Project Title:

Novel High Capacity Oligomers for Low Cost CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Solvents	Laboratory-Scale, Simulated Flue Gas

Primary Project Goal:

To develop a novel oligomeric solvent and process for carbon dioxide (CO_2) capture from post-combustion flue gases.

Technical Goals:

- Use molecular modeling to design new compounds with optimal heats of reaction (-8.5 to -10 kcal/mol).
- Design new oligomer solvents that have higher CO_2 solubility than current solvents.
- Achieve 25% greater CO_2 capacity than aqueous MEA.
- Achieve low solvent volatility.
- Achieve high reaction rate.

Technical Content:

Silicone based solvents, which may be either oligomeric (defined as short-chain polymers containing two to 20 repeat units) or small molecule species, will be developed. Silicones are known in the literature to be CO_2-philic. These materials are advantageous compared to aqueous amine technology because they have low volatility, do not require a carrier fluid such as water, and can be synthesized with a number of CO_2 capture sites per molecule, increasing the overall CO_2 capacity. In addition, silicones have a high degree of thermal stability, allowing the system to operate at higher temperatures. Polymer-CO_2 interactions have been extensively studied in the literature and several CO_2-philic functional groups, such as acetates, carbonates, and ketones, have been identified.

The development of the capture solvent has taken the following approach:

- Identify solvent backbones and functional groups (Figure 1), using a literature review, that are potentially CO_2-phillic (see Table 1 and Table 2).
- Use molecular modeling to predict favorable structures and heats of reaction.
- Synthesize Generation 1 solvents.
- Screen silicone solvents using high throughput screening (HTS) techniques.

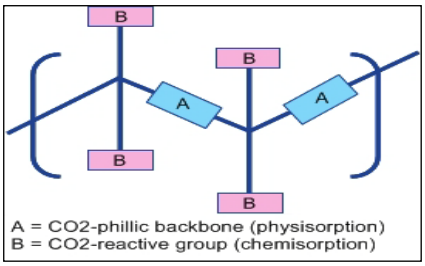
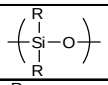
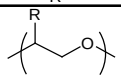
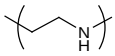
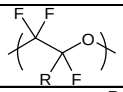
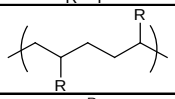
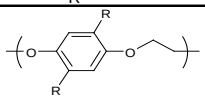
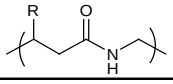
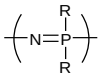


Figure 1: Solvent Concept

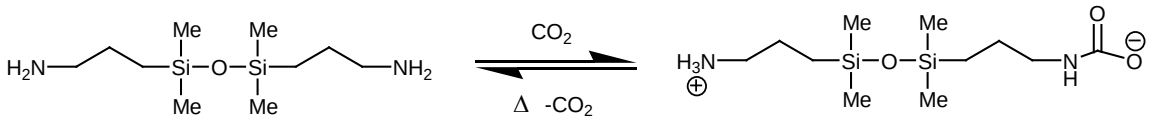
- Confirm materials by:
  - Nuclear magnetic resonance (NMR).
  - Boiling point, vapor pressure, flash point, viscosity, thermal stability, and CO_2 release characteristics.
- Downselect candidate solvents and synthesize.
- Estimate physical, chemical, and thermodynamic properties using modeling to further select candidates.
- Physically measure solvent properties.
- Conduct degradation and stability tests in the presence of CO_2, water, sulfur dioxide (SO_2), etc.
- Determine minimized cost of energy (COE) and an optimized capture process using power plant models.

Table 1: Examples of Solvent Backbone Candidates

		attribute						
backbone	**Structure**	physical state	cost (inexpensive)	synthetic availability	ease of derivatization	CO2-philic	stability	**total**
siloxane		9	5	9	9	9	9	**50**
alkyl ether		9	9	9	5	5	9	**46**
alkyl amino		5	9	9	5	9	9	**46**
perfluoroether		9	1	5	1	9	9	**34**
alkyl		9	9	9	5	1	9	**42**
aryl ether		1	5	5	5	5	5	**26**
alkylamido		5	5	9	5	5	5	**34**
phosphazene		5	1	5	5	5	1	**22**
Polystyrene		1	9	9	9	1	9	**38**
	physical state	must be low viscoisty liquid		9=liquid, 5=viscous liquid, 1=solid				
	cost (inexpensive)	should be < $10/lb		9=<$10/lb, 5=$10-2-/lb, 1=>$20/lb				
	synthetic availability	able to be made on large scale		9=commercial, 5 = small scale, 1 = laboratory				
	ease of derivatization	must be easily functionalized		9=easy, 5 = moderate, 1 = difficult				
	CO2-philic	physisorption		9=high, 5=moderate, 1=low				

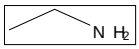
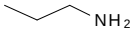
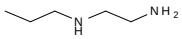
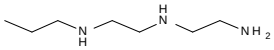
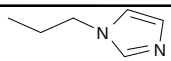
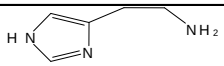
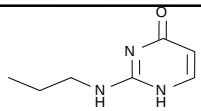
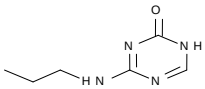
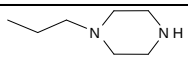
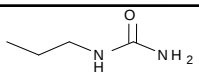
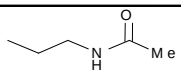
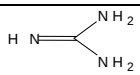
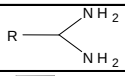
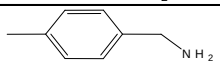
The solvent selection process splits the oligomers into backbones and functional groups so that physisorption and chemisorption are decoupled in the modeling of CO_2 solubility. Higher total scores indicate more promising candidates.

After HTS of various materials, one candidate solvent that showed much promise was 1,3-bis(3-aminopropyl)-1,2,3,3-tetramethyldisiloxane. The reaction of it and CO_2 is shown below:



Currently, the absorption process involves contacting the aminosilicone/glycol solvent system with gas phase CO_2. The viscosity of the system increases as CO_2 reacts until maximum CO_2 absorption is achieved. The solvent system remains a liquid and is transferred to a pressurized desorption chamber where it is heated, the CO_2 is released, and the lean solvent system is regenerated.

Table 2: Examples of Solvent Functional Group Candidates

		attribute					
Functional Group	**Structure**	CO_2 Capacity	Heat of Reaction	Kinetics	Ease of Attachment	Cost	**Total**
Aminoethyl		5	5	9	5	9	**33**
Aminopropyl		5	5	9	9	9	**37**
Aminoethylaminopropyl		9	9	9	9	9	**45**
Bis(aminoethyl)aminopropyl		9	9	9	9	9	**45**
Imidazole		1	1	1	9	5	**17**
Histamine		5	9	1	5	1	**21**
Isocytosine		5	5	5	5	1	**21**
5-Azacytosine		9	5	5	5	1	**25**
Piperazine		9	9	9	9	5	**41**
Urea		5	5	1	5	9	**25**
Acetamide		1	5	1	5	5	**17**
Guanidine		9	5	9	1	5	**29**
Amidine		9	5	9	9	5	**37**
Benzylamine		5	9	5	9	5	**33**

CO_2 capacity	9=high, 5=moderate, 1=low	
Heat of reaction	9=moderate, 5=low, 1=high	
Kinetics	9=fast, 5=moderate, 1=slow	(Reaction with CO_2)
Ease of attachment	9=easy, 5=doable, 1=difficult	

Table 3: Process Parameters for Aminosilicone/Glycol Solvents

	Parameter	**Current R&D Value**	**Target R&D Value**
Solvent Properties	Type of solvent	Amino silicone/ glycol	
	Molecular weight	248/150	
	Boiling point (Amino silicone/glycol)	132C@11mm Hg/ 125C@ 0.1mm Hg	
	Heat of reaction (kJ/mole CO_2)	45	
	CO_2 loading/working capacity*, wt.%	5.5-6%	
	Solvent concentration to stripper (mol/liter)		
	Heat capacity of solution (kJ/K/kg)	~2.1	
	Viscosity, cP (Glycol concentration)	@40 C <50(0%) --< 4500 (100%)	

Operating Conditions	Absorption temperature, °C		
	Absorption pressure (CO_2 partial pressure), atm.	0.1~0.15	
	CO_2 capture efficiency, %	>90	
	Regeneration method	thermal	
	Regeneration temperature, °C	100~150	
	Regeneration pressure, atm.	5~20	
Heat Integration	Required regeneration steam temperature, °C	120~170	
Miscellaneous	Solvent make-up rate, kg/kgCO_2	N/A	
Product Quality	CO_2 purity, %	N/A	
	N_2 concentration, %	N/A	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	
	Heat requirement, kJ/kgCO_2	N/A	
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	

Technology Advantages:

- Low volatility.
- Water not required as a carrier fluid, thus lowering heat capacity.
- Silicones have a high degree of thermal stability.

R&D Challenges:

Flexible short chain silicones have not been previously demonstrated as CO_2 absorbing solvents and thus a number of potential risks have been identified. The most significant technical risks include:

- Insufficient chemical and thermal stability of the solvents.
- Low CO_2 absorption and desorption rates.
- Excessively high heat of reaction.

Results To Date/Accomplishments:

- Selected solvent classes.
- Calibrated plant model for absorption cycles, stripping cycles, and cost calculations.
- Downselected aminosilicones solvent classes.
- Found that a glycol co-solvent aids in physi-sorption of CO_2 and decreases viscosity.
- Shown thermal regeneration of solvent after CO_2 capture.
- Demonstrated continuous CO_2 absorption by aminosilicone solvent system.
- Discovered aminosilicone solvent systems that show a >25% increase in loading compared to 30% MEA.
- Initial calculations show 48% COE with a path to 35%.

Next Steps:

- Optimize aminosilicone solvent system for maximum capacity.
- Develop methods for synthesizing larger quantities of selected solvents.
- Determine thermal stability and tolerance to impurities of selected solvents.
- Determine thermal stability.
- Construct continuous absorption/desorption unit which will allow determination of reaction rates, mass

transfer coefficients, robustness of the solvent system, and any special heating or cooling needs. • Estimate the impact of the solvent and capture process on the COE production.	
Available Reports/Technical Papers/Presentations: Presentation: Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 24-26, 2009, Pittsburgh, Pennsylvania.	
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