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Novel Tertiary Amine Solid Adsorbents Used for the Capture of Carbon Dioxide

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Presentation Outline

- Overview and Background
- Preliminary System Analysis
- Experimental Conditions and Results
- Conclusions

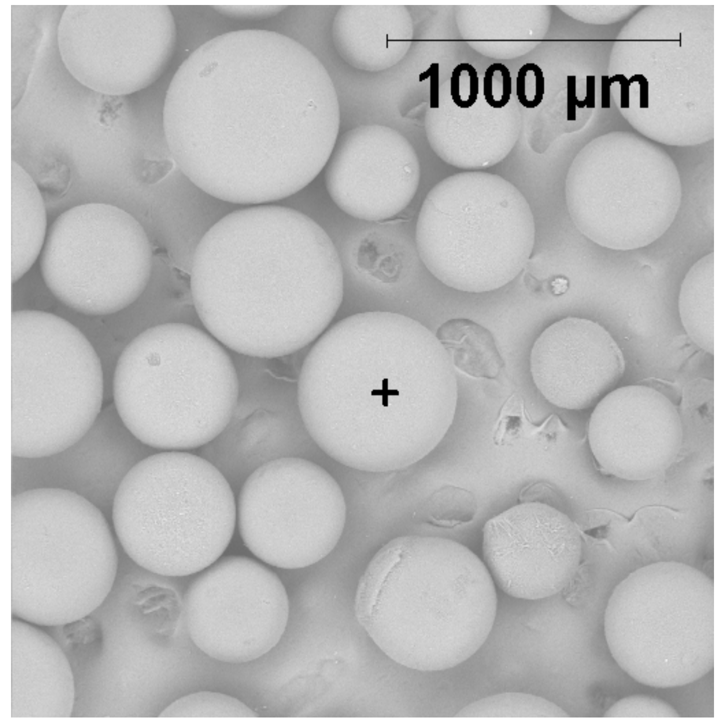
Overview and Background

Background – Carbon Dioxide Capture Technologies

Technical Challenges for Liquid Amine System

- Capture Capacities
- Energy Requires
- Mass and Heat Thermodynamics
- Amine Degradation
- Waste Products
- Corrosion Inhibitors
- Materials Balance

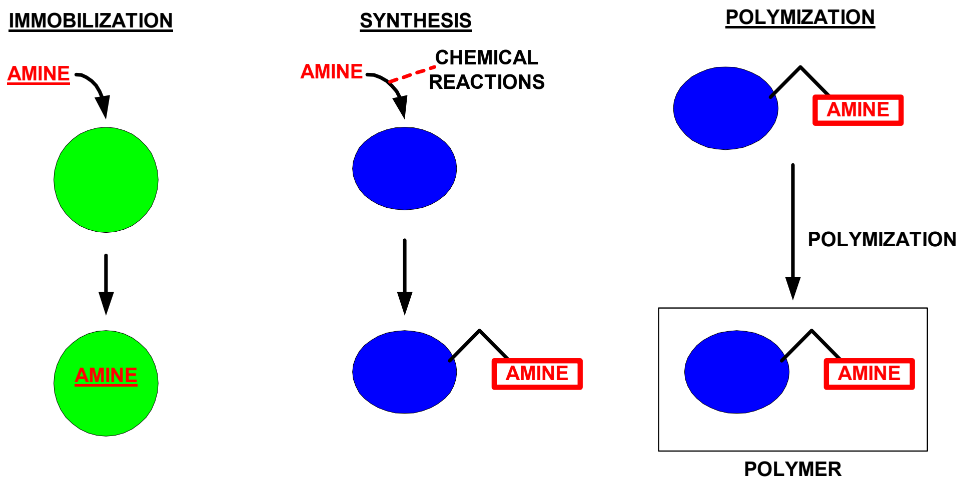
Solid Amine Adsorbents



To develop low-cost solid adsorbents to be used in an efficient process for the capture of CO_2 from flue gas streams

Background - Adsorbent Parameters

Adsorbent Pathways



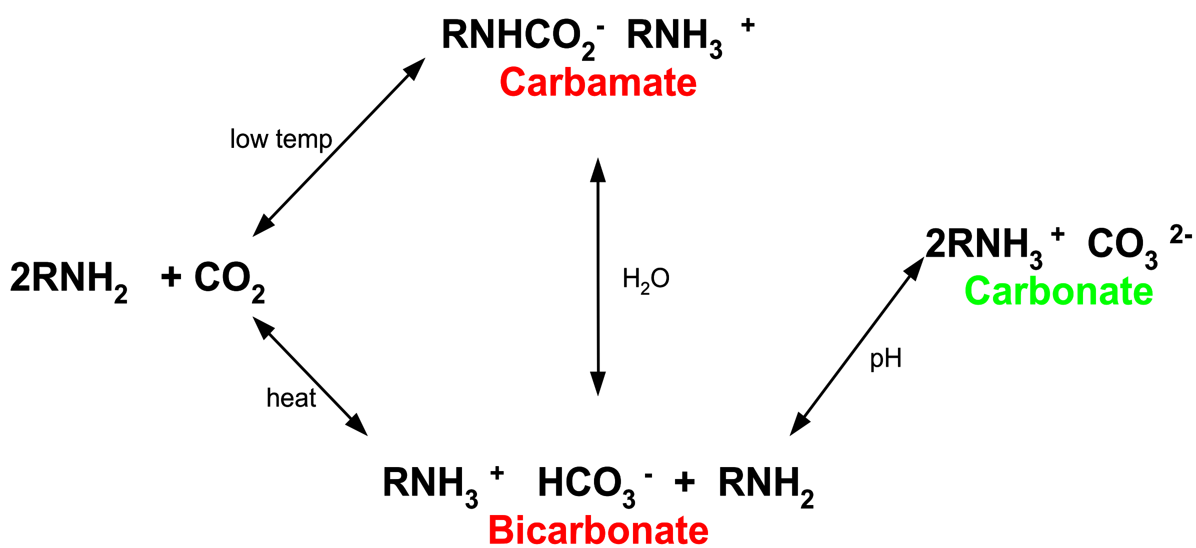
Performance and Cost

Adsorbent Criteria

- Basicity
- Vapor Pressure
- Viscosity
- Substrate
- Capture Capacity
- Temperature Stability
- Regenerable
- Durability
- Flue Gas Stream

Overview and Background

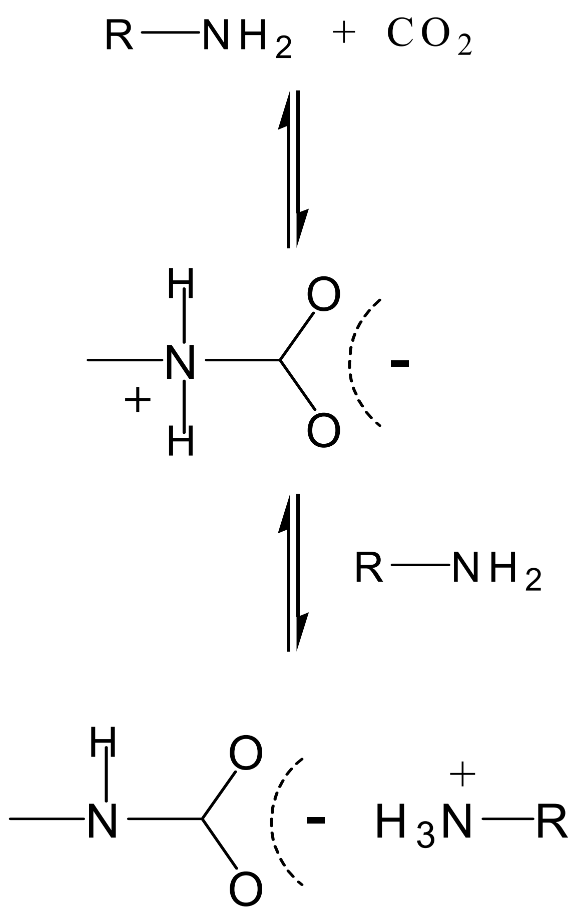
Proposed Reaction Sequence (in solution)



Hook, R. J., Ind. Eng. Chem. Res., ***1997,*** *36, 1779 -1790*

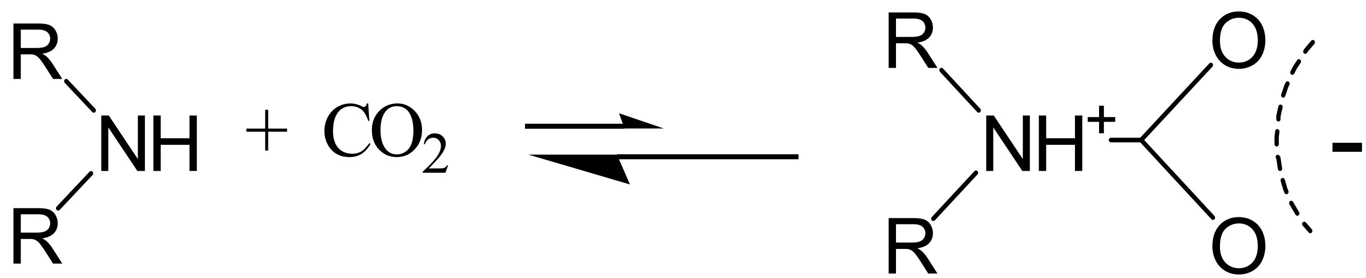
Overview and Background

Brief Background on Amine-CO_2 Chemistry



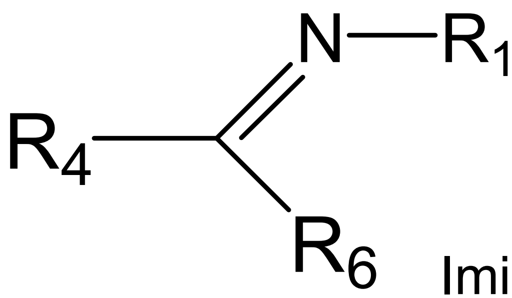
Conventional aqueous amine scrubbing of gas streams, 1940 – 1975; amine reacts with CO_2 to form the carbamate, proton transfer produces ion-counter ion product. This chemistry mandates the need for 2 amine groups to bind 1 CO_2 molecule

Overview and Background

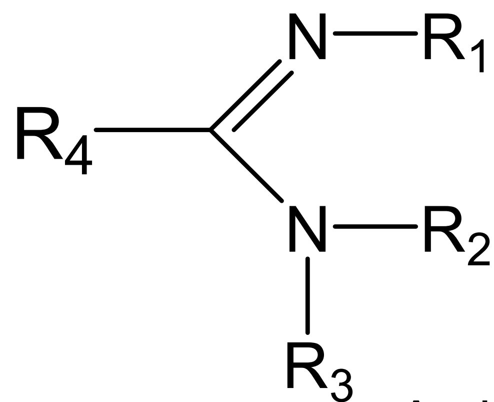


G. Sartori, Exxon, early 1970's: By using a hindered amine, the initial reaction between CO_2 and the amine to form the carbamate is inhibited, allowing proton transfer to the amine to dominate.

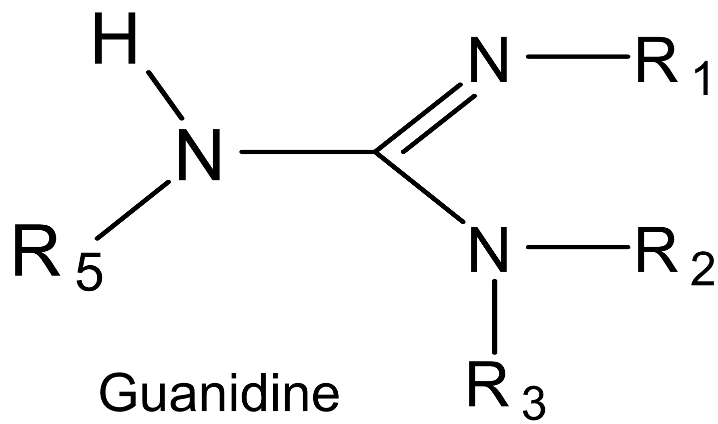
Carbon Dioxide Capture Interaction Groups



Imine



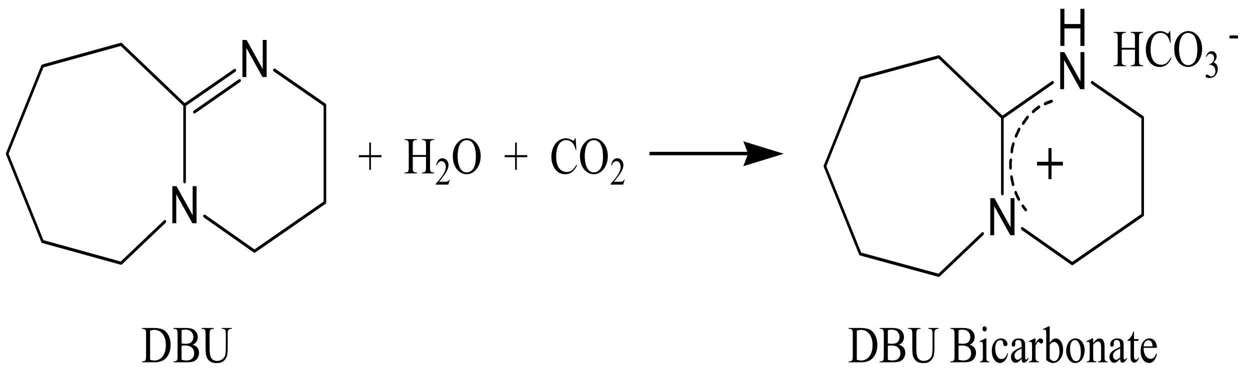
Amidine



Guanidine

Are strong bases that binds and interacts CO_2 reversibly chemical reaction at 1:1 molar ratio.

Fundamental Chemistry: Certain imino-functional compounds bind CO_2 reversible in a 1:1 fashion

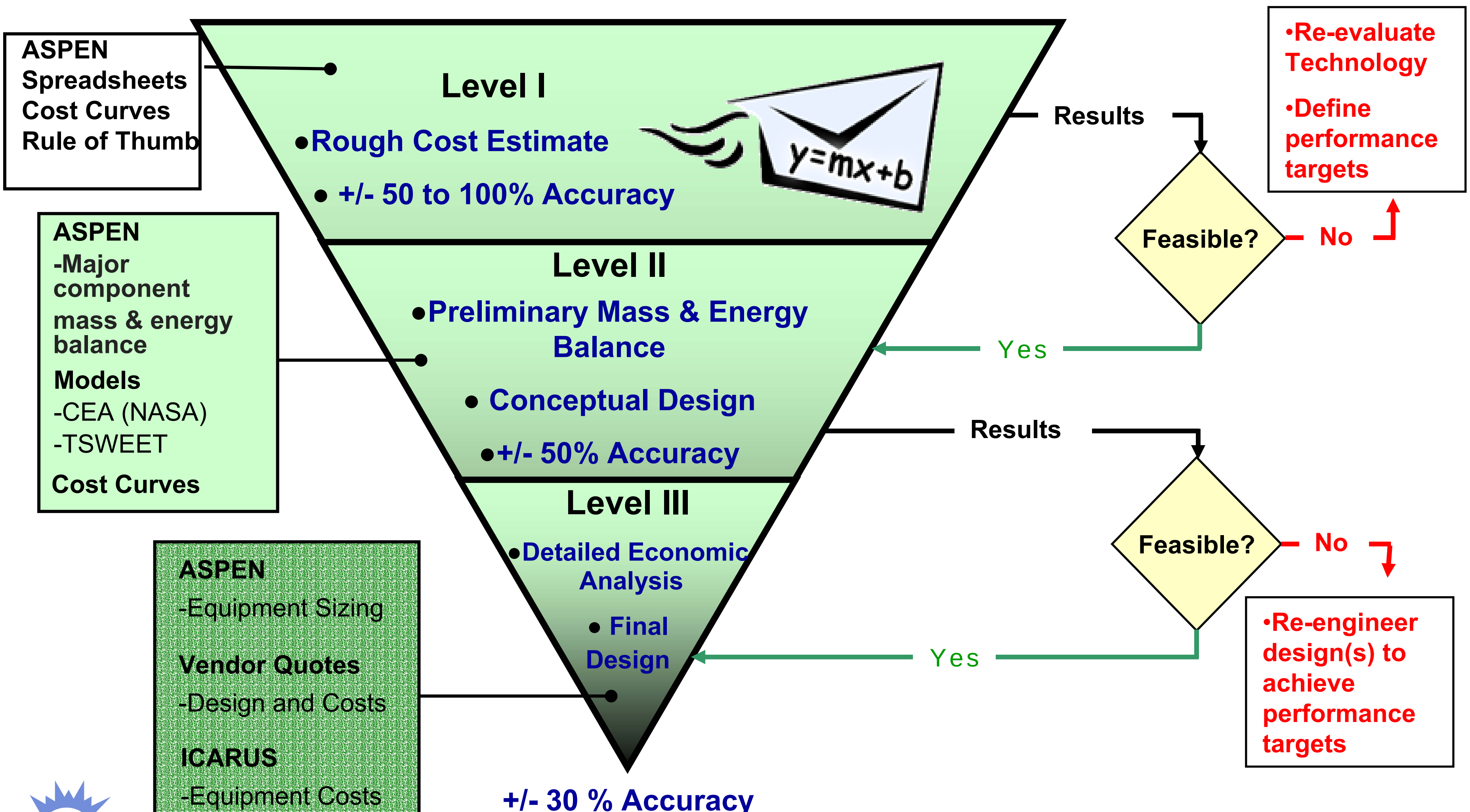


Diazabicycloundecane (DBU)

J. Org. Chem. 2005, 70, 5335-5338

Preliminary System Analysis

Systems Analysis Level of Detail



Solid Amine Adsorbent
Advantage

Reduction in Heating Capacities and Stripping steam for CO2 regeneration

Amine-Enriched Sorbents

Heat Capacity (Btu/lb-°F)		0.3
ΔT Regeneration		80°F

Regeneration Energy (Btu/lb CO_2)		
Sensible		183
Reaction	+	600*
Vaporization	+	0
Total	=	783

30% MEA [1]

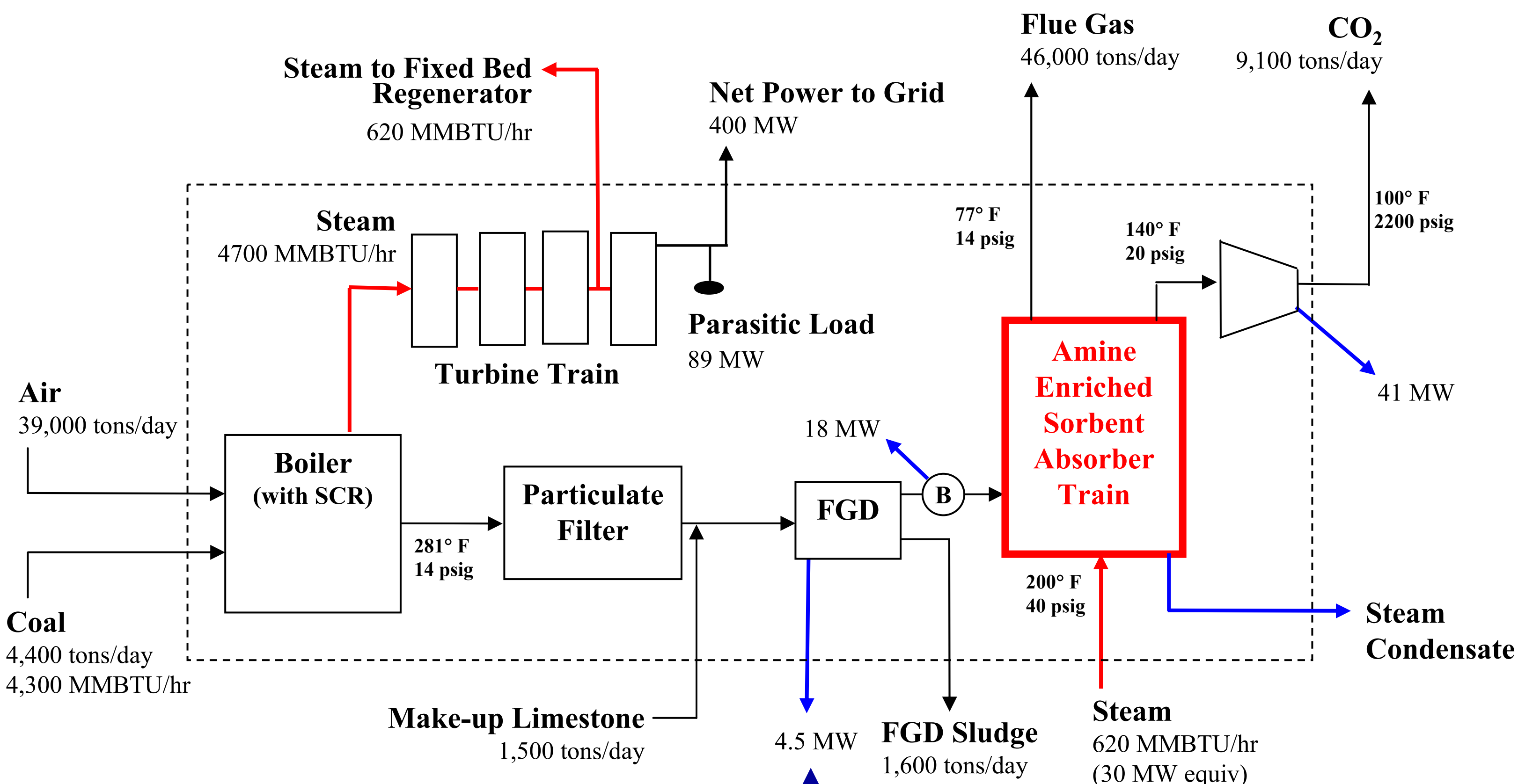
Heat Capacity (Btu/lb-°F)		0.9
ΔT Regeneration		105°F

Regeneration Energy (Btu/lb CO_2)		
Sensible		941
Reaction	+	703
Vaporization	+	290
Total	=	1,934

Reference:

1. Gottlicher,G., *The Energetics of Carbon Dioxide Capture in Power Plants*, U.S. Department of Energy, National Energy Technology Laboratory, 1999

System – Post Combustion



Exit Temperature = 140 °F or 60 °C

Solid Amine Adsorbent

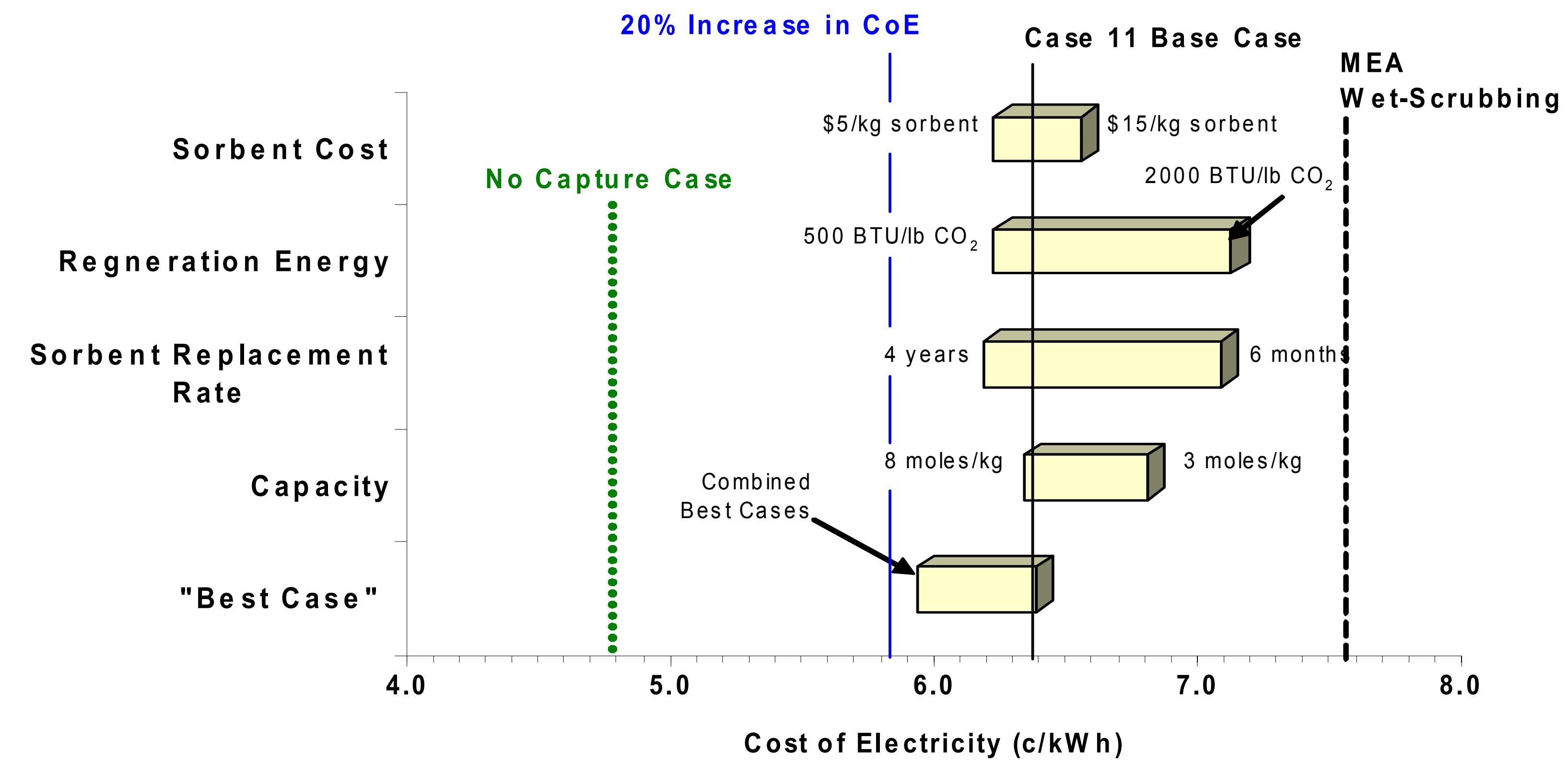
Advantanges

Higher CO2 carrying capacity per lb of sorbent

	30% MEA	Amine Sorbent
Density (lb/ft^3)	22	44
Working Capacity (lb CO_2/lb sorbent)	0.052	0.264
Mass sorbent per pound CO_2	19 lbs solution	3.8 lbs sorbent
Volume per Pound CO_2 (ft^3/lb CO_2)	0.8	0.08

10x Reduction in volume to treat equivalent amount of CO2

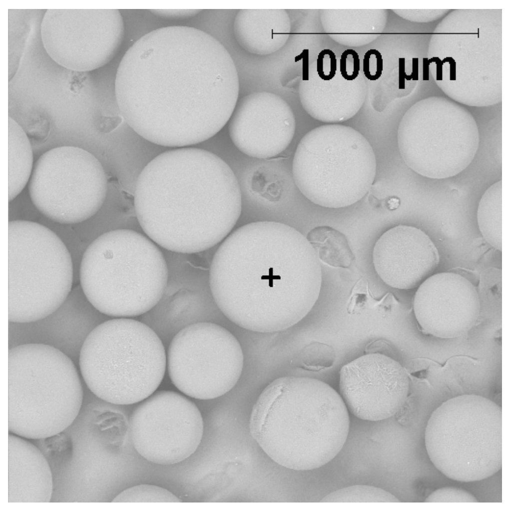
Preliminary System Analysis



Experimental

Materials and Reagents

- **Chemicals from Aldrich Chemicals**
  - 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)
  - Methanol Reagent Grade
- **Mitsubishi Chemicals**
  - Diaion ® HP2MG Poly methyl(methylacrylate) Bead – PMMA



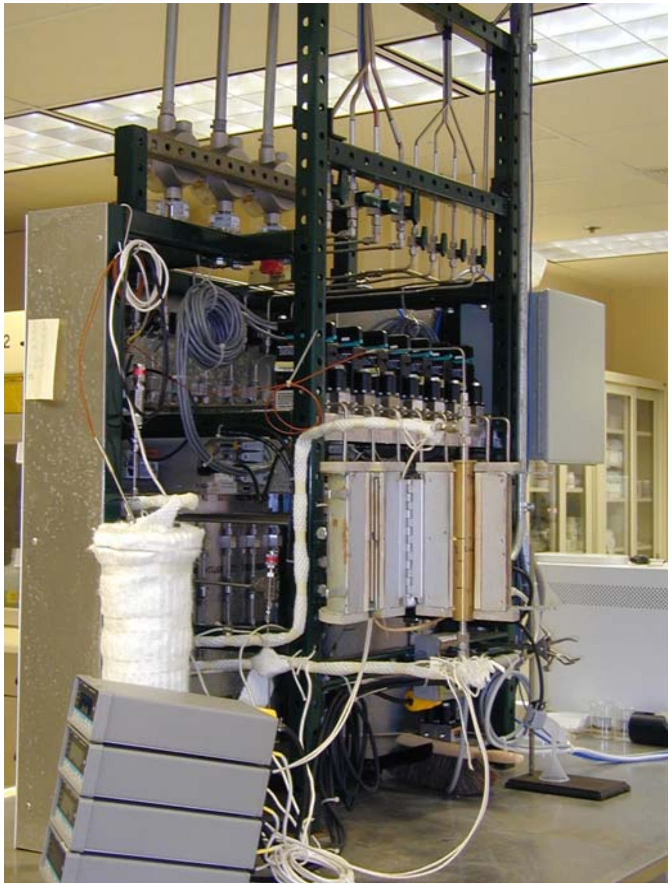
Particle size >250 µ m

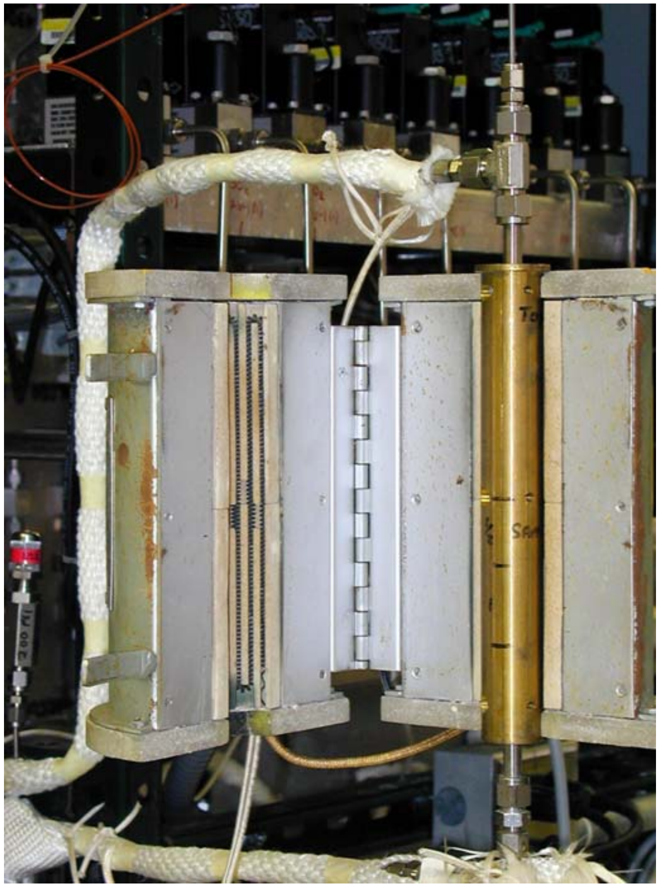
Preparation of Immobilized Adsorbents

- **75 grams of PMMA Beads placed in 300 ml of methanol and agitated**
- **Addition of the DBU at various weights ratio**
  - 7.5 grams 10 (Beads/DBU wt. ratio)
  - 15 grams 5 (Beads/DBU wt. ratio)
  - 30 grams 2.5 (Beads/DBU wt. ratio)
- **Heated over the temperature range of 25-90 °C**
- **Vacuum pressure range of 760-10 mmHg**
- **Stored in refrigerator until testing**

US Patent 5,876,488

NETL Carbon Dioxide Capture Reactor

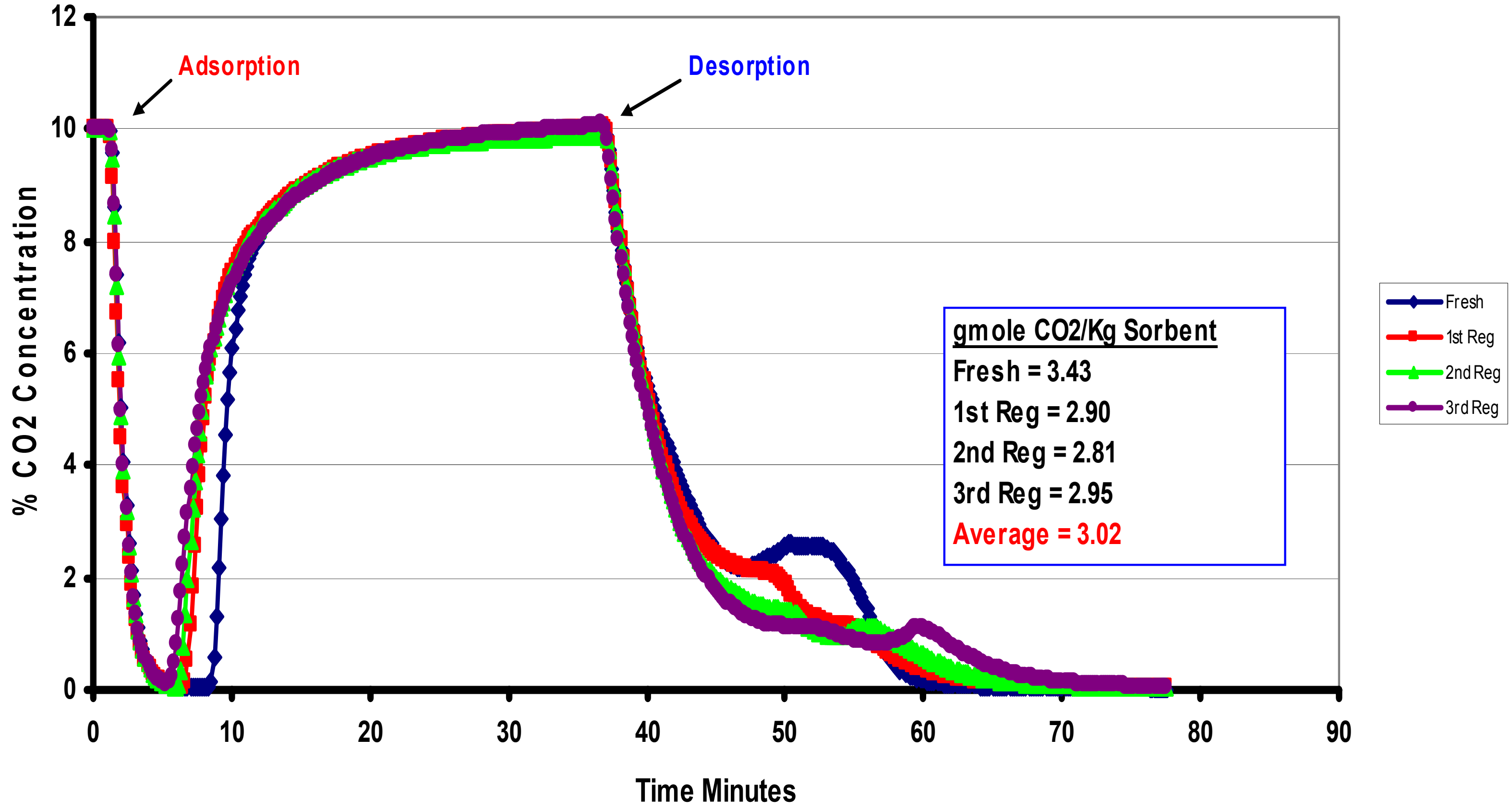




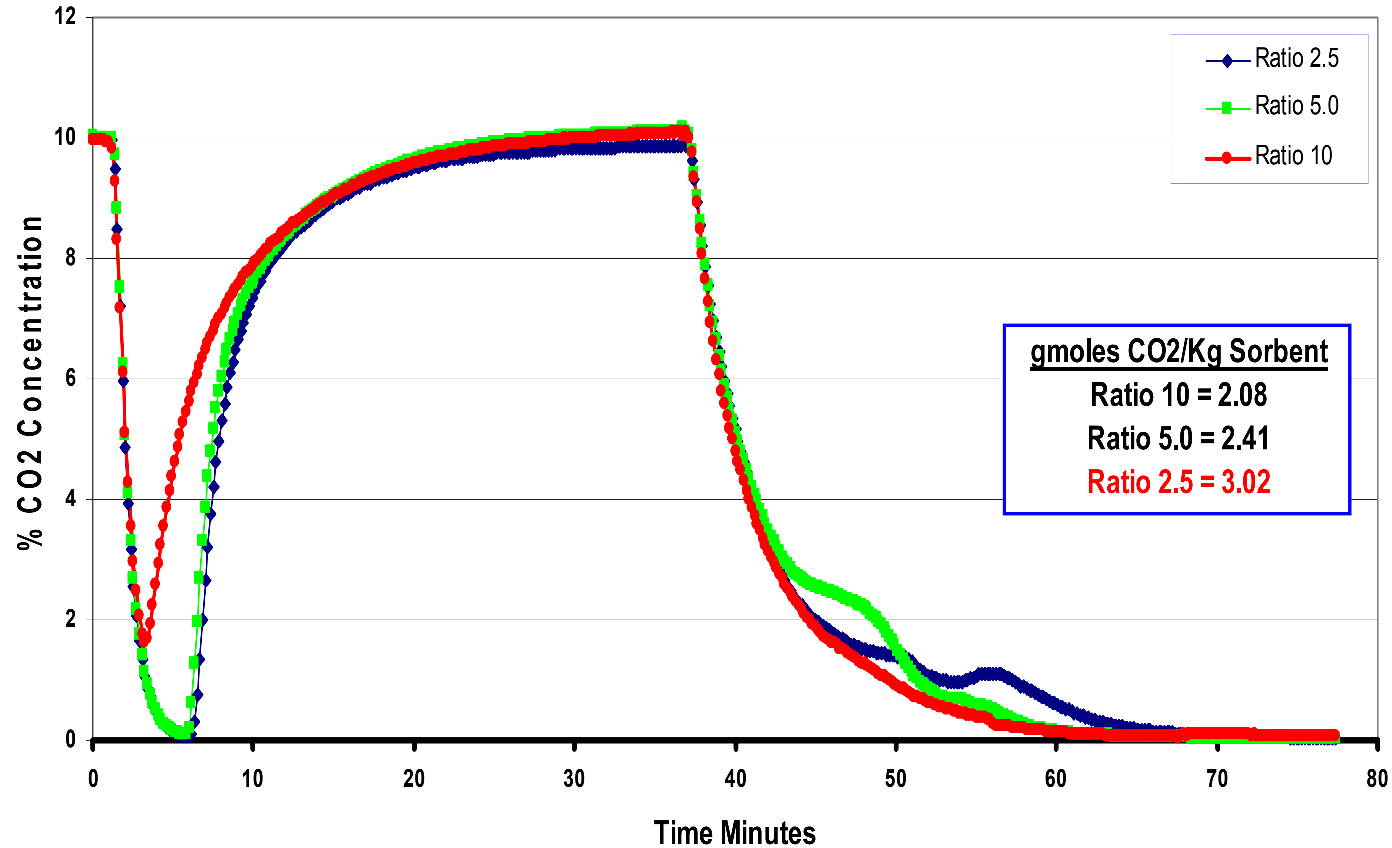
Experimental Conditions

- 1.0 Gram sample (Immobilized Secondary Amine Sorbents)
- He/2% H_2O Pretreatment at 25 ^oC (150 ml/min)
- 10% CO_2/2 % H_2O/He at 25-65 ^oC (100 ml/min) Adsorption
- He/2% H_2O at 90 ^oC (150 ml/min) Desorption
- Pfeiffer Vacuum OminiStar 300 Mass Spectrometer

Breakthrough Curve for DBU at 2.5 Loading Weight Ratio



DBU Loading Effect on the Performance of Immobilized Adsorbents at 25 C



Performance of PMMA/DBU Immobilized Adsorbent at 25 °C

Sorbent	Wt. Ratio PMMA/DBU	Surface Area m^2/g	Pore Volume ml/gram	gmole CO_2/ Kg sorbent
Diaion ® HP2MG[1]	NA	5.79	1.12	0.0
DBU-1	10	369	1.10	2.08
DBU-2	5	207	0.84	2.41
DBU-3	2.5	94	0.58	3.02

[1] Diaion ® HP2MG Poly methyl(methylacrylate) Bead – PMMA

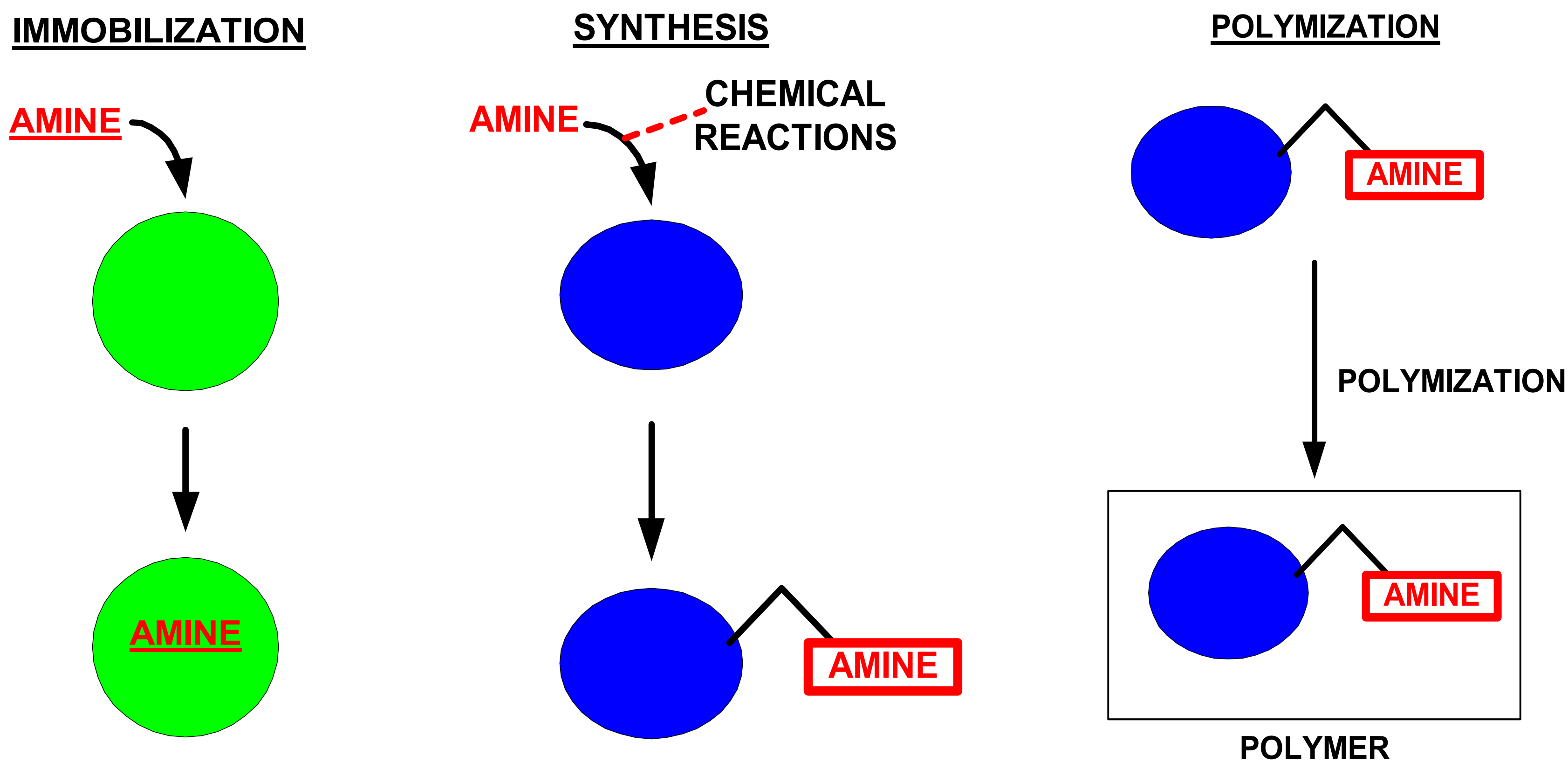
NETL

XPS Analysis of DBU-3 at Various Temperatures

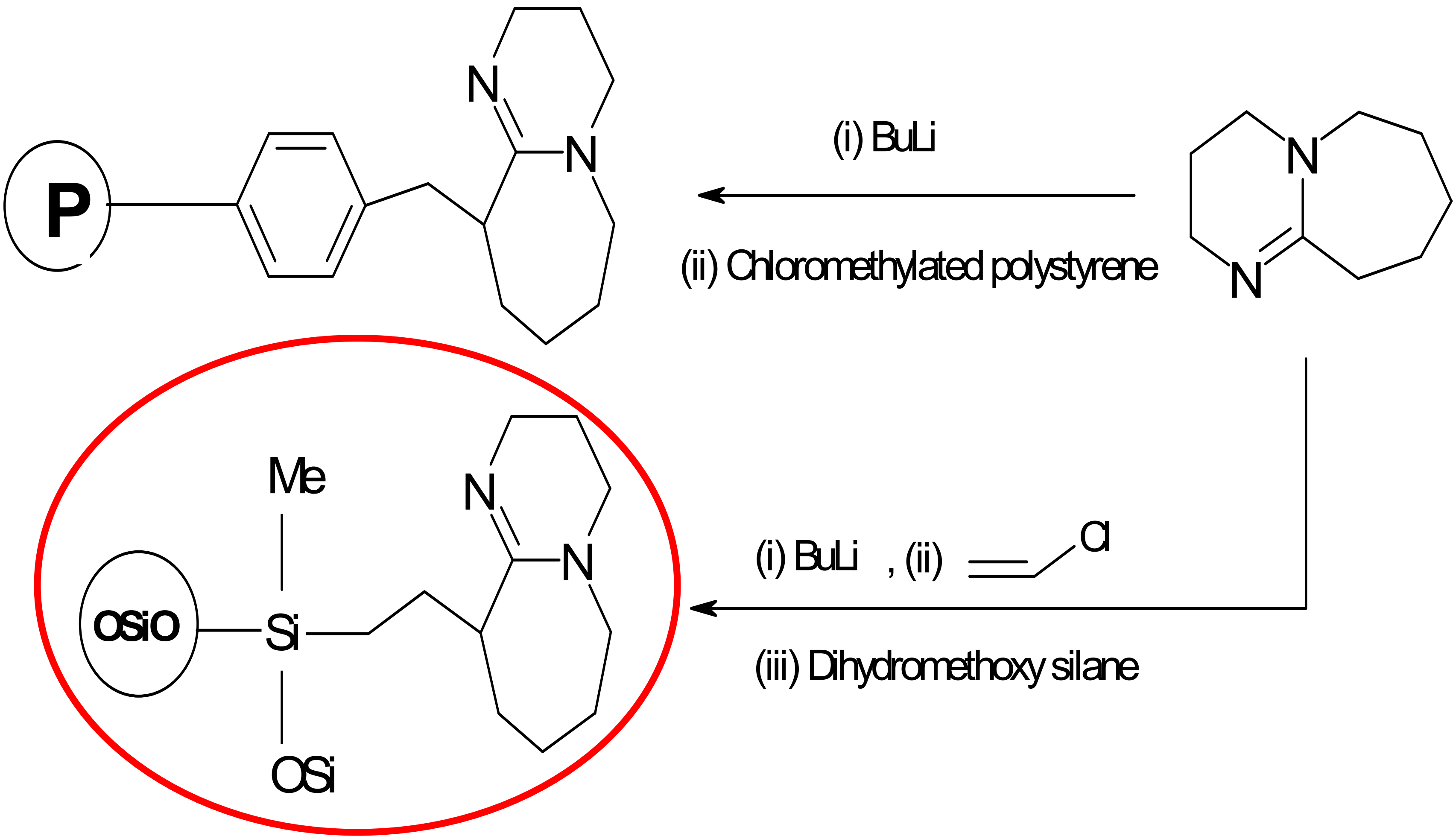
Temperature °C	gmole CO_2/ Kg sorbent	XPS N1s
25	3.02	1.03
45	2.47	NA
65	2.34	1.26

Good Stability of the DBU within the Diaion ® HP2MG Poly methyl(methylacrylate) Bead

Pathways to Solid Amine Adsorbents



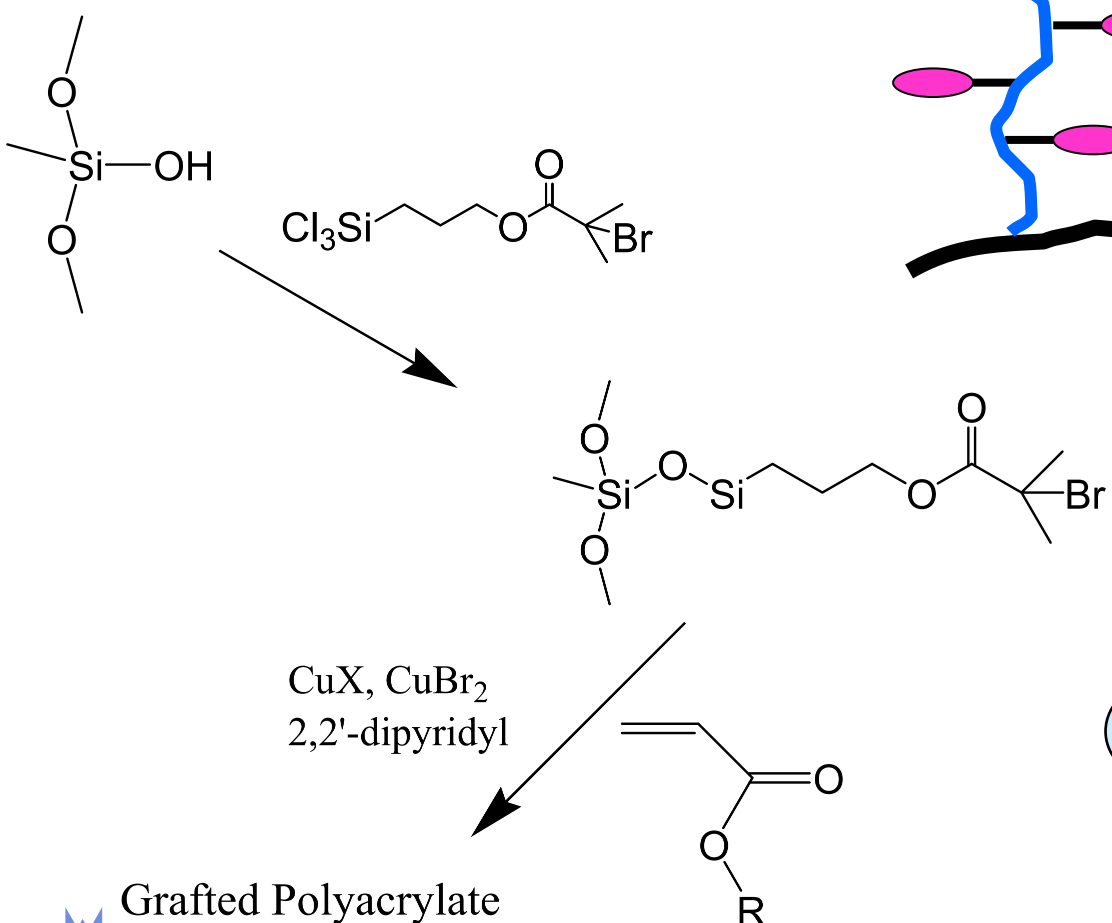
Initial Proof of Concept: A DBU-functional adsorbents

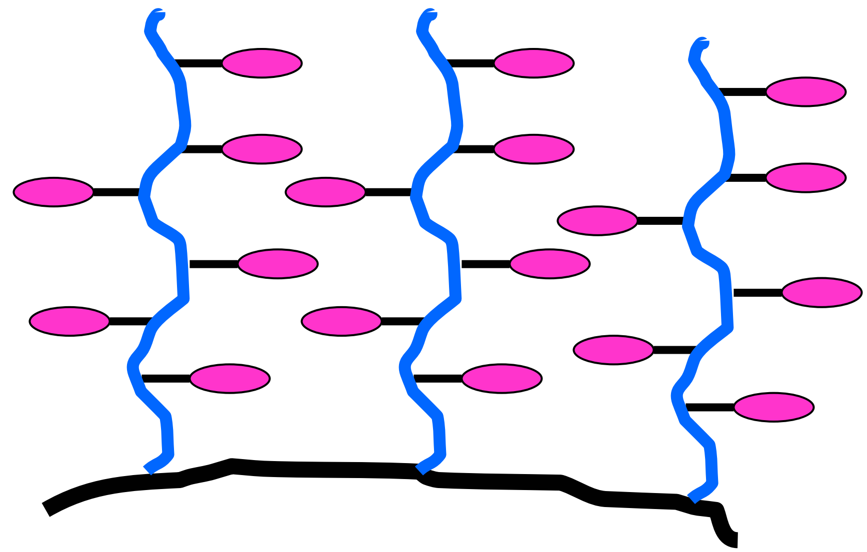


A DBU-functional silicone Adsorbent

Capture Temperature °C	gmole CO_2/Kg Sorbent	XPS N1s
25	3.31	4.2
45	3.26	NA
65	3.19	4.0

Polymeric DBU-acrylate





Increase Amine Loading

Polymeric Adsorbents

3-5 gmole CO_2/Kg Sorbent

Conclusions

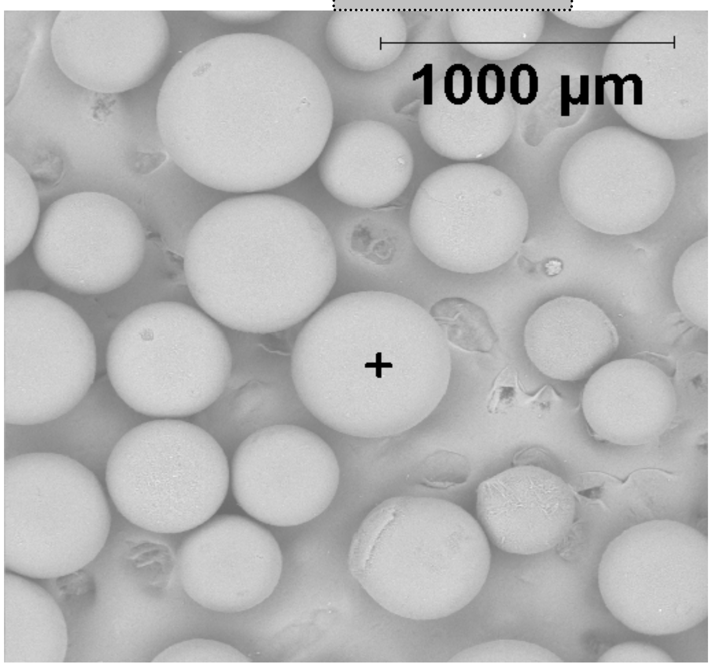
Conclusions

- The regenerable solid Tertiary adsorbents were capable of capturing carbon dioxide in levels greater than **3 gmole CO_2/Kg adsorbent** baseline.
- Adsorbents were capable of capturing CO_2 up to 65 ^oC.
- Tested in substrate systems.
  - Immobilization of DBU was stable
  - Synthetic Adsorbent was more at the higher temperatures
- Currently testing monomers and polymers of the imine and other amine based adsorbents **(3-6 gmoles CO_2/Kg adsorbent)**.

Acknowledgements

- ***Abbie Layne*** – Divisional Director of Separation and Fuels Processing Division
- ***Geo Richards*** – Focus Area Leader for Energy System and Dynamics

Preliminary System Conceptual Design



- Moving Bed
- Fluidized Bed
- Radial Bed
- Structural Bed