DOE Project NT0005287

Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture

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Chemical Engineering and Chemistry 22-Year Collaboration at Georgia Tech

- Jointly Directed Students and Postdoctorals
  - ✓Chemical Engineers
  - ✓Chemists
  - ✓> 50 PhDs Completed
- >50 Joint Research Grants
- >250 Publications and Presentations
- **2004 Presidential Green Chemistry Challenge Award**

Funding – $ in Thousands

By Budget Period, DOE and Cost Share

Expenditure	BP1 DOE	BP1 Share	BP2 DOE	BP2 Share	BP3 DOE	BP3 Share	Total DOE	Total Share
Personnel	372	92	417	101	434	87	1251	263
Equipment	92	62		120				150
Supplies	30		76		75		228	
Services	21		38		38		114	
Travel	9		9		9		27	
TOTAL	524	154	540	221	556	87	1620	462
Share %		23		29		14		22

Overall Project Performance Dates

First Year				Second Year				Third Year			
Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4

PROJECT MANAGEMENT, PLANNING, AND REPORTING

1-COMPONENT SILYL AMINE-BASED ILS

1-COMPONENT SILYL GUANIIDINE-BASED ILS

THERMODYNAMICS AND RATES OF IL FORMATION

OPTIMIZE CO_2 CAPTURE SOLVENT STRUCTURE

PROCESS DESIGN AND ECONOMIC ANALYSIS

Project Participants

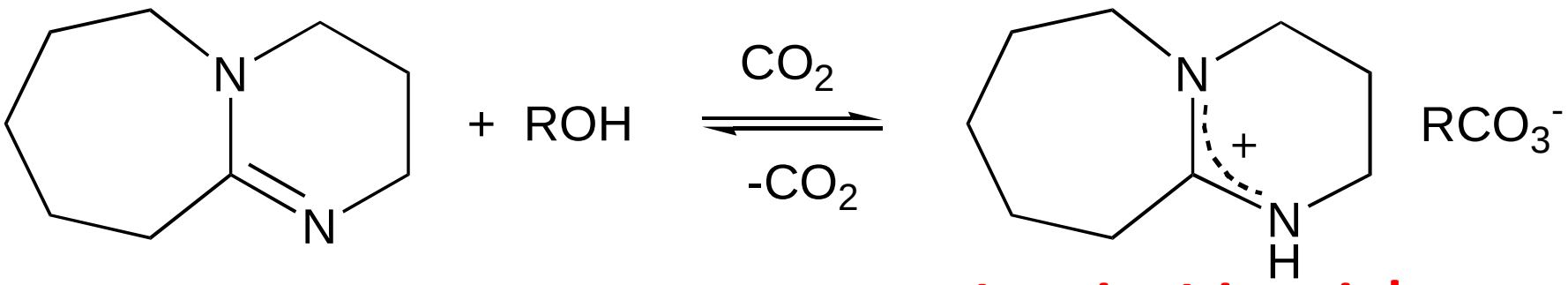
- Chemical Engineers and Chemists Supported on this Grant
  - ✓ Faculty – Charles Eckert, Charles Liotta
  - ✓ Postdocs – Elizabeth Biddinger, Manish Talreja, Manjusha Verma
  - ✓ PhD Students – Olga Dzenis, Ryan Hart, Gregory Marus, Amy Rohan, Emily Nixon, Amber Rumple
  - ✓ Undergraduate – Melissa Burlager
- Other Contributors
  - ✓ Research Scientist – Pamela Pollet
  - ✓ PhD Students – Kyle Flack, Jackson Switzer
  - ✓ Undergraduates – Sean Faltermeier, Paul Nielson, Jessica Doyle, Ashley Bembry, Poomrapee Jewanarom, Jordan Donaldson

Project Goal: CO_2 from Coal-Fired Power Plants

- Long-Term Goal
  - ✓ Capture 90% of CO_2 with less than 30% cost increase by 2020
- This Project
  - ✓ **Systematic Structural Changes to get Solvent with Optimum Balance of Properties**
    - ➢ Ease of Synthesis
    - ➢ High Capacity
    - ➢ Low Viscosity
    - ➢ Optimum Thermodynamic Properties
  - ✓ **Optimum Solvent**
    - ➢ Demonstrate Commercial Viability: Process Simulation
- **Bottom Line:** Superior Process for Post-Combustion CO_2 Capture from Coal-Fired Power Plants

Scientific Background: First Reversible Ionic Liquid (RevIL) – Amidine Absorbs and Releases CO_2

- DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene)
  - ✓ Absorbs CO_2 with Alcohol at Ambient T
  - ✓ Releases CO_2 with Inert Gas Sparge or at Higher T
  - ✓ All Done at Ambient Pressure – No High Pressure
  - ✓ Many Other Examples



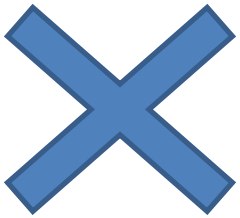
Molecular Liquid ⇌ Ionic Liquid

Jessop, Heldebrant, Li, Eckert, Liotta, *Nature* **2005**, *436*, 1102.

RevILs Proposed in This Work

- Silylamines

- Silylguanidines



  - Synthesis: Poor Yields
  - High molecular weight for liquid

RevILs: Dual Capture Mechanism

Chemisorption

Molecular Liquid $\xrightleftharpoons[-\,CO_2]{+\,CO_2}$ Rev. Ionic Liquid

Added Capacity By **Physisorption**

Rev. Ionic Liquid $\xrightarrow{+\,CO_2}$ CO_2 Swollen Ionic Liquid

Silylamine Library

Acronym	Structure
TMSA	
TESA	
CHDMSA	
PDMSA	

Acronym	Structure
TEtSA	
TPSA	
THSA	
FSA	

Silylamine Library

Acronym	Structure
TMSA	
TESA	
CHDMSA	
PDMSA	

Unstable in air and moisture

Turn into solids after CO_2 reaction

Silylamine Synthesis

General hydrosilylation reaction to form trialkylsilylatedamines

- Easy One Step Synthesis with High Yields
- Characterization: NMR, FT-IR, Elemental Analysis
- Easily Change Structure by Changing R_1 & R_2

Properties: CO_2 Capture

- **Absorption Capacity (Chemical and Physical)**
  - **<u>Chemisorption</u>: Equilibrium Constant $K(T)$**

$$K = \frac{a_{IL}}{a_{ML}{}^2 a_{CO2}} = \frac{x_{IL}\gamma_{IL}}{(x_{ML}\gamma_{ML})^2 \cdot \frac{f_{CO2}}{f^{\circ}_{CO2}}} = \frac{x_{IL}\gamma_{IL}}{(x_{ML}\gamma_{ML})^2}$$

K_x (T) : FT-IR

K_γ (T) : COSMO-RS

  - **<u>Physisorption</u>: CO_2 solubility in IL: Henry's Law Constants $H_{CO2,IL}(T)$**

$$H_{CO2,IL} = \frac{P_{CO2}}{x_{CO2}}$$

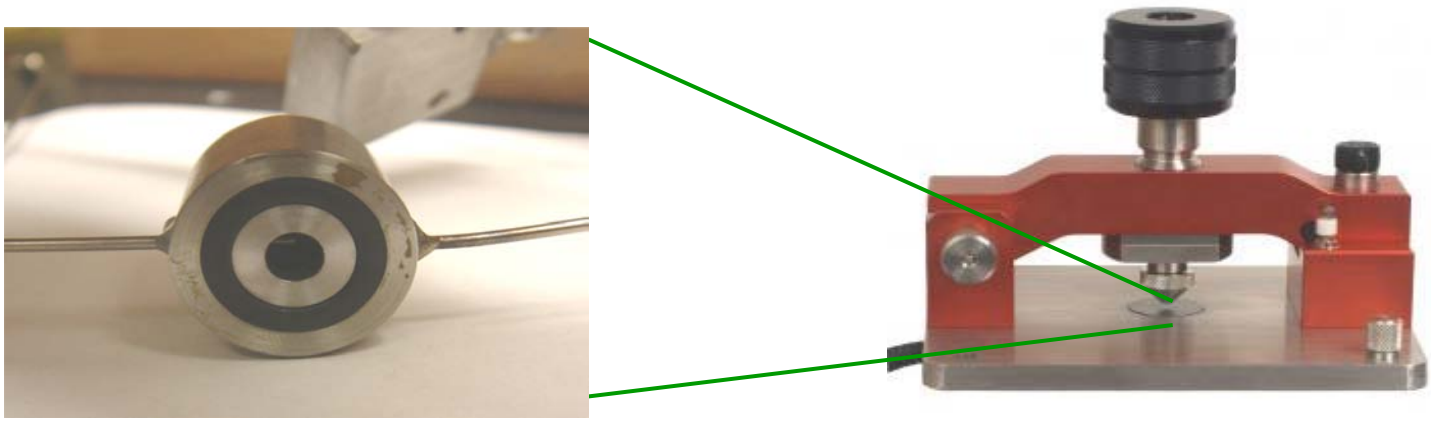
$H_{CO2,IL}$ (T) : FT-IR

- **Viscosity (pre and post capture)**

Cone and Plate Viscometer

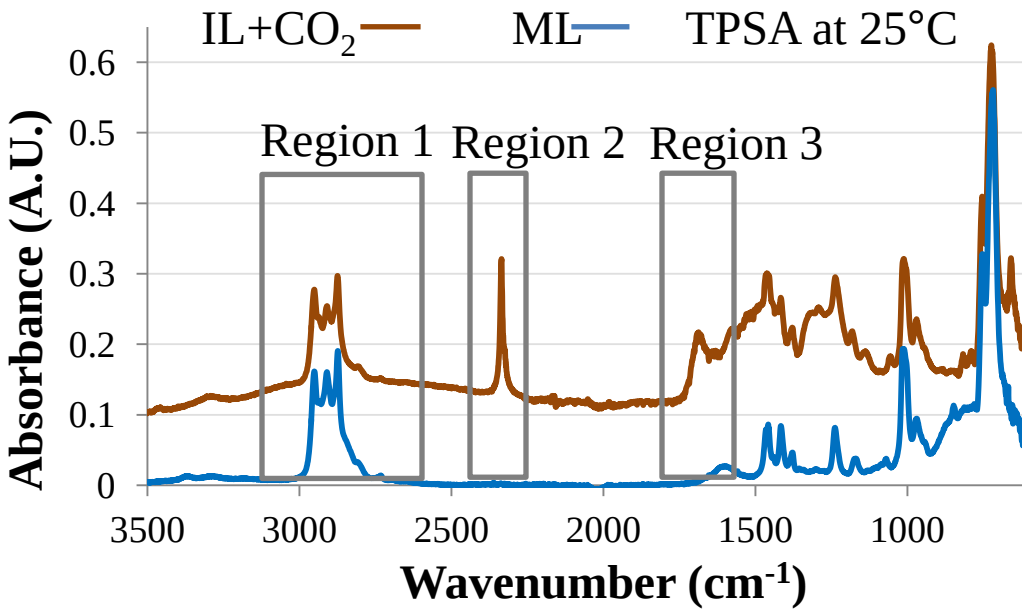
Custom Design Sample Cell for ATR FT-IR

- Custom built in collaboration with *Prof. Sergei Kazarian*
  - ✓ Ease of assembly, operation, and maintenance
  - ✓ Low volume, high pressure, high temperature
  - ✓ *In situ* measurements



ATR-FTIR

- **Peak area measurements + Beer-Lambert Law**



Region 1 and 3: Chemisorption
Region 2: Physisorption

Region 1 (3100-2600 cm^{-1})
- C-H stretch vibration
- NH_3^+ vibration (IL)

Region 2 (2400-2260 cm^{-1})
- Asymmetric CO_2 stretch

Region 3 (1740-1520 cm^{-1})
- N-H deformation (ML)
- C=O stretch vibration (IL)

COSMO-RS

(COnductor-like Screening MOdel for Real Solvents)

Predictive tool for thermodynamic equilibria of fluids
Work Done by Collaborators Outside of this Project

- **Quantum chemical calculations:** Molecular surface charges
- **Extract molecular interaction energies**: Electrostatic, vdW, H-bonding
- **Statistical thermodynamics**: Calculate thermodynamic properties: Vapor pressure, boiling point, activity coefficients

Properties: CO_2 Release

- **Regeneration Energy**

$$mC_p\Delta T + \Delta H_{rxn} + \Delta H_{desorption}$$

m : mass (related to capacity)

C_p : heat capacity of CO_2 rich solvent

ΔT : $T_{reversal} - T_{capture}$ (40 °C)

ΔH_{rxn} : Amine-CO_2 reaction enthalpy

$\Delta H_{desorption}$: CO_2-IL mixing enthalpy

Ruzicka & Domalski method

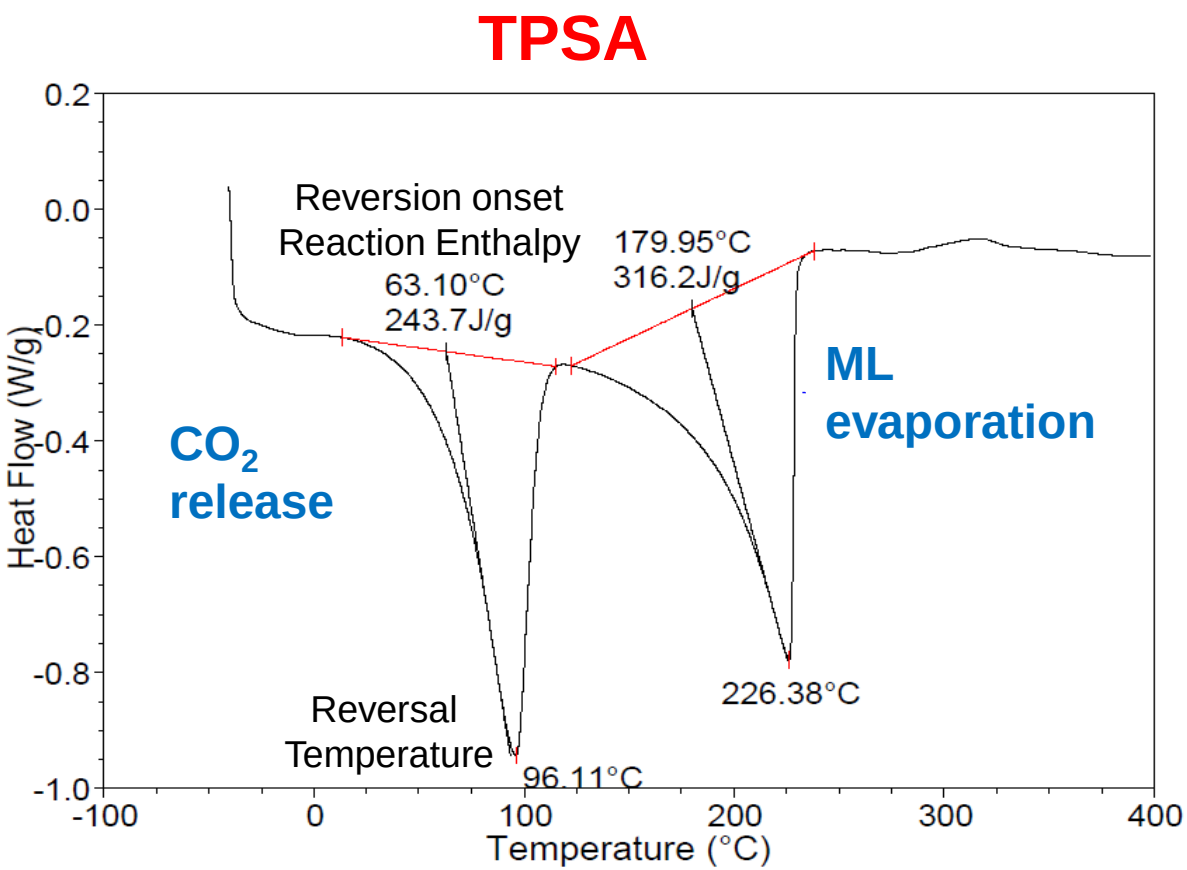
DSC

FT-IR

Refractive Index

- **Recyclability**

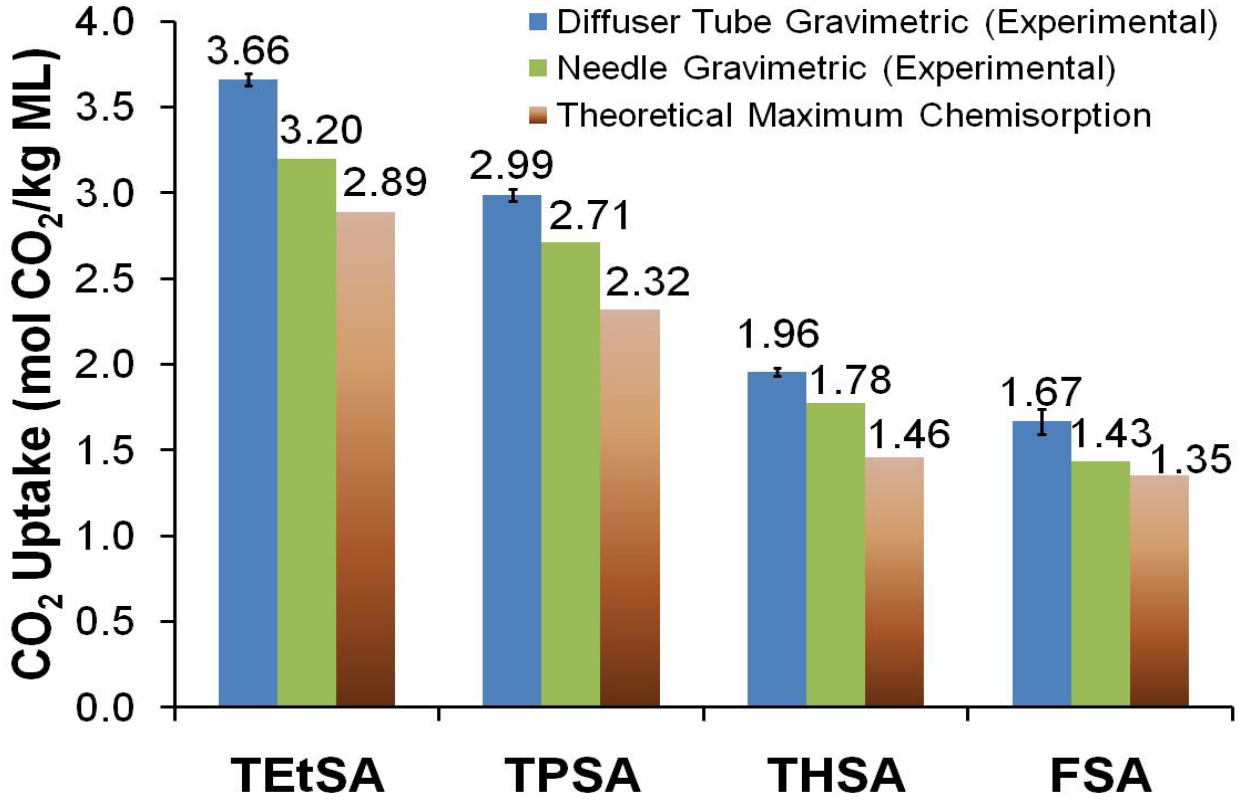
CO_2 Release: DSC Analysis



DSC: Preformed Ionic Liquid @ 5°C/min from -40°C to 400°C

RESULTS

Capacity Comparison, Experimental vs Theoretical for Chemisorption Only

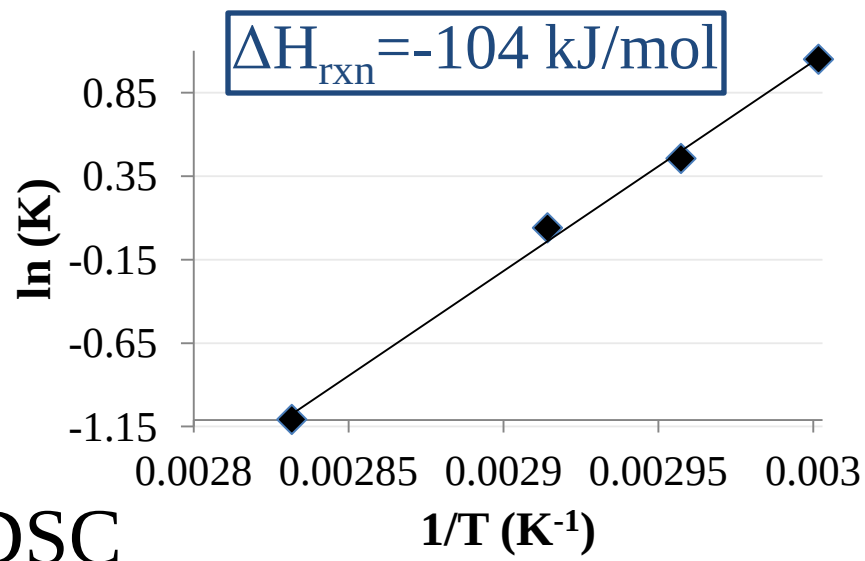


- **Capacity decreases with higher molecular weight**

Equilibrium Constant

Temperature (K)	Equilibrium Constant , K
60	2.8
65	1.6
70	1.0
80	0.3

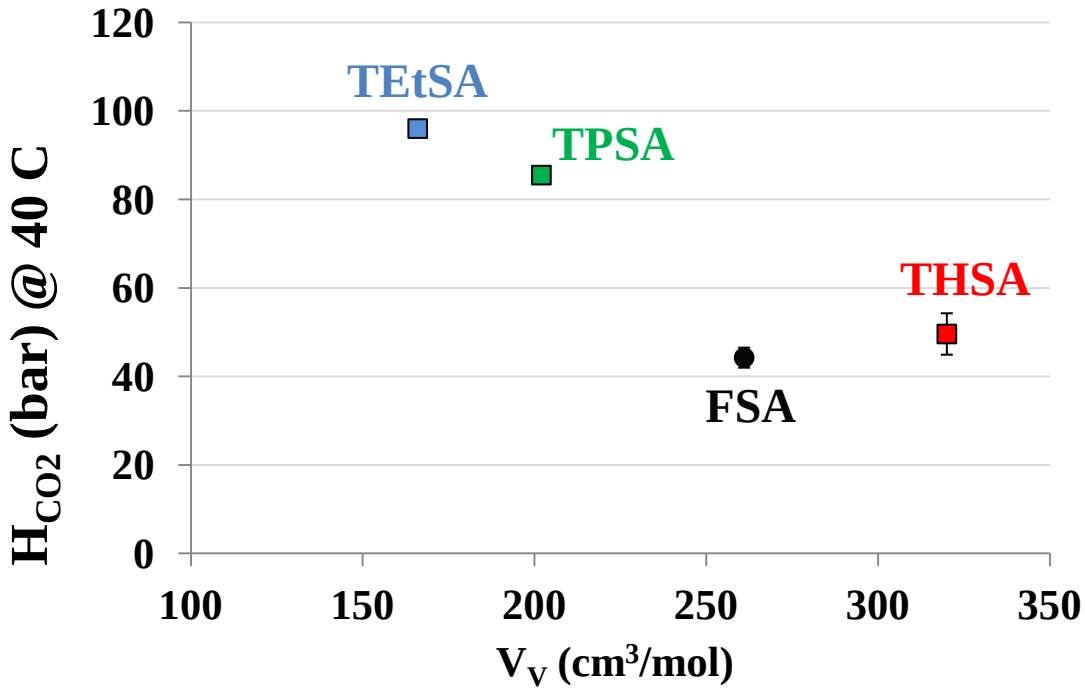
$$\frac{d(lnK)}{dT} = \frac{-\Delta H_{rxn}}{RT^2}$$



- ΔH_{rxn}= -110 kJ/mol from DSC

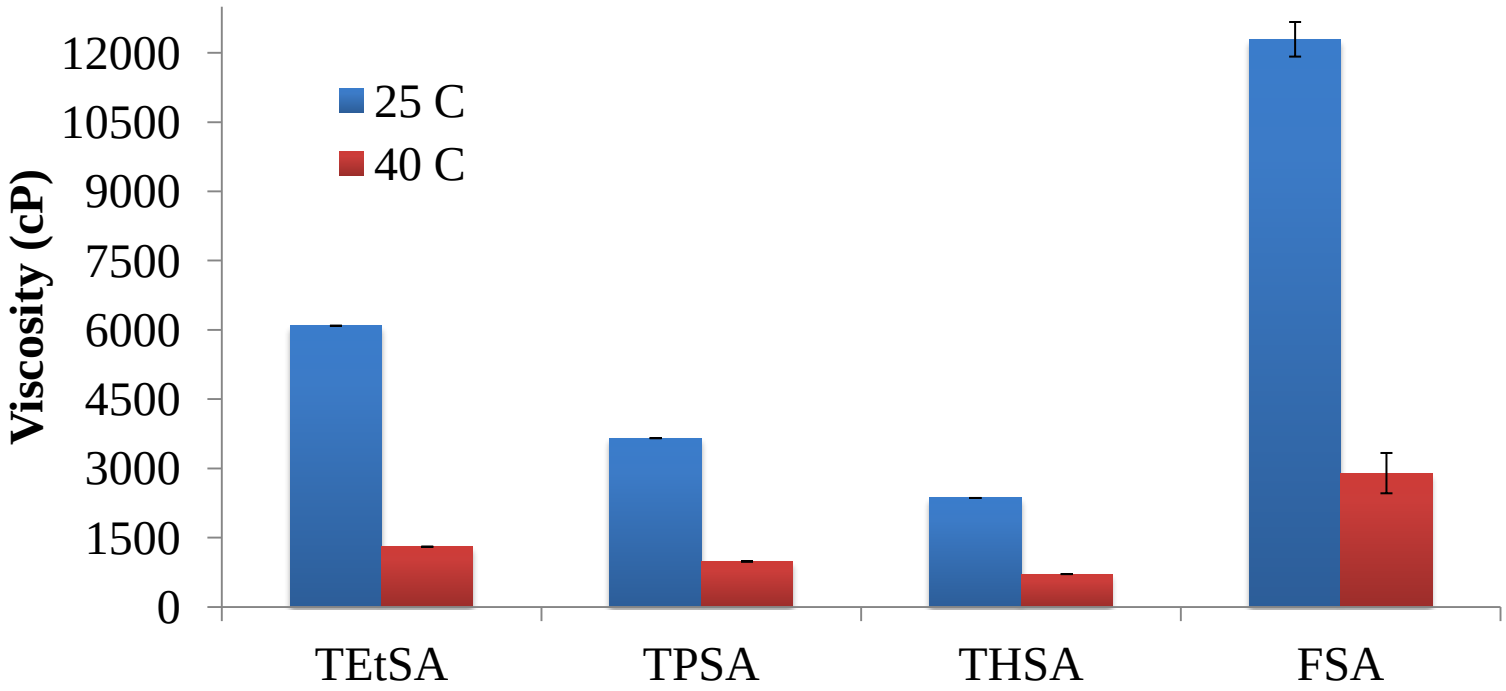
CO_2 Capture: Henry's Law Constants

- **Henry's Law constants $H_{CO2,IL}$ (40 °C)** $H_{CO2,IL} = \frac{P_{CO2}}{x_{CO2}}$



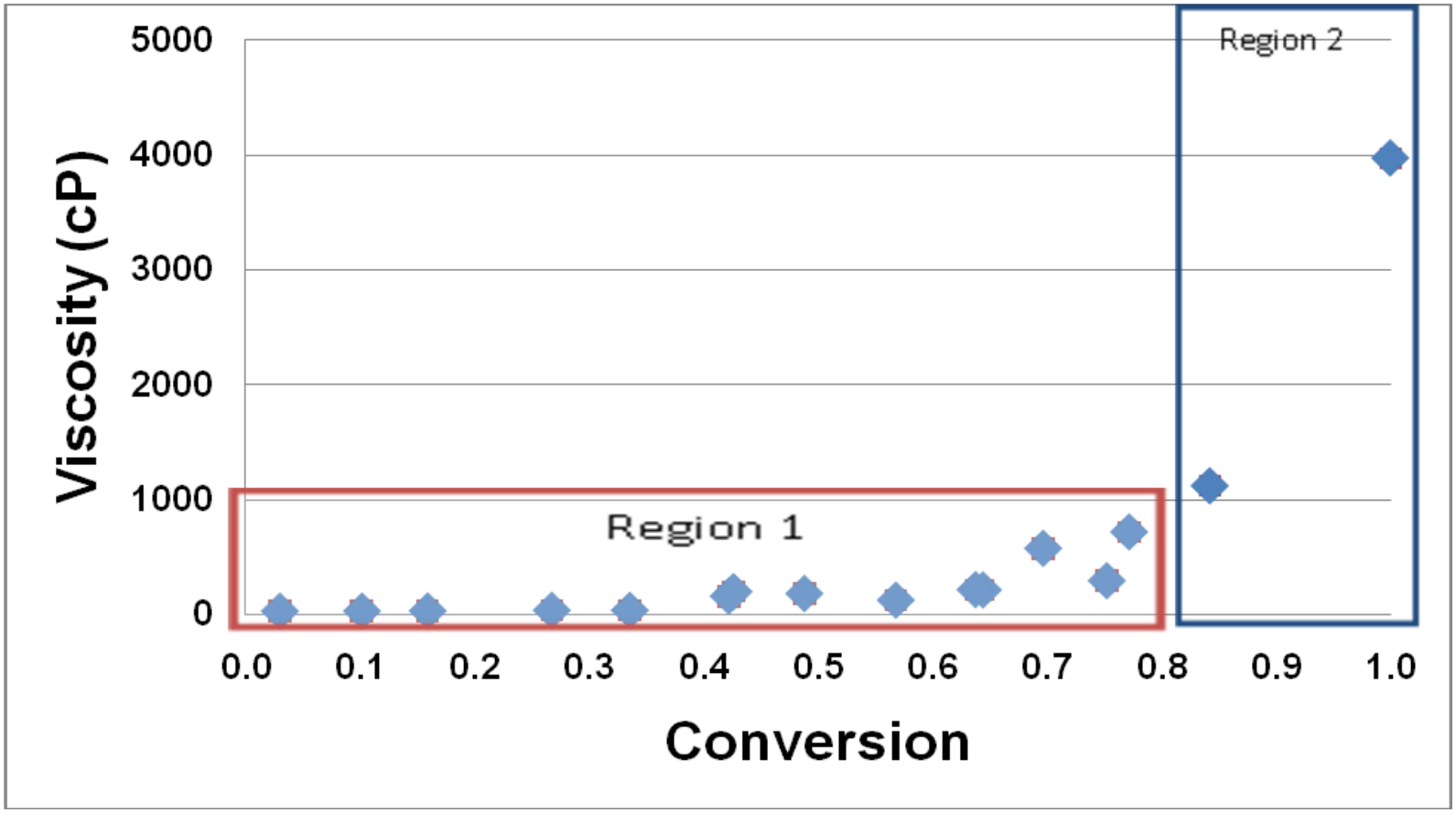
- CO_2 solubility increases with increasing void volume
- Increased CO_2 solubility in fluorinated compound

Project Challenge: Viscosity of Ionic Liquids



- **Decreases with increasing chain length (packing)**
- **Increases with fluorination (increased intermolecular bonding)**

Viscosity vs. Extent of Reaction

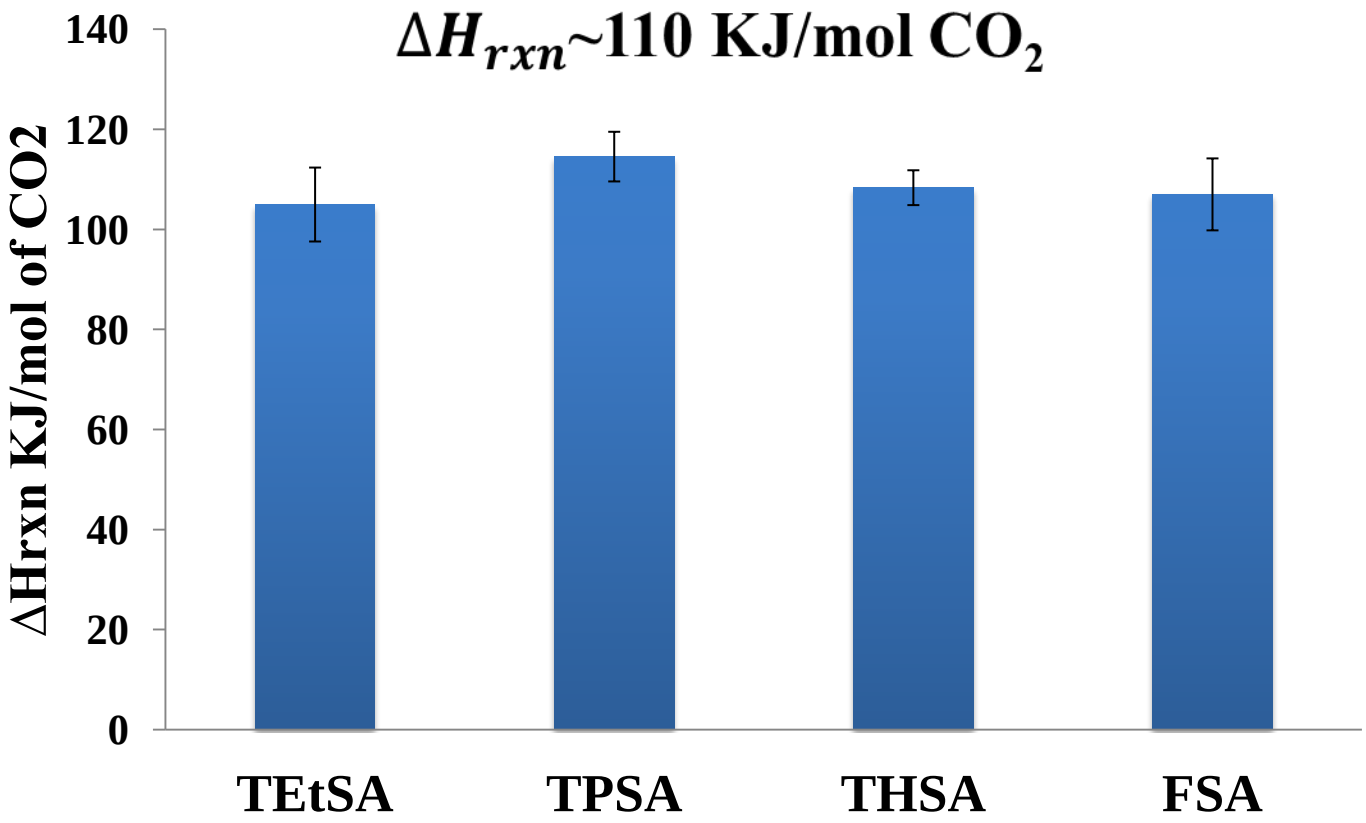


- **Viscosity is a non-linear function of conversion**

Potential Management of Viscosity

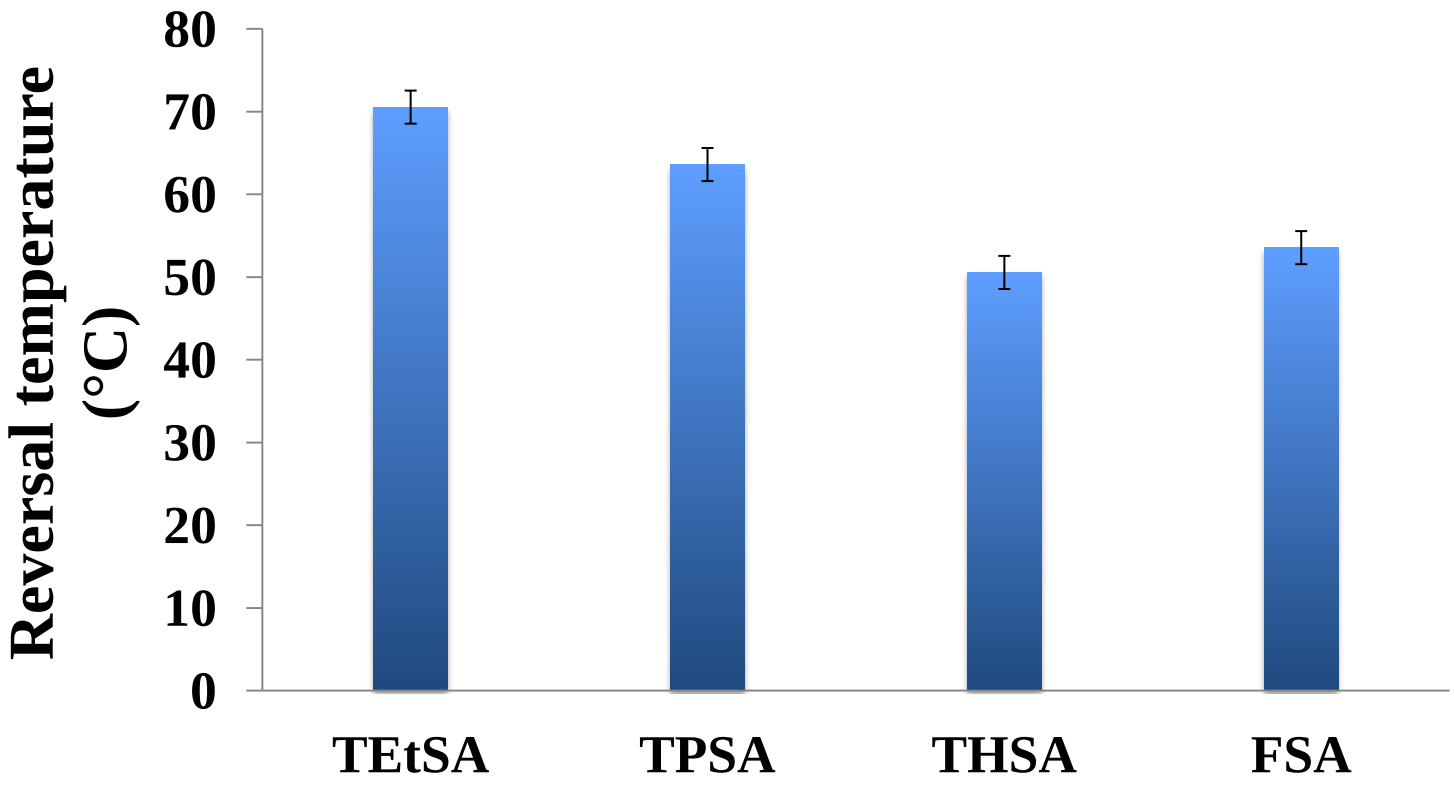
- Reaction Slightly Less than Complete
- Add Water
  - ✓ Always Present, 10-15%
- Water Also Increases Capacity
  - ✓ Forms Bicarbonate in Presence of Amine

Reaction Enthalpy



- **Not affected by the structural changes studied**
- **Same reaction (primary amine and CO_2)**

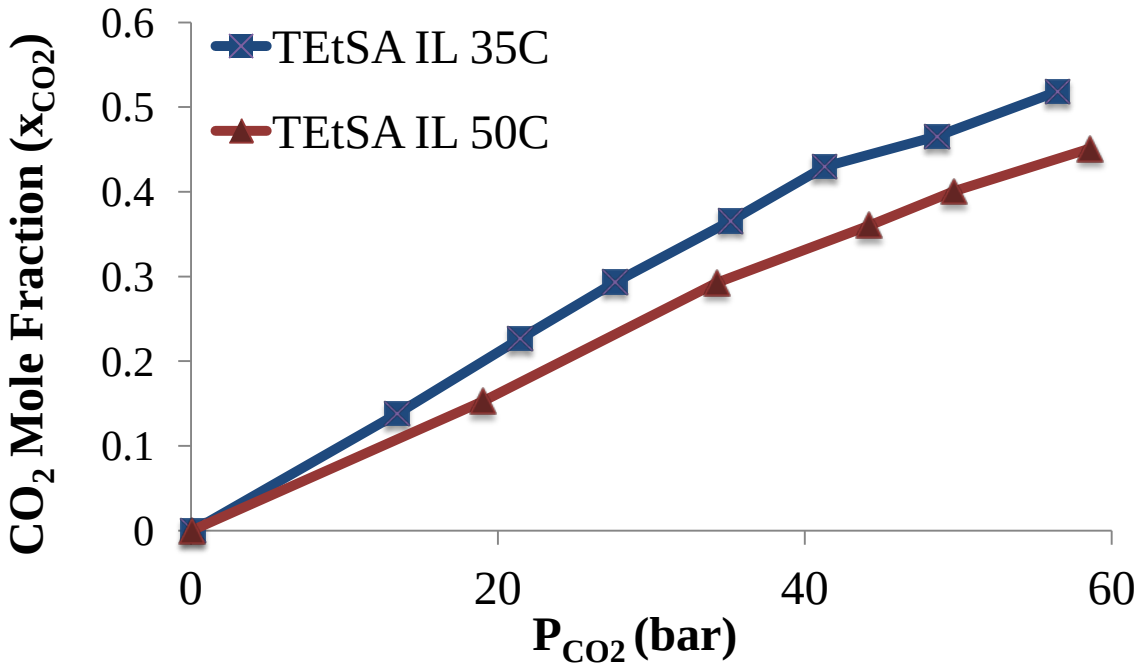
Reversal Temperature



- **Decreases with longer chains (entropic effects)**

Dissolution Enthalpy

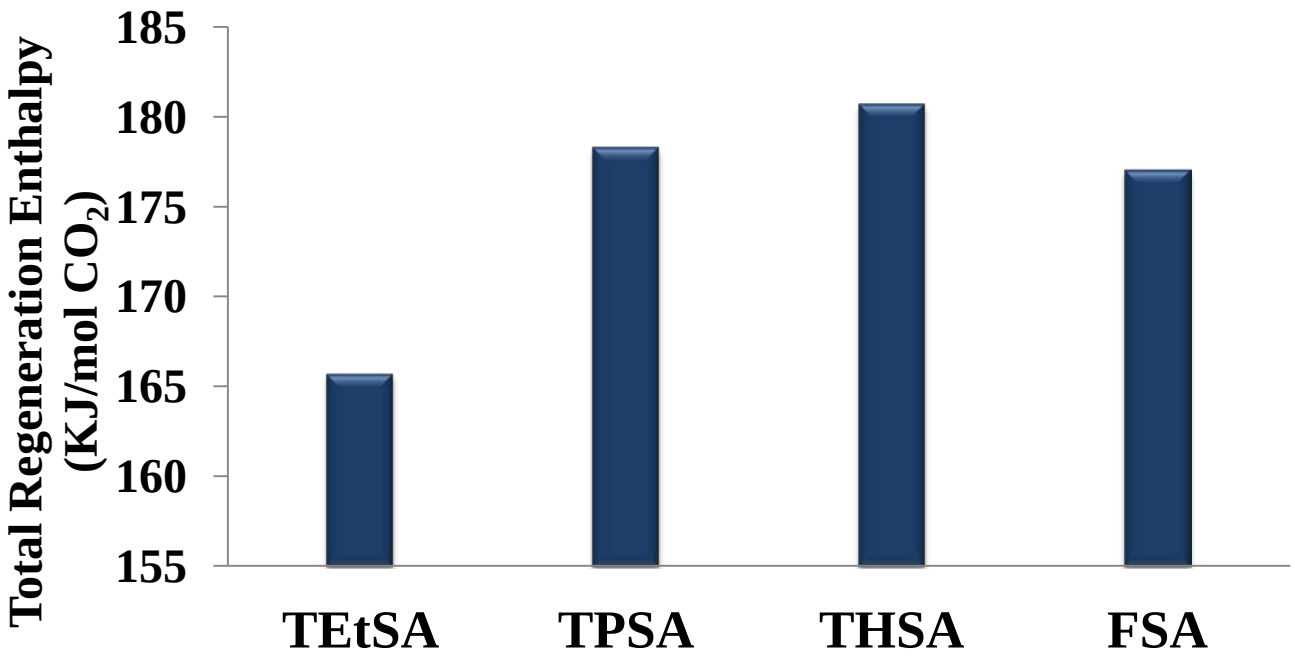
$$\Delta H_{dissolution} = R\left(\frac{d(\ln P)}{d(1/T)}\right)_{x1}$$



- **Calculated from CO_2 solubility data in IL (FT-IR)**
- **Dissolution enthalpy ~ 15 KJ/ mol CO_2 (14% of ΔH_{rxn})**

Regeneration Energy

$$mC_p\Delta T + \Delta H_{rxn} + \Delta H_{desorption}$$

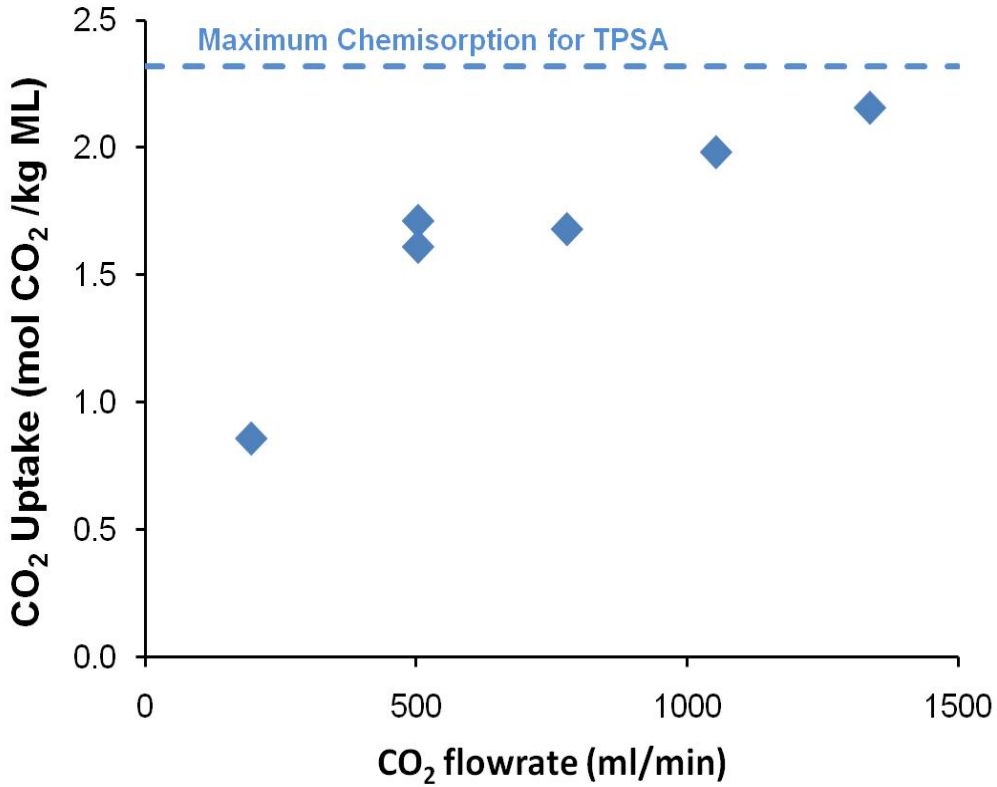


- **Flue Gas Conditions (40 °C ; 1 bar ; 15% CO_2)**
- **Negligible physisorption**

Kinetics and Mass Transfer

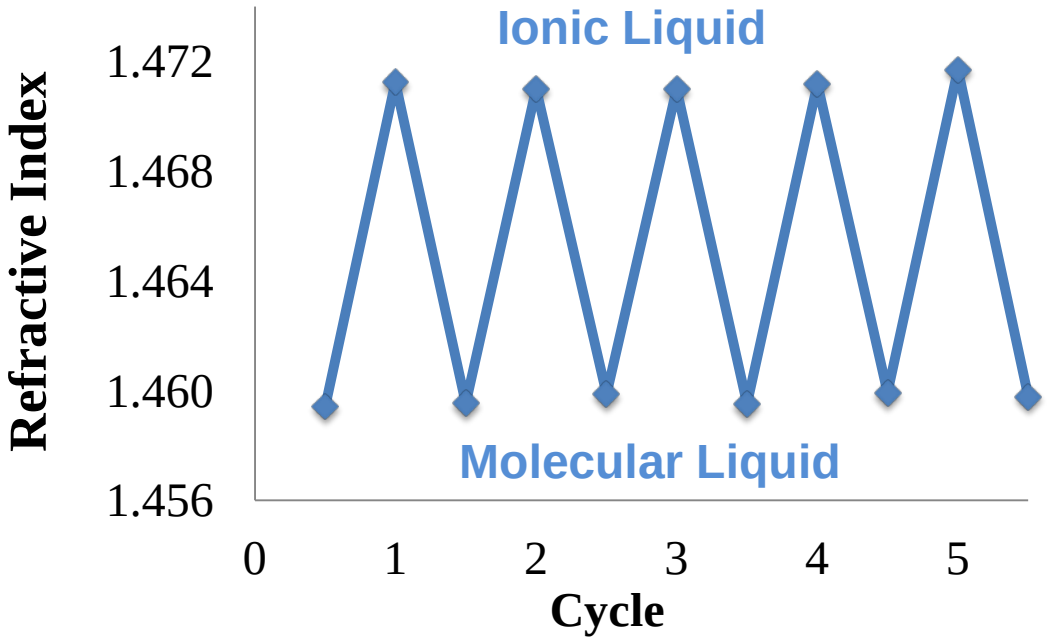
- Reaction instantaneous
- Absorption is mass transfer limited
- All flowrates: excess CO_2, yet more agitation, more absorption

Graph is for TPSA, 60 sec, 25C

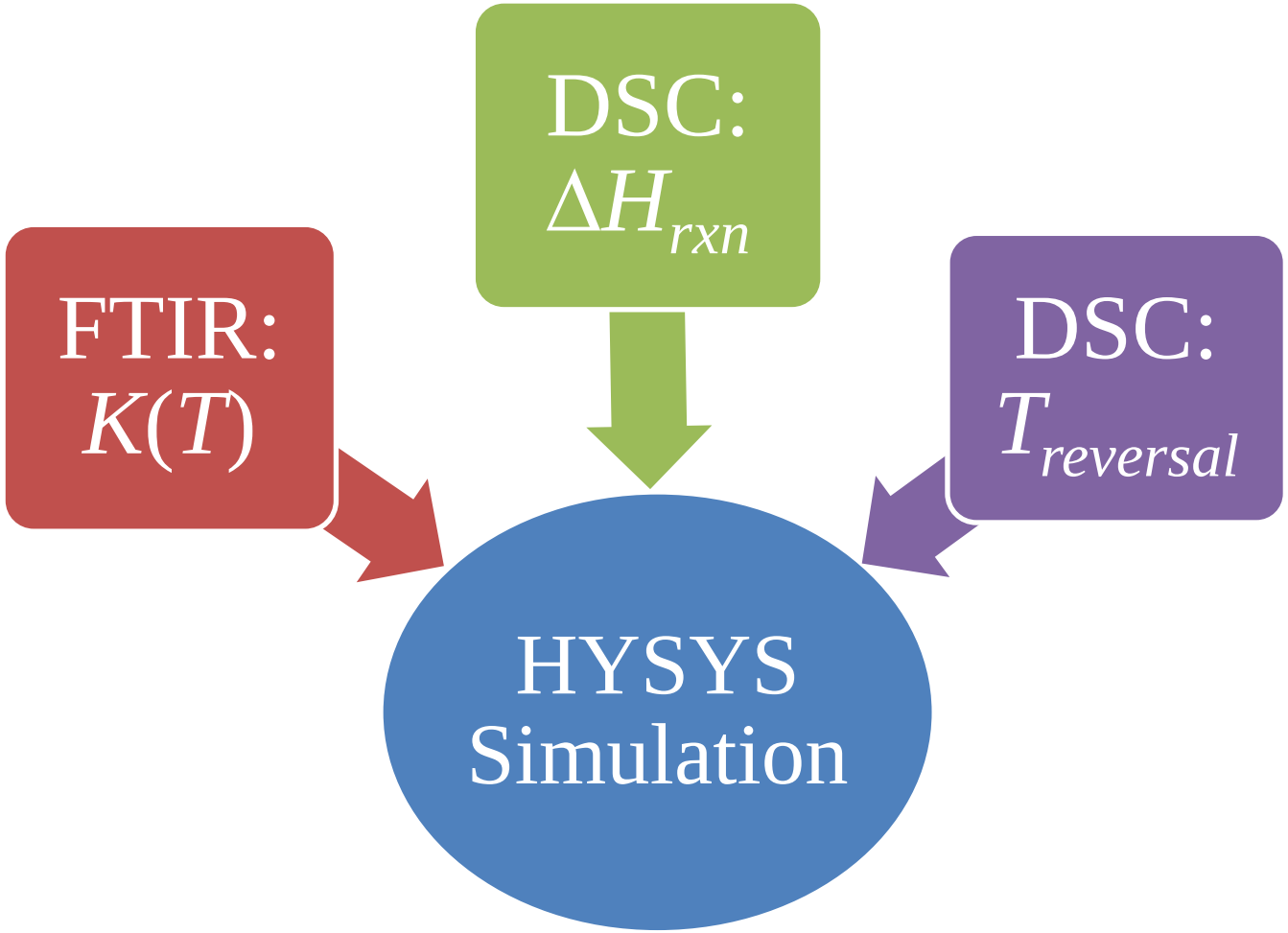


Recyclability of RevILs (TPSA)

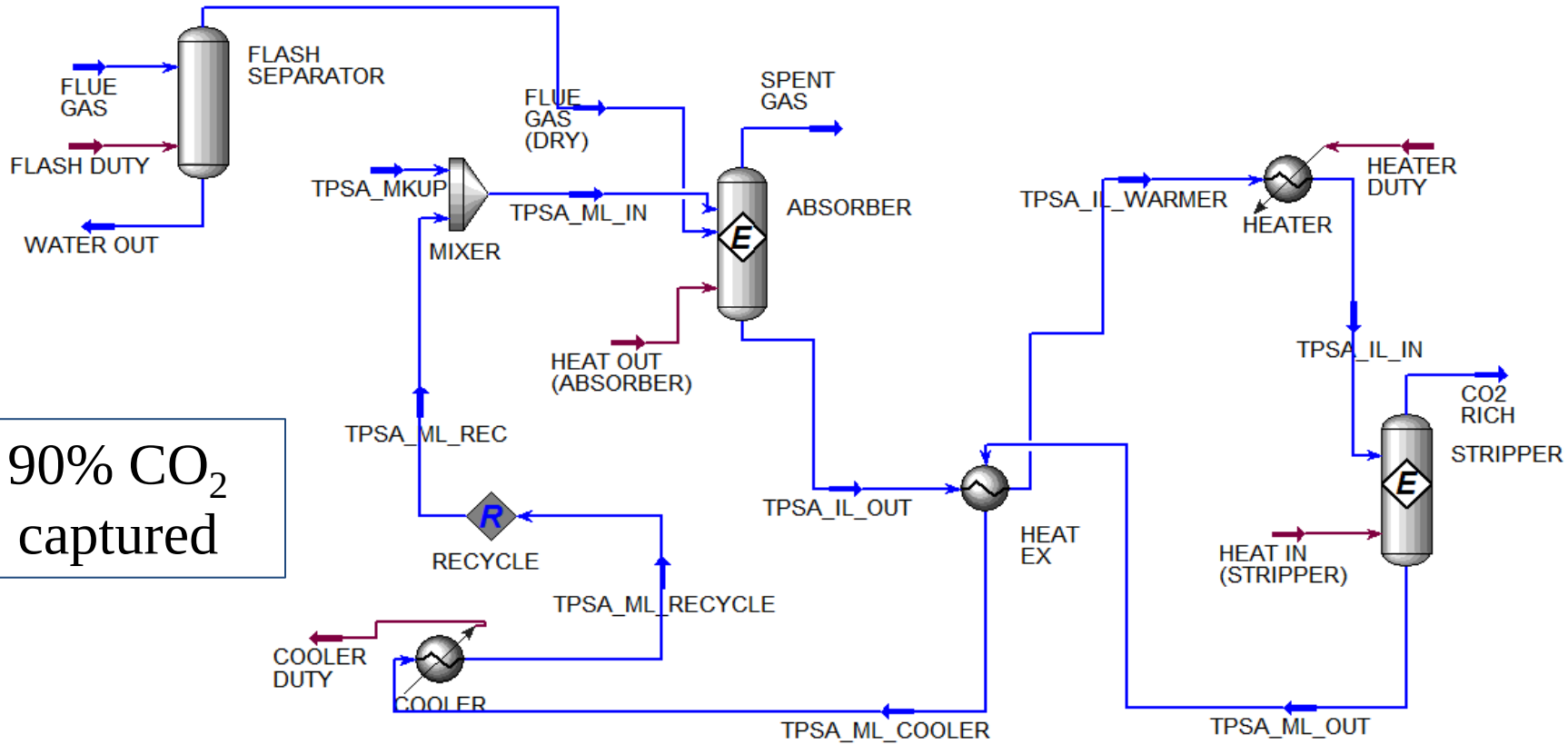
- CO_2 capture: 1 atm CO_2 and room temp.
- CO_2 release: heating at 100°C for 1-1.5hrs
- **5 cycles with consistent behavior**



Integrating Experimental Data into Process Design



HYSYS Simulation



90% CO_2 captured

- Preliminary Estimate for TPSA: 1.4 MJ/kg CO_2
- Literature Value for 30% Aq. MEA: 4 MJ/kg CO_2

Conclusions

- Developed RevILs as carbon capture solvents:
  - ✓ **Minimize water**
  - ✓ **Dual capture** mechanism
  - ✓ **Structure-property relationship** based approach
- **Physisorption is less energy intensive** than chemisorption
- **RevILs are promising** alternatives to aq. alkanolamines

Support From DOE Has Generated...

- 5 Articles Published, 2 More Submitted
- 8 Invited Presentations
- 13 Conference Presentations, 3 More Upcoming
- 7 Collaborations:
  - ✓ 4 Academic
  - ✓ 3 Industrial
- 6 Students Have Finished
  - ✓ Vittoria Blasucci, PhD ChBE (Exxon)
  - ✓ Ryan Hart, PhD ChBE (Exponent)
  - ✓ Manish Talreja, Postoc ChBE, (Dow)
  - ✓ Olga Dzenis, MS ChBE (Wink Engineering)
  - ✓ Melissa Burlager, BS ChBE (Grad School)
  - ✓ Greg Marus, PhD ChBE (Albemarle)

Project Objectives and Timing: Milestones

Milestone Title	**Finish**	**Verification Method**
A Complete Project Management Plan	9/30/08	PMP approved by DOE COR
B 1-Comp. Silyl Amine-Based ILs	06/30/10	Successful Synthesis and Characterization
C 1-Comp. Silyl Guanidine-Based ILs	02/28/11	Successful Synthesis and Characterization
D Thermo & Rates of IL Formation	6/30/11	Successful Measurements
E Optimize CO_2 Capture Solvent Structure	10/31/11	Optimal Solvent Identified
F Process Design and Economic Analysis	10/31/11	Design and Scaleup Completed
G Write Final Report	12/31/11	Final Report Submitted

Future Testing & Development

- This Project
  - ✓Complete Determination of Optimum RevIL
  - ✓Design and Economic Analysis
- Next Project
  - ✓IL Scaleup for Economic Manufacture
  - ✓Address Rates, Transport Issues
- Scale-Up Potential
  - ✓Already Working with Industrial Partner ConocoPhillips