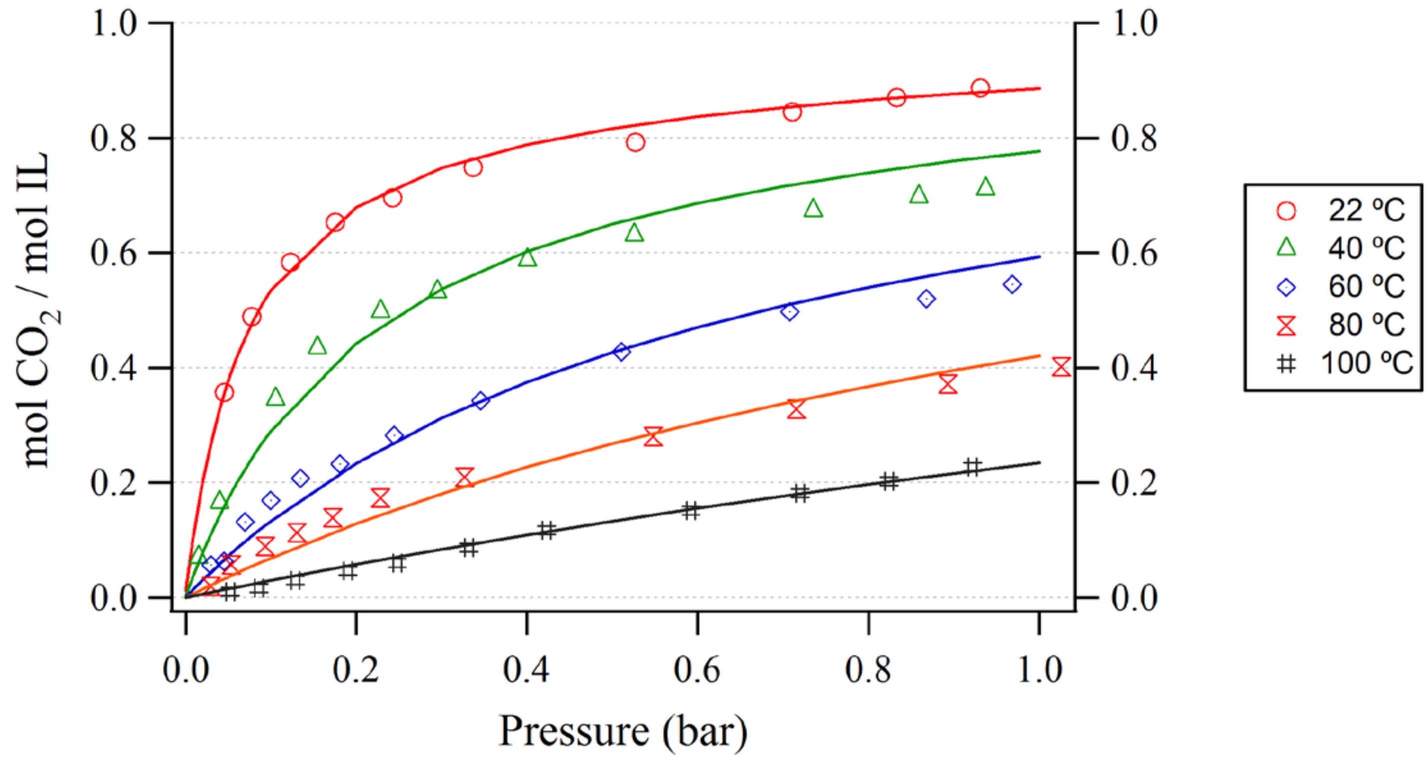


Electronic structure predictions, Mindrup and Schneider

Progress and Current Status: Capacity

$P^+(C_6H_{13})_3C_{14}H_{29}$



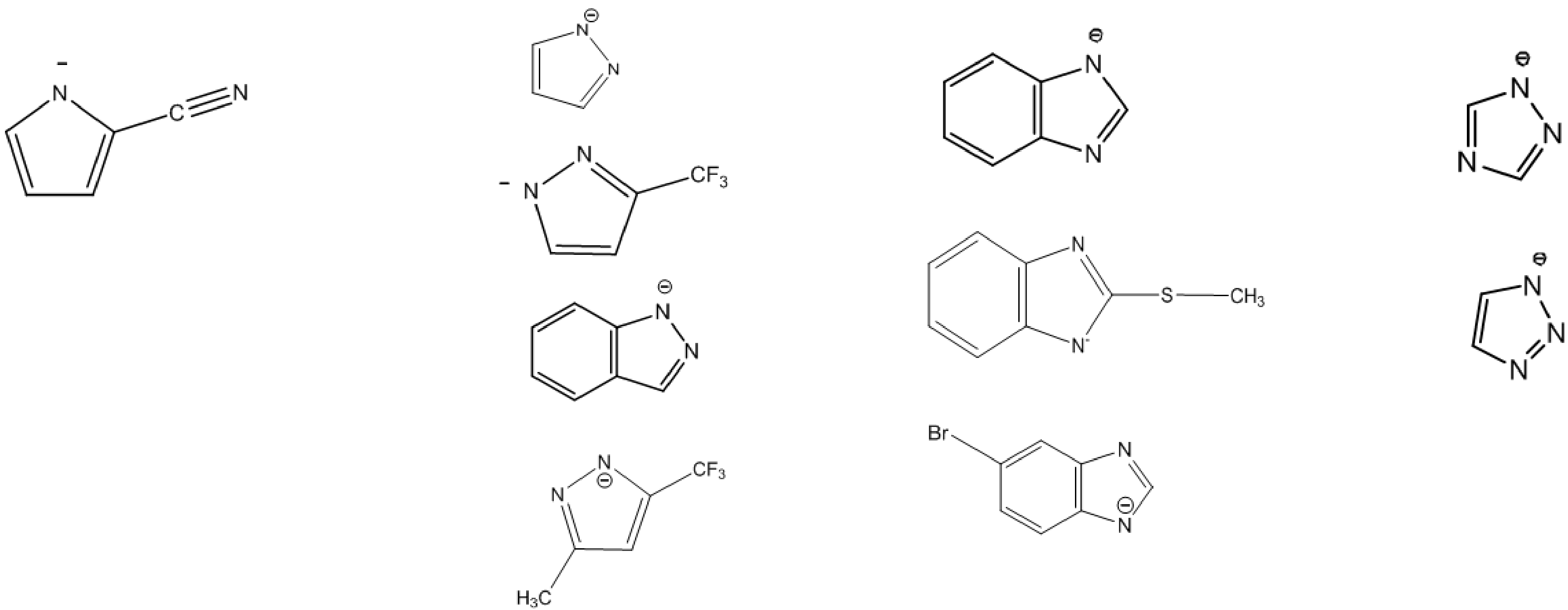


Experimental confirmation, Gurkan et al.: approaches 1:1 IL to CO_2 binding ratio

Progress and Current Status: Viscosity

- **Showed how to eliminate viscosity increase**
  - **Remove hydrogen bonding sites through use of aprotic hetrocyclic anion (AHA) ILs**

pyrrolides | pyrazolides | imidazolides | triazolides

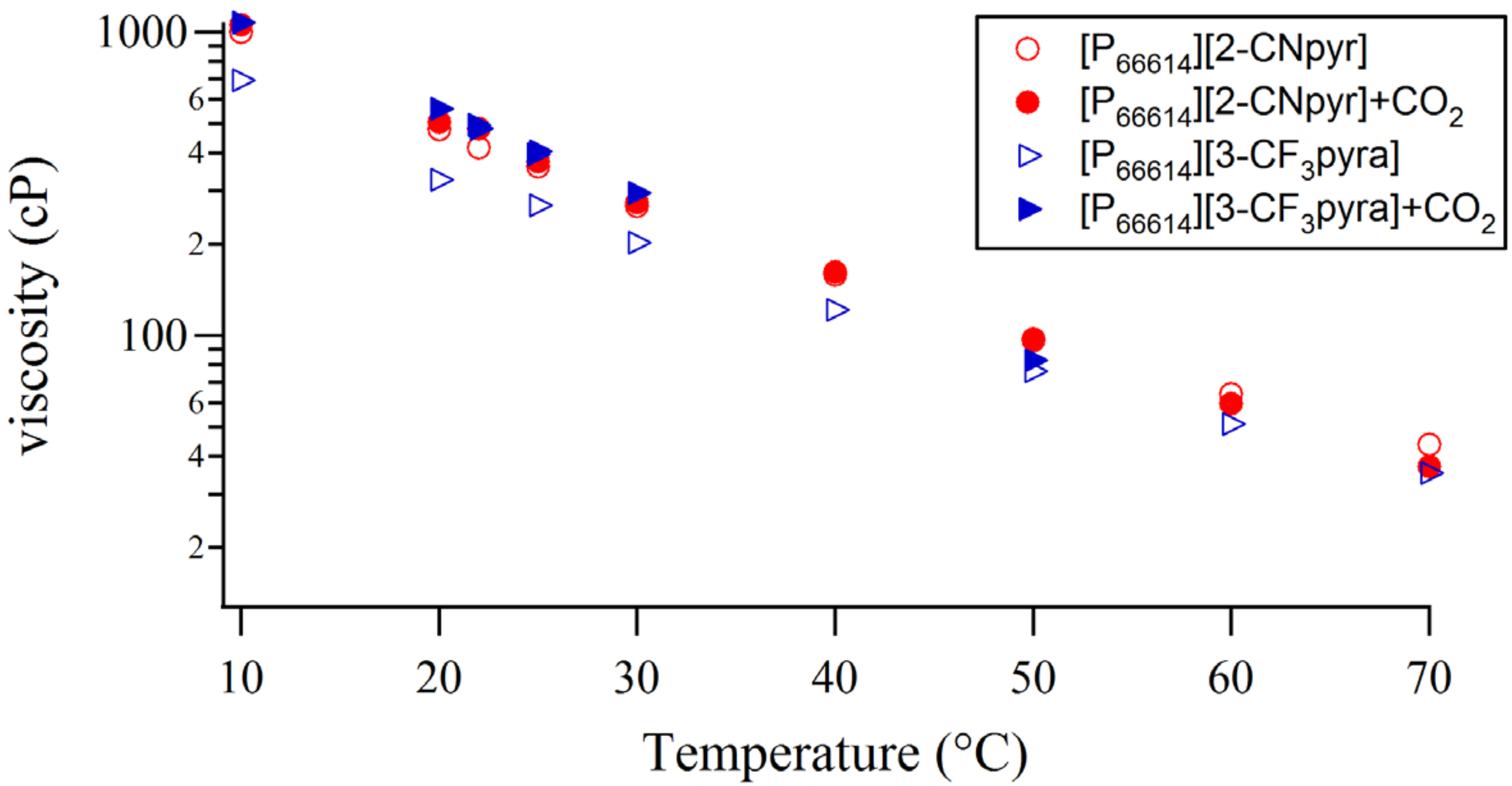


$-80^{o}C < T_g < -65^{o}C$

$260^{o}C < T_{decomp} < 330^{o}C$

Progress and Current Status: Viscosity

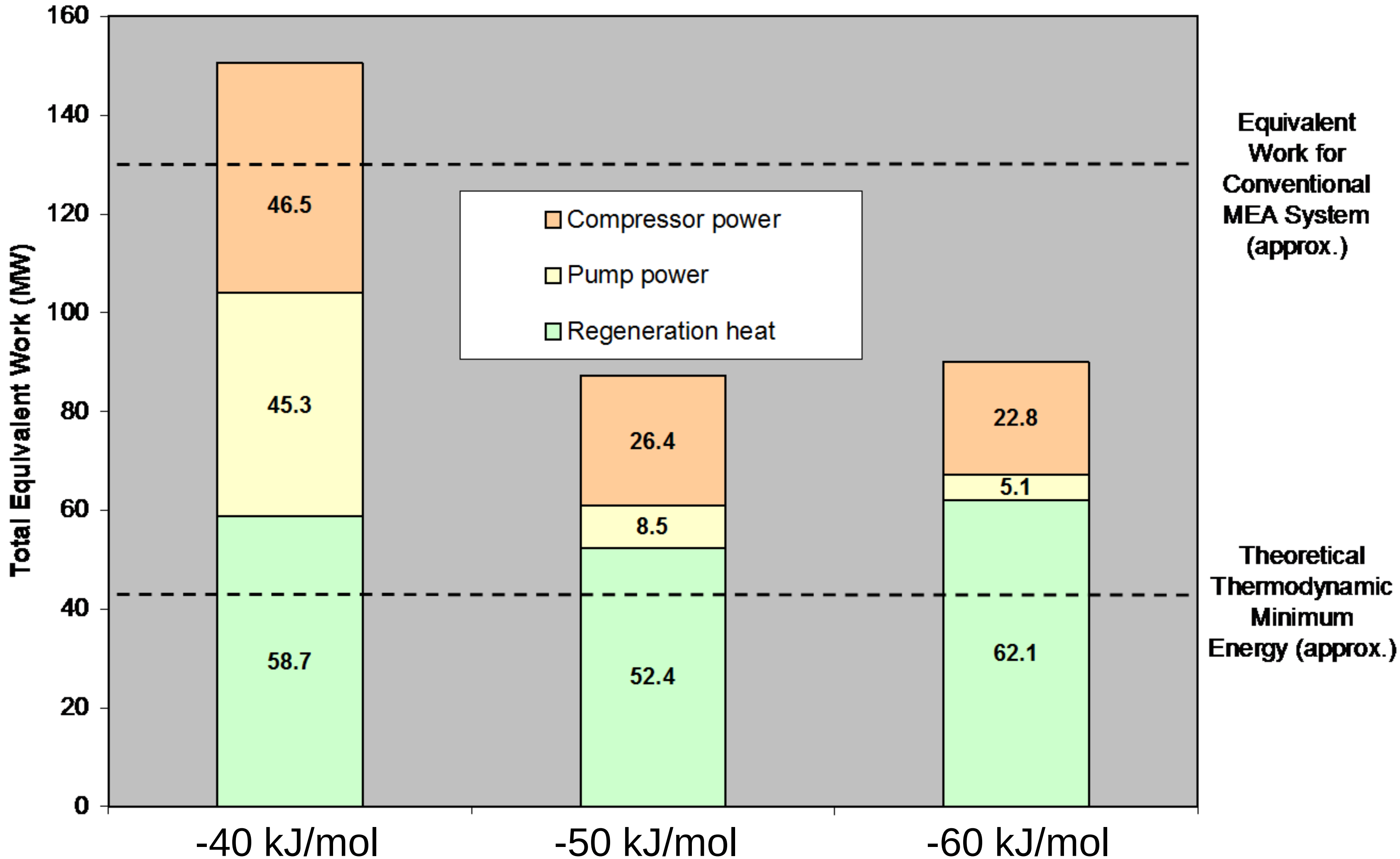
Very small viscosity increase when saturated with CO_2 at 1 bar and 22 °C



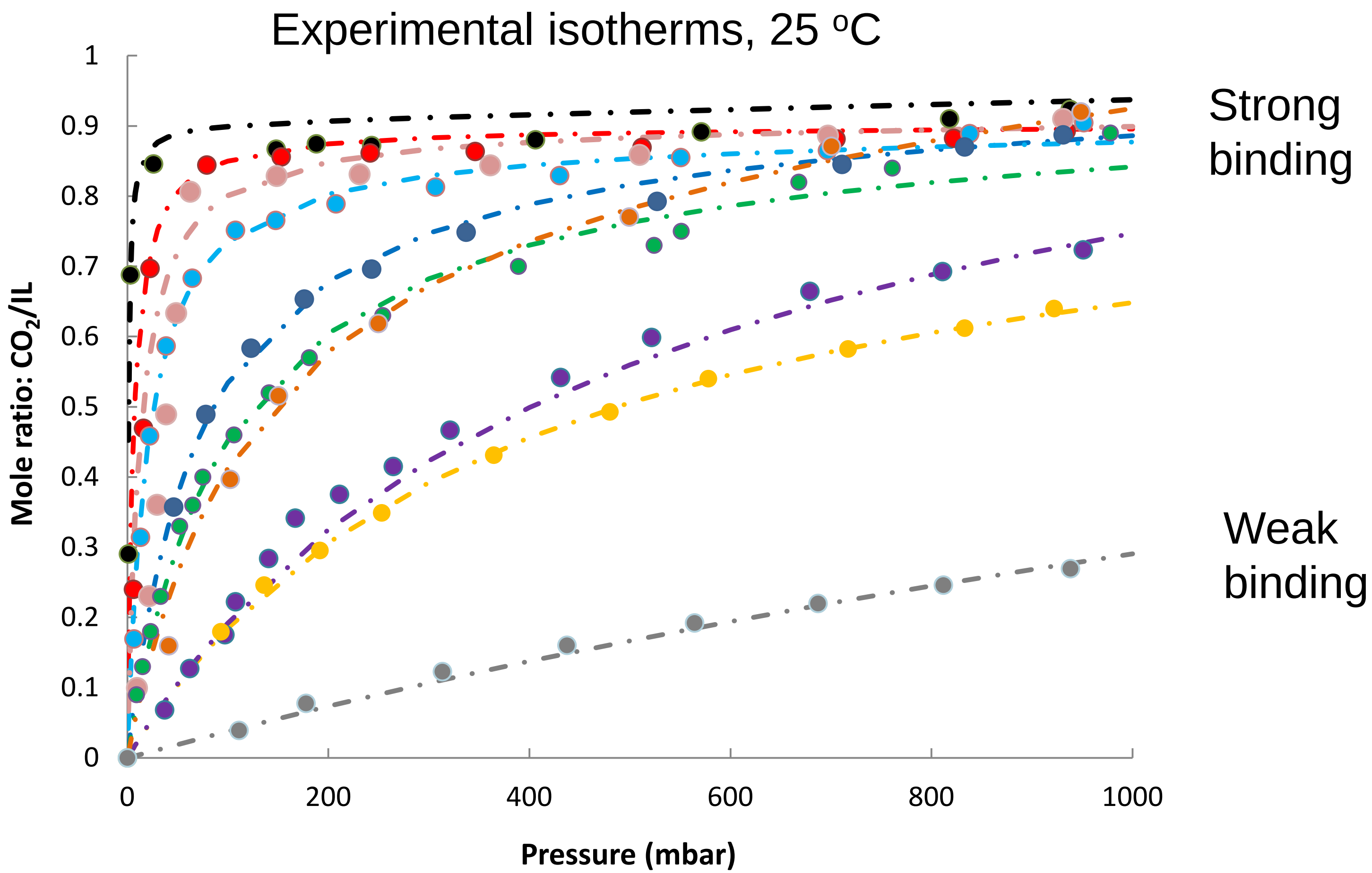
Progress and Current Status: Enthalpy

- **Enthalpy of reaction can be tuned**
  - **Large enthalpy**
    - **Increases capacity of absorption**
    - **Increases regeneration energy, temperature**
  - **Small enthalpy**
    - **Less capacity at absorption conditions**
    - **Decreases regeneration energy**
  - **Optimal determined from process modeling (Trimeric)**

Progress and Current Status: Enthalpy



Progress and Current Status: Enthalpy



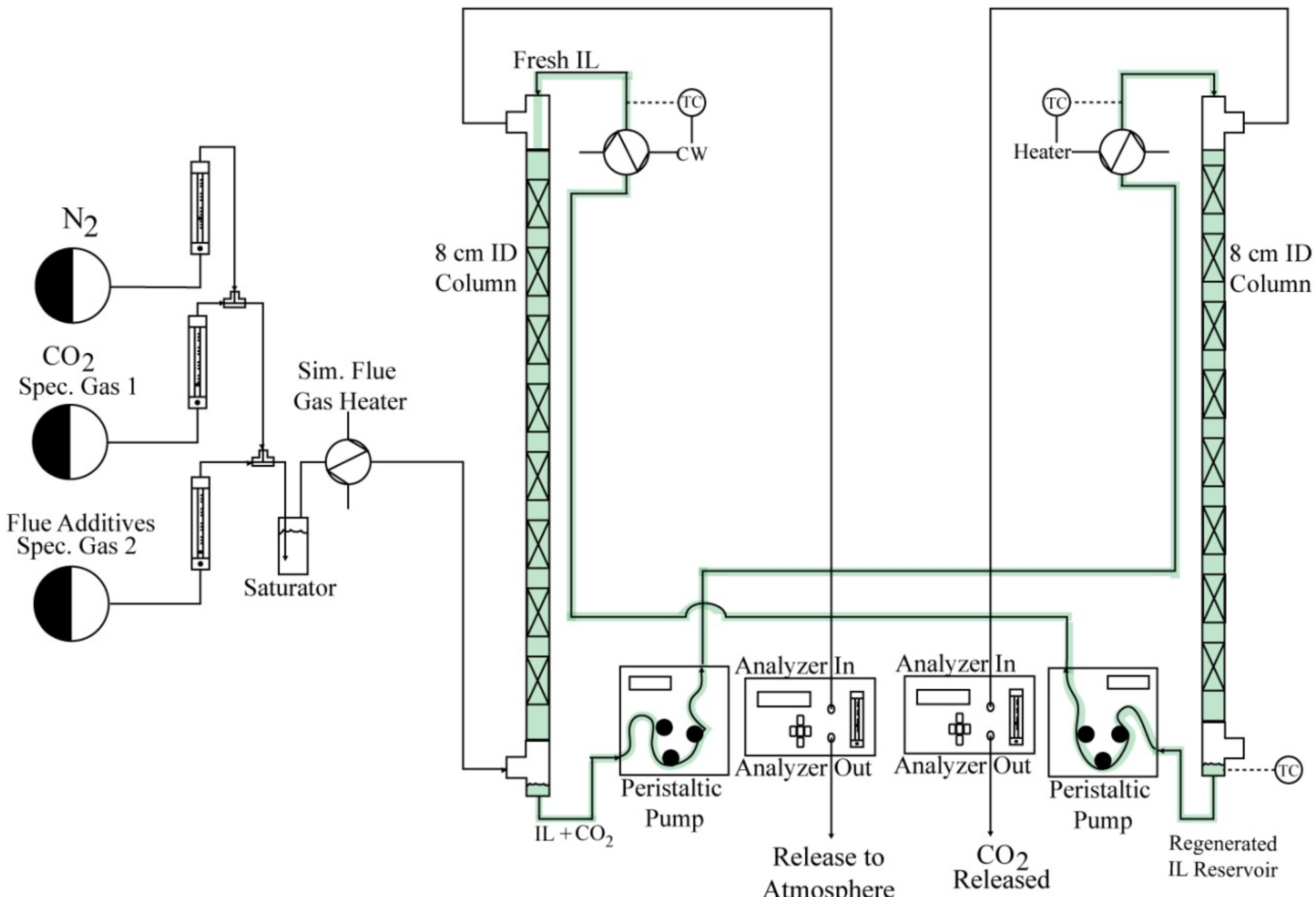
Developed many different ILs with enthalpies ranging from -15 to -100 kJ/mol

Progress and Current Status: Enthalpy

- **NDIL0046 was best IL known by original project end date**
  - **Slightly too low binding energy than optimal**
  - **Project extended to 9/30/12 to enable search for better ILs**
- **11 new ILs made and tested with better binding energies**
  - **Koei1, Koei2, Koei3, Koei4, Koei5**
  - **NDIL0063, NDIL0071, NDIL0080, NDIL0088, NDIL0091, NDIL0094**
- **None deemed acceptable**
  - **Unstable in presence of water + CO2 (Koei1,Koei2,NDIL0063,NDIL0071,NDIL0091)**
  - **Inconsistent capacity results, unexpected chemistry (NDIL0088)**
  - **Purity problems, making stability determination impossible (Koei4,Koei5,NDIL0080,NDIL0094)**
  - **Prohibitive cost (Koei3)**

Good possibility if Koei can discover cheaper production method

Progress and Current Status: Operability via Lab-Scale Testing



- Continuous operation
- Can run columns separately
- 2 liter liquid samples

Progress and Current Status: Operability via Lab-Scale Testing

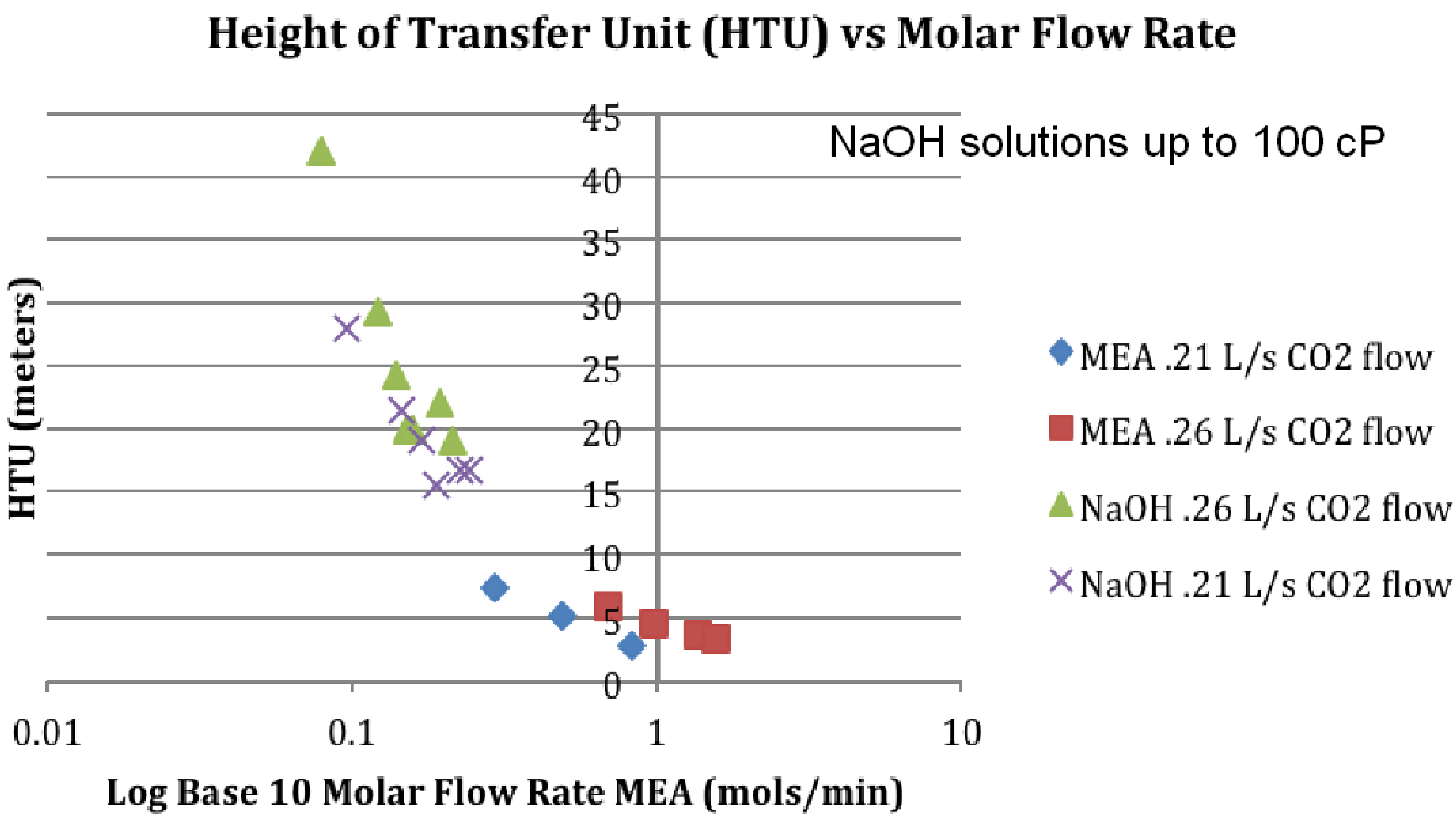
- We have run continuous steady-state operation of absorber and regenerator
- Verified with MEA
- Ran with EMD0005
- Koei delivered 25 liters of NDIL0046 in June, 2012
- Running NDIL0046
- B&W to run NDIL0046
  - Similar absorber/stripper system
  - Wetted wall column
  - Corrosion testing

Figure 1: Image of the lab-scale unit constructed for Task 18.

“Structured Packing”

- We have to deal with a very viscous material in a laboratory size column, 2.5 cm in diameter

HTU for (viscosity) test fluids



HTU results for EMDIL

Ionic Liquid Flow Rate (ml/s)	CO2 Flow Rate (L/s)	Molar Flow Ratio CO2/IL	CO2 in %	CO2 out %	HTU Value m
3 ml/s	.16	1.48	11.25	10.1	16.37
3 ml/s	.12	1.11	11.3	9.5	10.9
3 ml/s	.10	.92	11.6	9.1	7.47
3 ml/s	.08	.74	10.1	7.3	6.48
1.5 ml/s	.04	.74	14.1	12.2	12

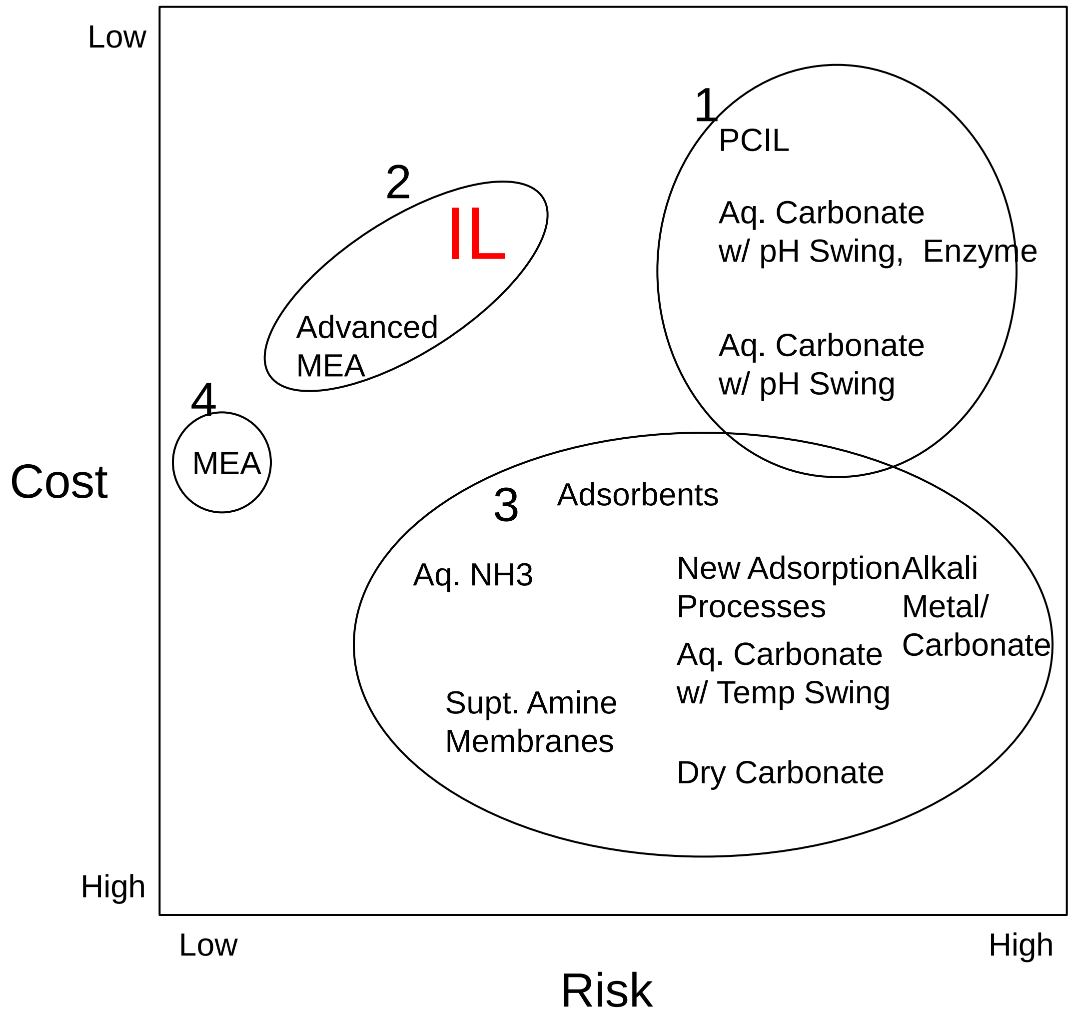
Progress and Current Status: Commercialization Study

1 - Potential for low cost but very high risk

2 - Potential for lower cost at moderate risk

3 - Currently cost estimates and risk are high

4 - Low risk but high cost



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Progress and Current Status: Commercialization Study

- Risk vs. Cost
  - Risk profile indicates multiple solutions should be pursued
  - Development and deployment cost is large, suggesting down-selects should be made early
  - Focus on processes with potential to be substantially less expensive than MEA, even if risky
  - IL process and lower-energy variations of the MEA process should continue to be pursued as retrofit options
- Scale-up of the IL-based CO_2 capture process to the point of full-scale demonstration is doable in ten years or less.
  - Multi-step sequential scale-up, not including full-scale demonstration, is an estimated $60 million.
  - Construction and 1 ½ years of operation of the full-scale demonstration separation process will cost roughly $600 million.
- Study being updated in response to NETL comments

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Critical Path Milestone	Original Planned Completion Date	Revised completion date	Actual Completion Date	Comments
Initiate force field development and modeling	09/01/07		06/15/07	
Initiate synthesis of Generation 1 compounds	12/01/07		06/15/07	
Initiate physical property measurements Generation 1 compounds	03/01/08		09/01/07	
Complete preliminary economic, engineering and systems analysis	07/15/08		09/01/08	
Initiate modeling of Generation 2 compounds	09/01/08		09/01/08	
Initiate synthesis of Generation 2 compounds	12/01/08		09/01/08	
Initiate physical property measurement Generation 2 compounds	03/01/09		03/01/09	
Complete Phase II engineering and systems analysis	07/15/09		07/15/09	
Initiate bench scale experiments	08/01/09		11/15/09	
Complete TSA analysis	11/30/09		12/03/09	
Completion of bid package for lab scale unit	05/31/10		NA	Design to be done in house
Complete test plan for lab scale system	06/30/10		06/30/10	
Identify best Generation 3 ionic liquid; deliver topical report on IL	07/31/10		07/17/10	
Complete updated economic analysis	07/31/10		08/04/10	
Down-select process configuration	08/01/10		03/10/10	Decision to use absorption made soon after Task 11.0 completed
Delivery of Gen 2 ionic liquid for lab scale process	02/28/11		03/10/11	
Complete construction and testing of lab scale system	02/28/11		02/28/11	Construction completed 9/30/10; testing completed Feb., 2011
Begin operation of lab scale system	03/01/11		03/15/11	Began after receipt of Gen 2 sample
Complete Generation 3 solvent optimization activities	08/31/11	01/31/12	2/15/12	Delayed due to earthquake
Delivery of Gen 3 ionic liquid for lab scale process	10/31/11	05/01/12	06/14/12	Delayed due to EH&S holdup in Japan
Complete operation of lab scale system with Gen 2 IL	10/31/11		12/01/11	Extra testing done while waiting for Gen 3 IL delivery
Complete operation of lab scale system with Gen 3 IL	02/29/12	8/31/12		Began testing with NDIL0046 July 2012
Deliver final commercialization report	02/29/12			Draft submitted, revisions being made
Complete final economic, engineering and systems analysis	02/29/12	05/31/12		Now 9/1/12 due to due to delay in property transmission to Trimeric

All but three milestones completed

Actively working on final milestones

No problems anticipated

Plans for future testing

- Scale up to next level
  - Work with a partner company with scale-up experience
  - Synthetic flue gas
  - Slip stream
  - Have held discussions with Matric, B&W, Southern Company

- Process chemistry research to make ILs at scale for lower cost
  - Current liquid-phase batch processes too expensive
  - Gas phase continuous process: $5-20/kg
  - Can Koei3 be made more cheaply?

- Improve process simulations
  - Rate-based models / data

3. Steam train: 300 PSI, 650 F (25 points)

The Union Pacific Railroad has always been known for having some of the biggest, heaviest and most powerful locomotives. This was the case during the steam era and for a while during the diesel era until diesel electric locomotives became completely standardized.

One of most powerful late era steam locomotives was the Union Pacific 9000 series

UNIVERSITY OF NOTRE DAME

CBE20260
Spring 2012
Final Exam
5/8/12

1. Further analysis of a steam locomotive. (70 points)

The Union Pacific Challenger class of locomotives was designed and built in the late 1930's and early 1940's. The wheel arrangement was 4-6-6-4 which means 4 lead wheels, 2 sets of 6 drive wheels and 4 trailing wheels. These locomotives were "articulated", that is they had a joint in the frame between the sets of drive wheels that allowed them to better follow curves. One of these magnificent machines is still operating as a display engine and you can track its location on the *Union Pacific* website. If