CO_2 Binding Organic Liquids for Post Combustion CO_2 Capture

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Project Objectives

Develop novel non-aqueous CO_2 scrubbing solvents and capture process that could substantially reduce the parasitic energy load and corresponding increase in cost of electricity (COE) for post-combustion CO_2 capture

Performance Targets

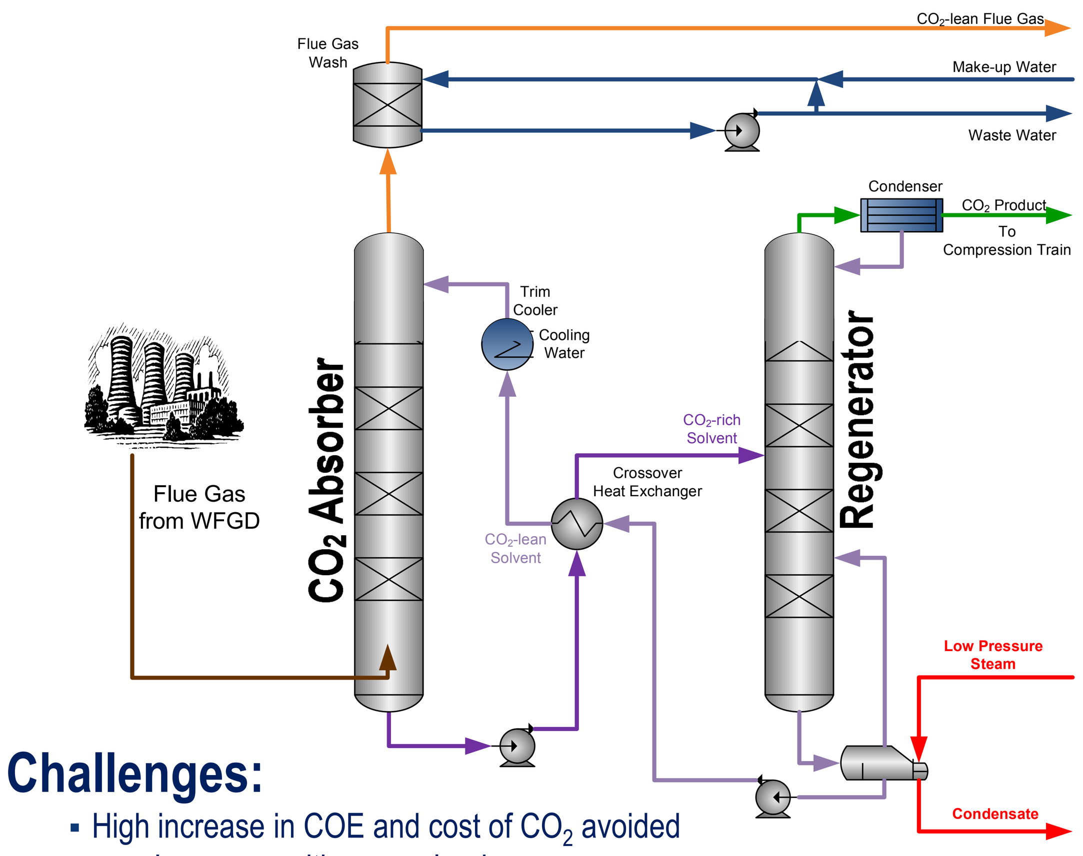
- Power Performance:
  - Reboiler Duty < 2.0 GJ/tonne CO_2
  - Plant Efficiency Point Loss < 7 points
- Economic Indicators:
  - % Increase in COE < 50%
  - Cost of CO_2 Avoided < $45/tonne CO_2

Background

Aqueous-amine Solvent Systems:

Only commercially-available capture technology

Monoethanolamine (MEA) **Hindered Amines**



Challenges:

- High increase in COE and cost of CO_2 avoided
  - Large parasitic power load
    - High heat of absorption, regeneration temperatures, and compression
  - High capital and operating costs
    - Expensive materials of construction due to corrosivity of solvents
    - High degradation rates due to O_2 and SO_2 in flue gas
    - Evaporative losses and wastewater treatment requirements

Cost and Energy Requirements of State-of-the-Art Amine Solvents

Basis: 450 MW_e Coal-fired Power Plant

Solvent	Parasitic Energy [%]	Cost [$/ton CO_2 removed]			Cost of CO_2 [$/ton CO_2]†
		Power	Capital	Operating	Removed
30 % MEA[1]	27	29	17	8	52
KS-1[2]	22	23	14.4	8.4	46

†Assumed $80/MWh

Current Situation

- Current DOE post-combustion research target for ***increase in COE (ICOE) is 35%***.
- Current state-of-the-art technologies are estimated to be ***75-100%***.

Path to Reducing ICOE and Cost of CO_2 Avoided

ICOE Break Down[1] = 56% Power Consumption + 33% Capital Expense + 11% Operating Expense

$$q_R = \left[\frac{C_P(T_R - T_F)}{\Delta\alpha}\cdot\frac{M_{sol}}{M_{CO_2}}\cdot\frac{1}{x_{sol}}\right] + \left[\Delta H_{V,H_2O}\cdot\frac{p_{H_2O}}{p_{CO_2}}\cdot\frac{1}{M_{CO_2}}\right] + \left[\frac{\Delta H_{abs,CO_2}}{M_{CO_2}}\right]$$

Sensible Heat — Heat of Vaporization — Heat of Absorption

Solvent	C_p [J/g K]	Δh_{abs} [kJ/mol]	Δh_{vap} [kJ/mol]	X_{solv} [mol solvent/ mol solution]	$\Delta\alpha$ [mol CO_2/ mol solvent]	Reboiler Heat Duty [GJ/tonne CO_2]
MEA (30%)	3.8	85	40	0.11	0.34	3.22
Lower Energy Solvent System	↓	↓	↓	↑	↑	↓

- Aqueous systems have similar properties such as high heat capacities, heats of absorption and vaporization, and high dilutions
- Reboiler heat duties are similar and can only be *improved marginally* by lower heats of absorption or increase in concentration of amine.

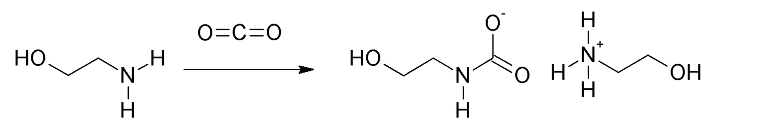
References

1. Rochelle, G. T. (2009). "Amine Scrubbing for CO_2 Capture." *Science* **2009,** 325, 1652-1654
2. http://www.co2management.org/proceedings/Masaki_Iijima.pdf
3. Heldebrant, D.J. et al. (2008). "Organic liquid CO2 capture agents with high gravimetric CO2 capacity." *Energy Environ. Sci.,* **2008**, 1, 487–493.

Approach

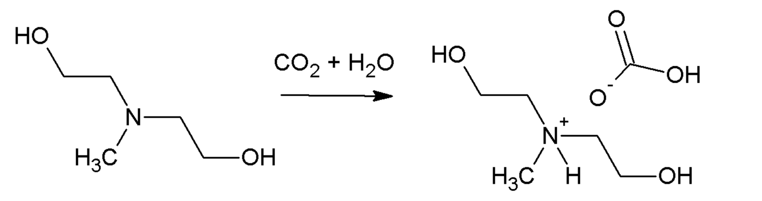
- Non-aqueous, organic-based solvent systems
  - Desirable physical and chemical properties to lower reboiler duty
- Alternative reaction pathways to conventional carbamate and bicarbonate chemistry

Primary and secondary amines: Carbamate formation



Regeneration Temp. = 120°C
Absorption Rate ≈ 10,000 s^{-1}
(Flue gas Conditions)

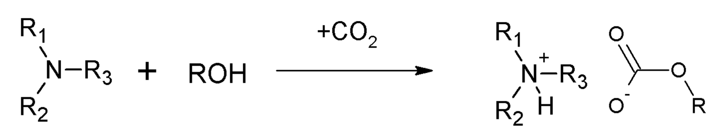
Tertiary hindered amines: Bicarbonate formation



Regeneration Temp. = 90°C
Absorption Rate ≈ 10 s^{-1}
(Flue gas Conditions)

Alternative, non-aqueous reaction: Alkylcarbonate formation

(CO_2 Binding Organic Liquids (CO_2BOLs) originally proposed by Heldebrant et al.[3])



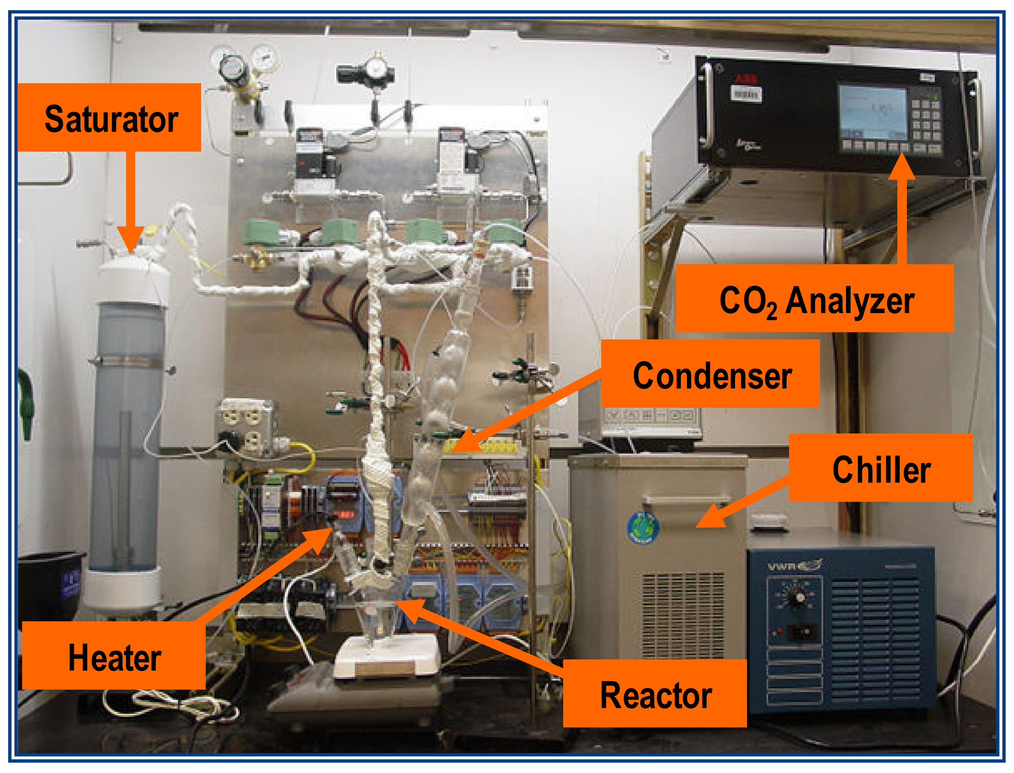
Regeneration Temp. < 70°C
Absorption Rate ≈ not determined

Technical Challenges for Existing CO_2BOLs Systems

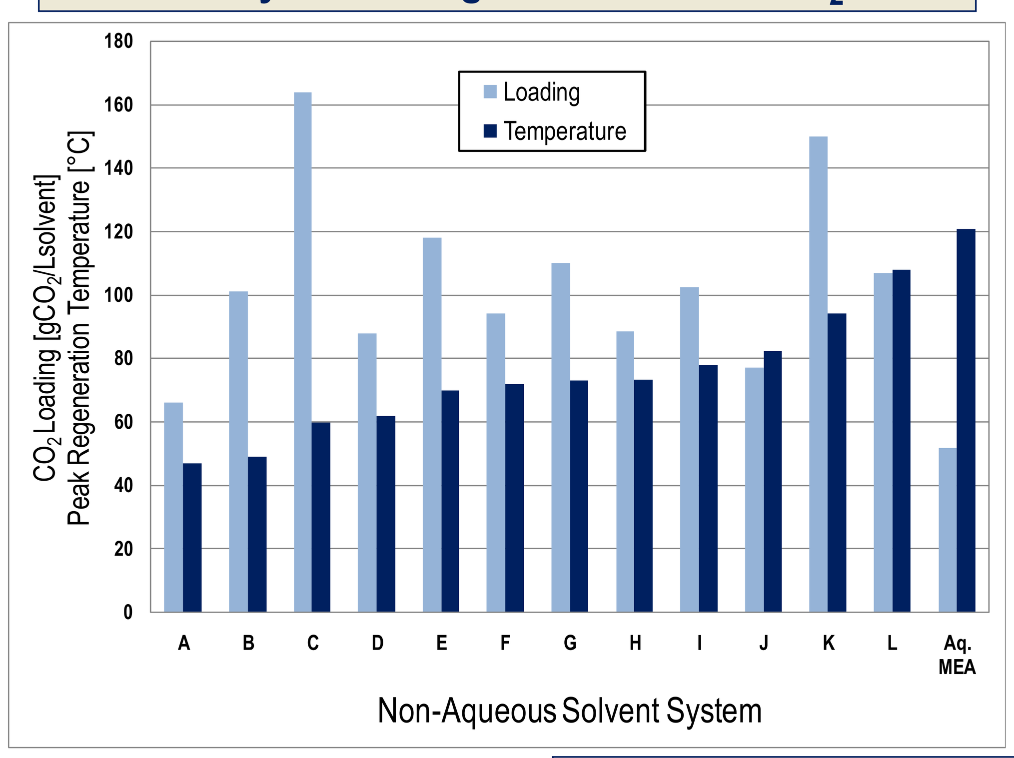
- Chemical degradation by water
  - Water reacts with many alkoxide bases producing the hydroxide anion
  - CO_2 is absorbed as a bicarbonate salt requiring more energy for regeneration
- Physical accumulation of water from flue gas in solvent
  - Flue gas from wet FGD is saturated (~15%) with water vapor
  - Water can condense or be desiccated by non-aqueous solvents in the Absorber vessel under optimal absorption conditions until VLLE is established
- Viscosity of solvent should be low for optimal mass transfer of CO_2 from gas to liquid
- Solids formation in rich solvent
  - Many solvents form insoluble solids at high CO_2 loadings
  - Solids can accumulate in packing or other undesirable areas in the process
- Foaming
  - Many aqueous and non-aqueous solvents foam when purged with gases
  - Anti-foaming agents must be added to avoid entrainment

Experimental Results

Highly Automated Solvent Evaluation System



Preliminary Screening of RTI's Novel CO_2BOLs



Advantages

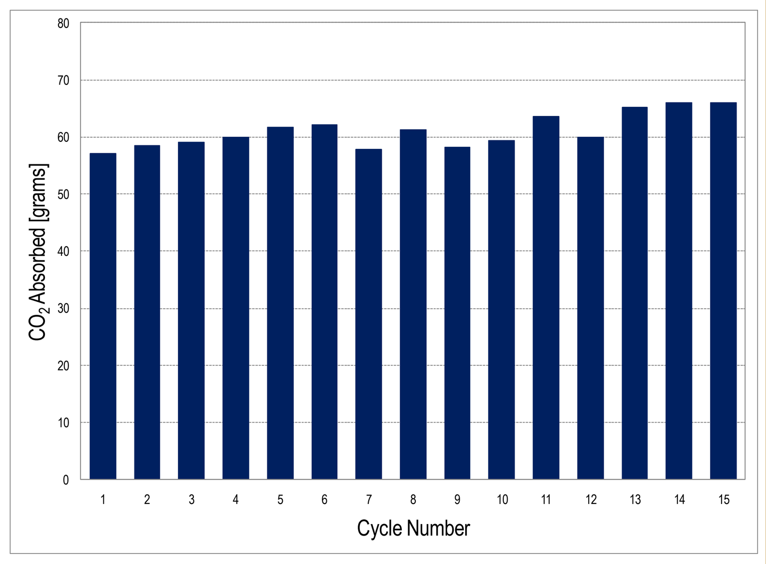
- Low regeneration temperatures
- High loading capacities
- Not degraded by water

Experimental Results (cont'd)

Selective Alkylcarbonate Formation in the Presence of Water

Absorption:
Temperature: 30°C
Flue Gas Composition:
14%CO_2, ~3 % H_2O
4% O_2, 50 ppm SO_2
Balance N_2

Regeneration:
Temperature: Ramp to 80°C
Gas Composition:
N_2 Purge



Water accumulation is a major hurdle for non-aqueous systems

- Solvent systems with low water solubility form separate liquid phase
- Water balance can be maintained without distillation and offer low-energy separation options
- Regenerator can utilize low regeneration temperature

Robust CO_2BOLs are water tolerant

Lowering Power Load and ICOE

Solvent	C_p [J/g K]	Δh_{abs} [kJ/mol]	Δh_{vap} [kJ/mol]	X_{solv} [mol solvent/ mol solution]	$\Delta\alpha$ [mol CO_2/ mol solvent]	Reboiler Heat Duty [GJ/tonne CO_2]
MEA (30%)	3.8 ↓	85 ↓	40 ↓	0.11 ↑	0.34 ↑	3.22 ↓
Lower Energy Solvent System	2.0	30*	38	0.3*	0.6*	1.97

*Experimentally measured data

Beneficial Characteristics of RTI's CO_2BOLs

- Lower specific heat capacity (C_P)
- Lower heat of absorption (Δh_{abs})
- Lower solvent vapor pressure at regen. T (p_i)
- Lower solvent dilution (Increasing x_{solv})
- Increased CO_2 working capacities ($\Delta\alpha$)

Challenges facing RTI's CO_2BOLs

- Lower absorption T for optimal capture
- Water accumulation due to condensation or desiccation of water from flue gas
- Evaporative losses in Absorber
- Degradation by flue gas contaminants (O_2, SO_2)
- Cost of solvents

RTI's CO_2BOLs have the potential to reduce all COE contributors

Significantly lower energy penalty

- Proper selection of non-aqueous solvents can lead to a solvent system with superior physical and chemical properties compared to aqueous amine systems
- Alkylcarbonates offer a lower energy alternative to conventional carbamate and bicarbonate chemistries
- RTI's novel CO_2BOLs are stable in the presence of water

Lower Capital Costs

- Simple process configuration, similar to conventional processes
- Potential for process simplifications
- Potential for less expensive materials of construction

Lower Operating Costs

- Potential for reduced solvent make-up costs
  - Evaporative losses can be minimized
  - Less prone to oxidation than conventional amines
  - SO_2 absorption is reversible

Technology Development Plan

Transitioning from novel solvent concept to commercial

	Previous Work			Current Project		Future Development			
Yr	2009-10			2010-13		2014-15		2016-18	2019+
TRL	1	2	3	4	5	6	7	8	9

Proof of Concept/Feasibility — Prototype Testing at Power Plant

Laboratory Validation

- Comprehensive solvent screening
  - Identify solvent systems that exhibit:
    - Working capacity > 0.4 mol CO_2/mol sol
    - Regeneration temperature < 120°C
    - Heat of reaction < 80 kJ/mol CO_2
    - Minimal solvent degradation
  - Determine thermodynamic and physio-chemical properties for novel systems
- CO_2 capture process modeling
  - Develop comprehensive process model
  - Evaluate novel process configurations and integration schemes
  - Compare performance with conventional solvent systems

Relevant Environment Validation

- Bench-scale testing to assess solvent performance
  - Continuous flow, 10 kg/day CO_2 capture unit operated using simulated flue gas
  - Long term (1,000 hours) performance stability testing with high-fidelity flue gas
  - Collect process and scale-up data to support simulation and pilot-scale unit design efforts
- CO_2 capture process modeling
  - Update process models
  - Techno-economic analysis
- Preliminary engineering design package for a pilot unit

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