CO_2 Capture with Enzyme Synthetic Analogue

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Funded by:

arpa·e

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Program Team

- Hamilton Sundstrand
  Review of CO_2 separations system testing

- Columbia University
  Modification of Synthetic Analogue (Prof. Gerard Parkin's group)

- WorleyParsons, LLC
  Review of power plant -coupled system performance and cost models

- CM-Tec, Inc.
  Custom Chemical Synthesis

- GL Chemtec Int'l, Ltd.
  Custom Chemical Synthesis

- Consultants:

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Catherine Thibaud-Erkey, PhD	Chemical Engineering
Bart Van Hassel, PhD	Membrane Science
George Zafiris, PhD	Chemical Engineering

United Technologies

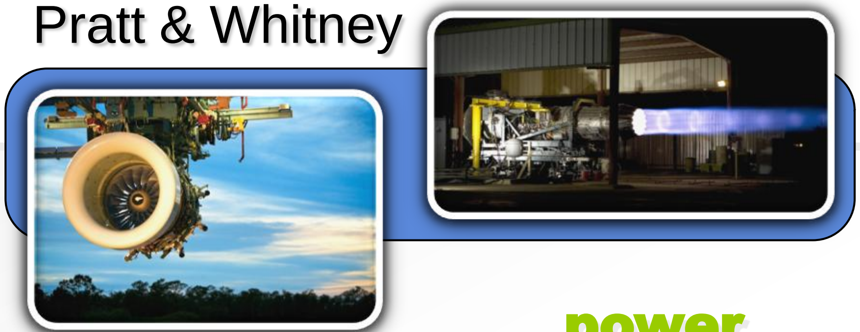
Business units

2009 Revenues

$52.9 billion

aerospace systems

Pratt & Whitney



Sikorsky

Hamilton Sundstrand

power solutions

UTC Power

building systems

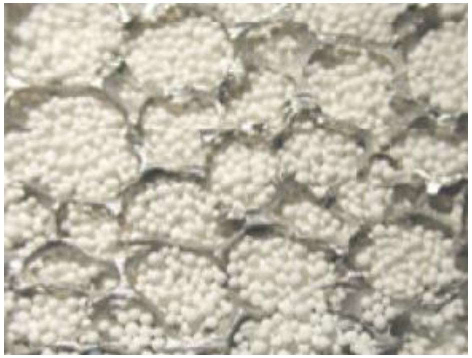
Carrier

UTC Fire & Security

Otis

Hamilton Sundstrand: CO_2 Capture for Space Applications

- CAMRAS: CO_2 And Moisture Removal Amine Swing bed
- Prototype delivered to NASA JSC (currently TRL6)
- Baselined for Orion; Lunar Lander; and new space suit
- Regeneration by space vacuum
  (heat for Mars environment)
- Heat exchange between adsorption/desorption
  maintains system isothermal



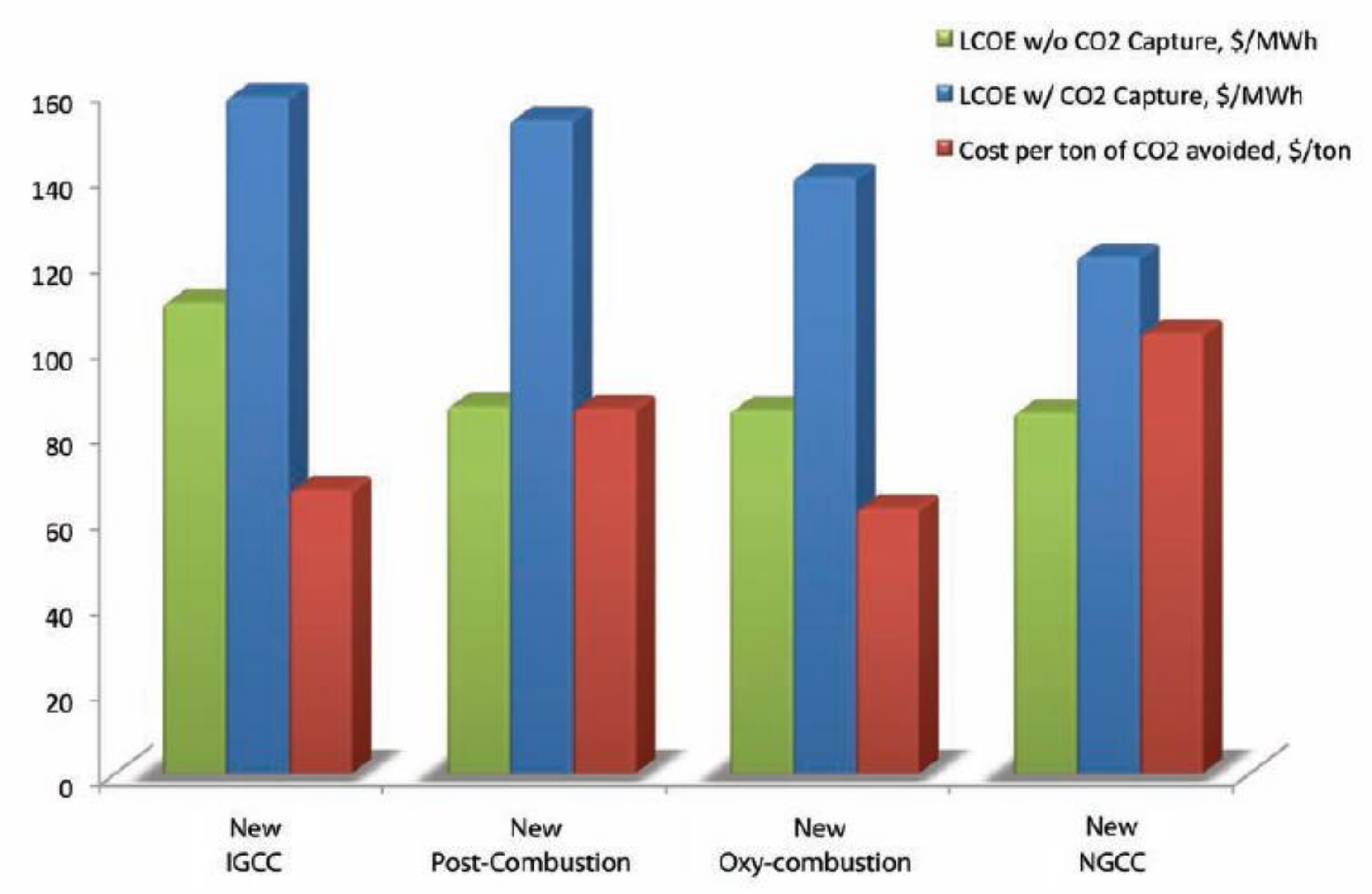
HS solid amine sorbent
in metal foam

Prototype CAMRAS system

Volunteers and NASA JSC scientists testing the CAMRAS system

Post-Combustion CO_2 Capture from Power Plants

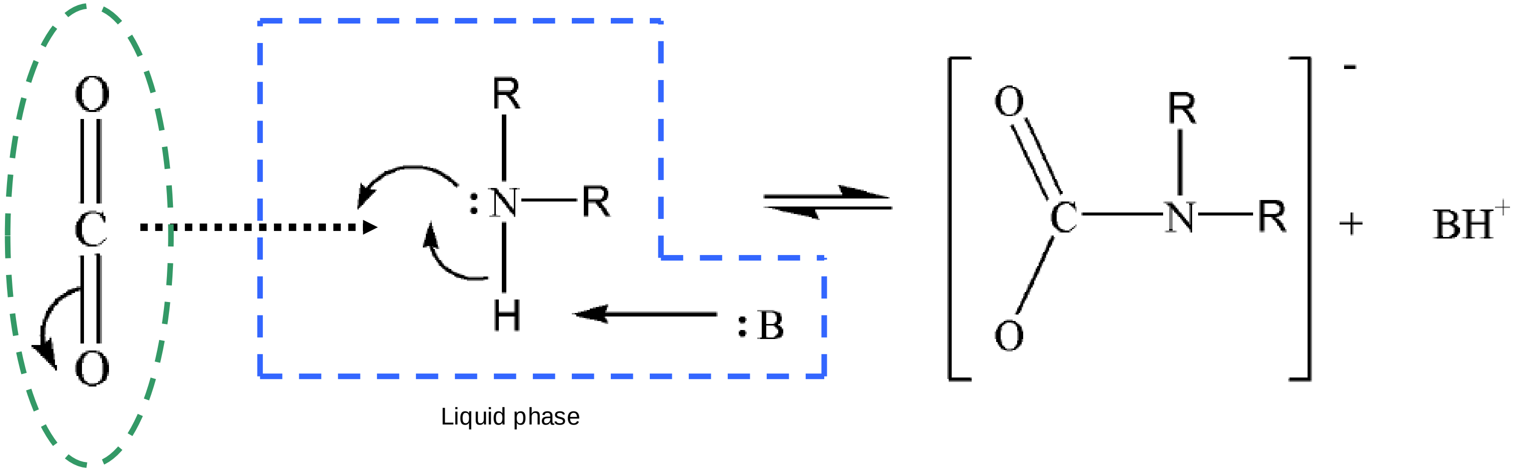
Technologies exist, but COE would almost double



Source:
DOE/NETL Advanced CO_2 Capture R&D Program
Technology Update: September 2010

Existing technology: Reaction between Liquid Amines and CO_2

High cost can be traced to limitations in chemistry



Gas phase

	Pulverized Coal Boiler			
	PC Subcritical		PC Supercritical	
	Case 9	Case 10	Case 11	Case 12
CO_2 Capture	No	Yes	No	Yes
Gross Power Output (kW_e)	583,315	679,923	580,260	663,445
Auxiliary Power Requirement (kW_e)	32,870	130,310	30,110	117,450
Net Power Output (kW_e)	550,445	549,613	550,150	545,995
Coal Flowrate (lb/hr)	437,699	646,589	411,282	586,627
Natural Gas Flowrate (lb/hr)	N/A	N/A	N/A	N/A
HHV Thermal Input (kW_{th})	1,496,479	2,210,668	1,406,161	2,005,660
Net Plant HHV Efficiency (%)	36.8%	24.9%	39.1%	27.2%
Net Plant HHV Heat Rate (Btu/kW-hr)	9,276	13,724	8,721	12,534
Raw Water Usage, gpm	6,212	12,187	5,441	10,444
Total Plant Cost ($ x 1,000)	852,612	1,591,277	866,391	1,567,073
Total Plant Cost ($/kW)	1,549	2,895	1,575	2,870
LCOE (mills/kWh)[1]	64.0	118.8	63.3	114.8

(Exhibit 4-46, DOE/NETL - 2007 / 1281)

High regeneration energy:

1) Reaction forms stable compound
2) ~70% of total mass is water

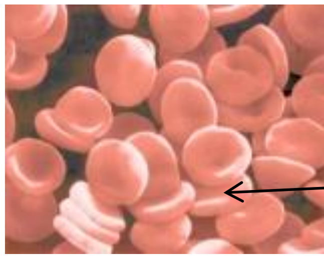
Slow kinetics:

1) CO_2 diffusion through liquid phase
2) Alignment with base and amine (low probability for reaction)

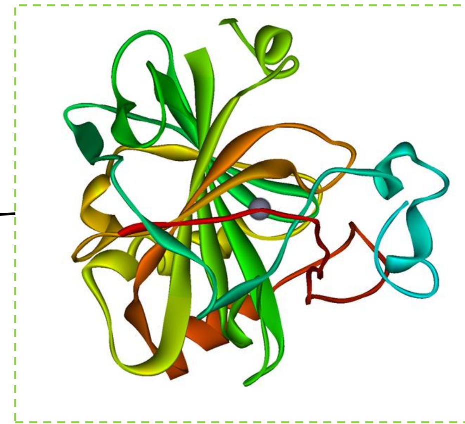
Nature's Solution: Carbonic Anhydrase

One of the fastest enzymes known; ancient and ubiquitous

Red blood cells



Carbonic anhydrase



$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

k_{cat} ~ $600{,}000 s^{-1}$

Limitations with using CA directly:

Not "designed" for harsh environments
Thermodynamically unstable, sensitive to pH
High cost

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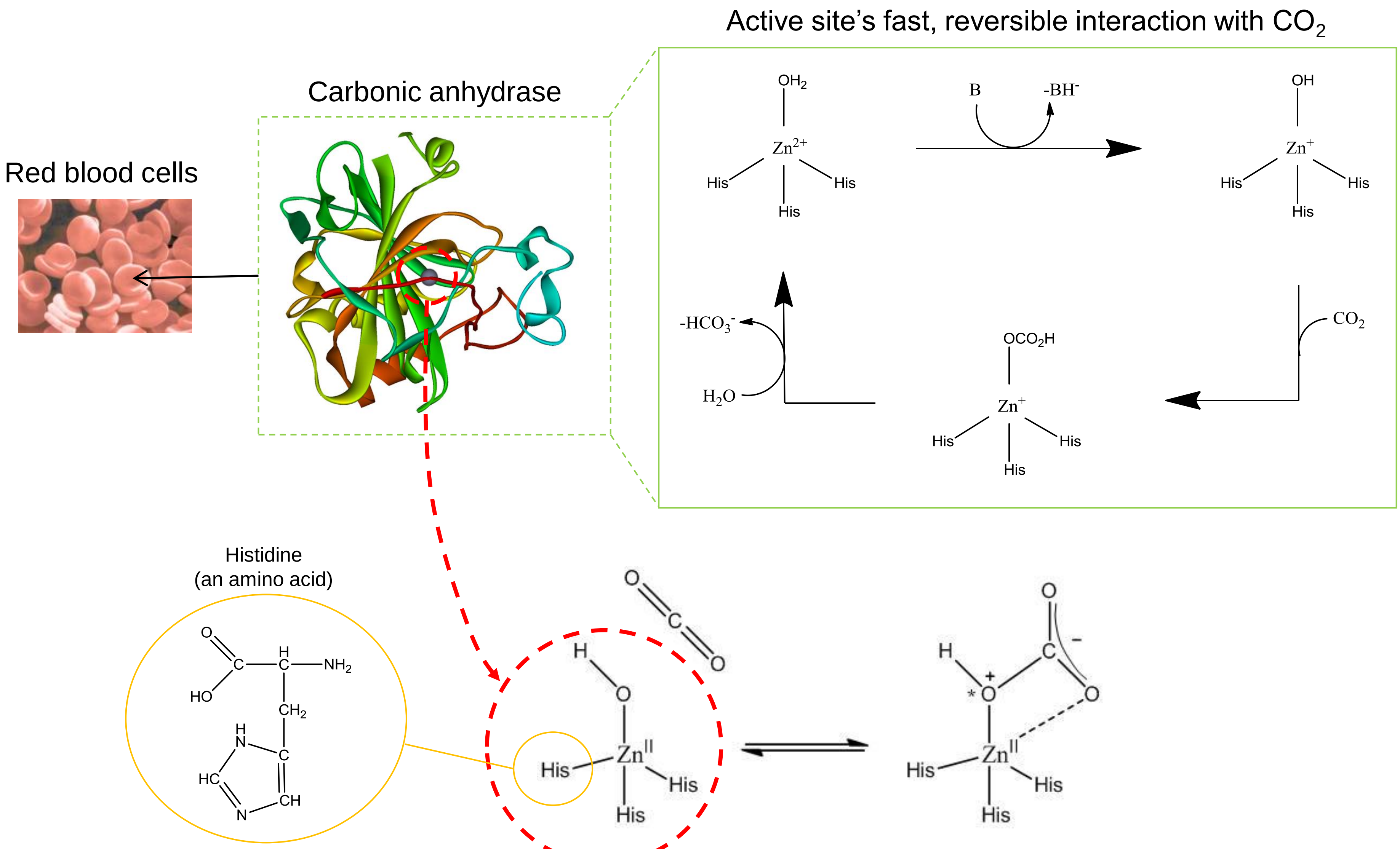
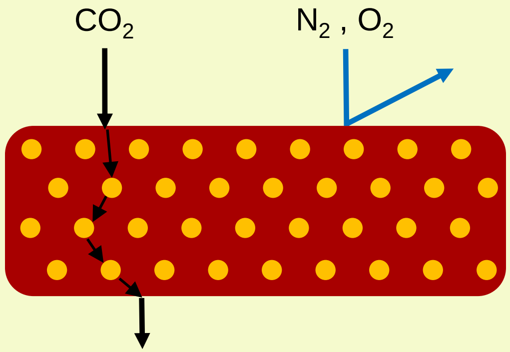
Overview of CA Structure & Function

Active site stereochemistry key for fast, reversible interaction with CO_2



Proposed Approach: Membrane-based Separation

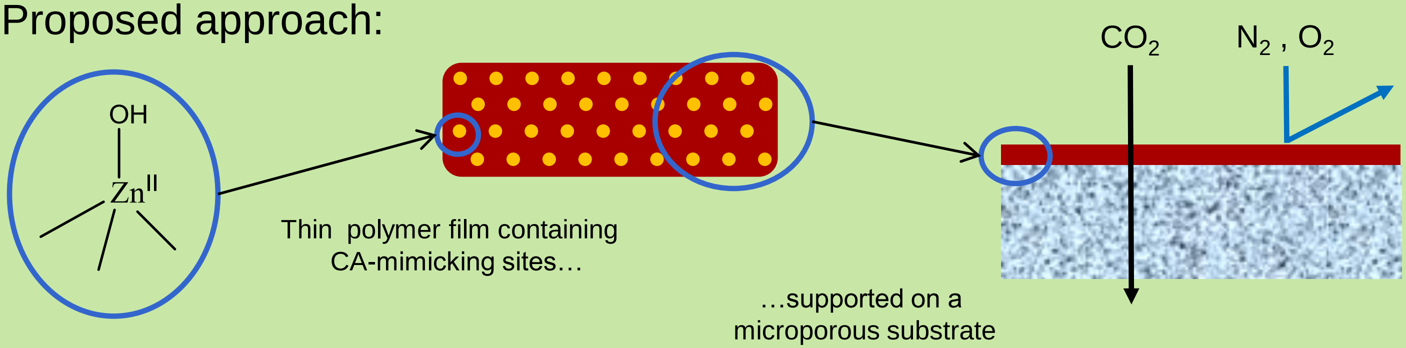
CO_2 transport facilitated by carriers mimicking enzyme active site



"Ideal" membrane:

- CO_2 transport is facilitated by specialized "carriers" within a barrier film
- Requires sites exhibiting fast and reversible interaction with CO_2

Proposed approach:



- ~30% lower CO_2 capture cost compared to liquid amines
- ~2 billion tons/yr CO_2 from existing coal-fired power plants
- Modular, skid-mounted configurations; no moving parts
- Flexibility to start with smaller system, gradually increase to 90% CO_2 capture

Key Questions

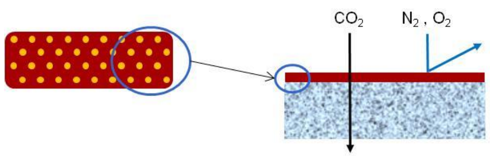
How does a membrane-based separation system compare to current benchmark (liquid amines)?

How do we maintain Zn-OH in tetrahedral coordination within a polymer matrix?

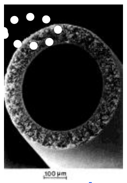
What is the effect of flue gas contaminants?

First Task: Separation System Feasibility Study

Simulation compares membrane vs. benchmark amine system

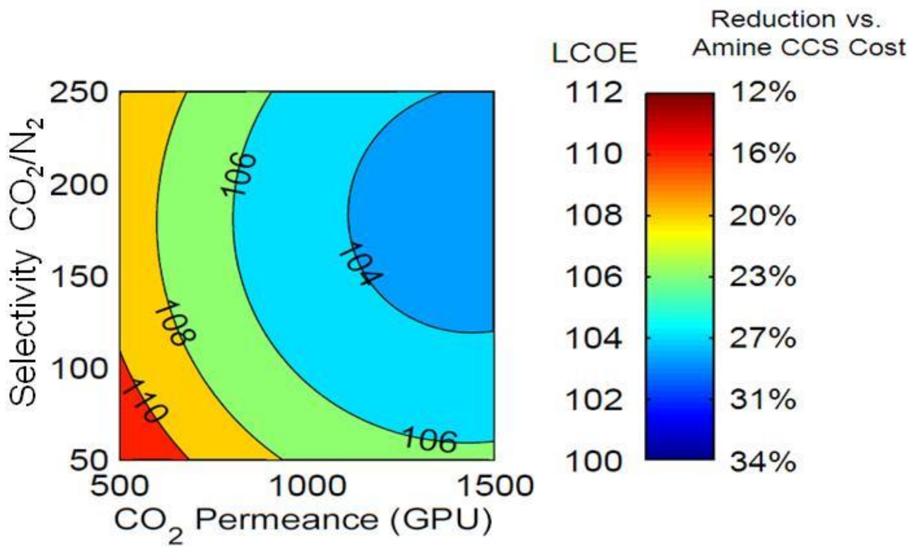


Synthetic analogue/
polymer thin-film

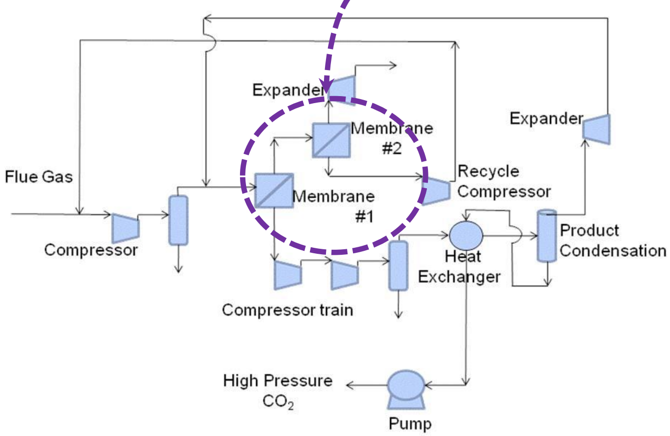


Porous substrate

Membrane
module



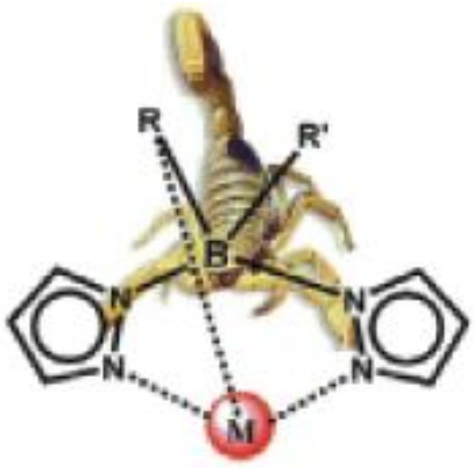
Membrane properties mapping

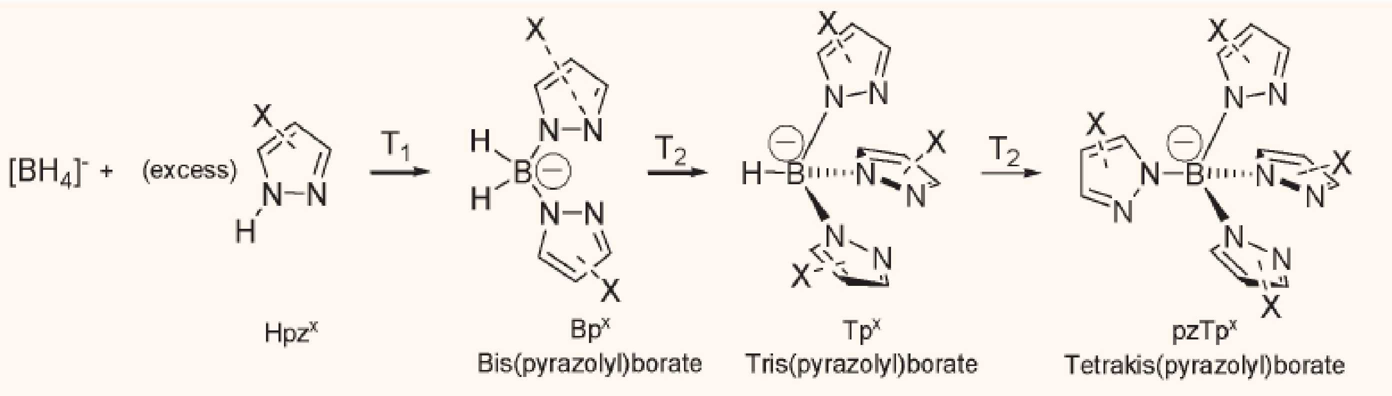


Simulated separation system (simplified)

“Scorpionates” (Poly-Pyrazolyl-Borates)

Modern tripodal ligants “force” metals into tetrahedral coordination

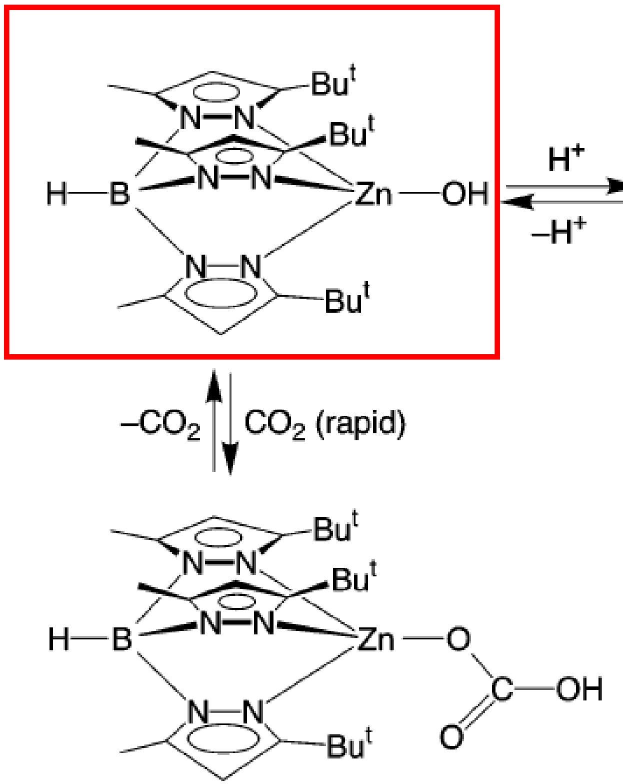


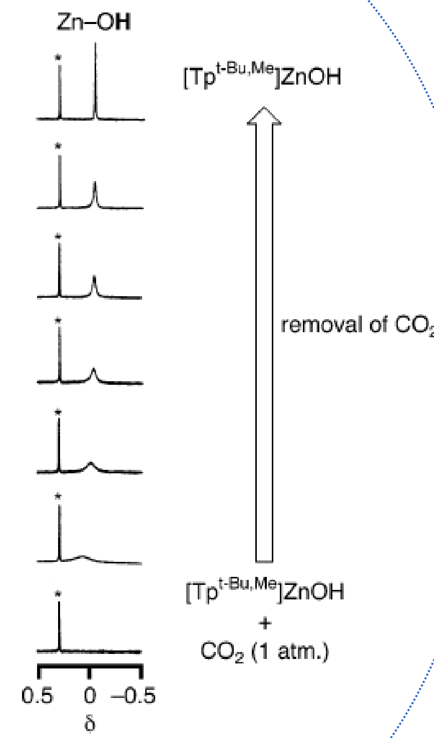


Trofimenko, S. “Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligants”, Imperial College Press, London 1999

$[Tp^{t\text{-}Bu,Me}]ZnOH$: a “Scorpionate” Synthetic Analogue for CA

Demonstrated fast & reversible interaction with CO_2





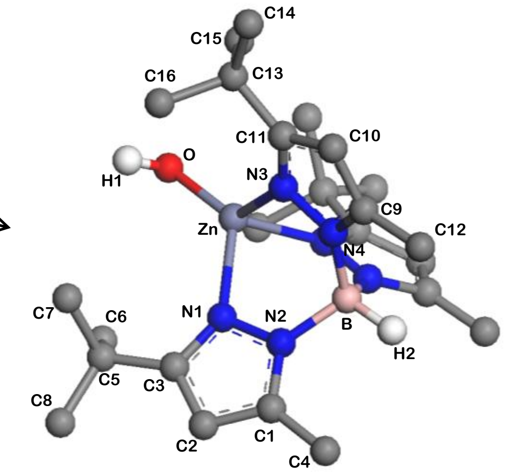
G. Parkin, Chem. Rev. 2004, 104, 699-767

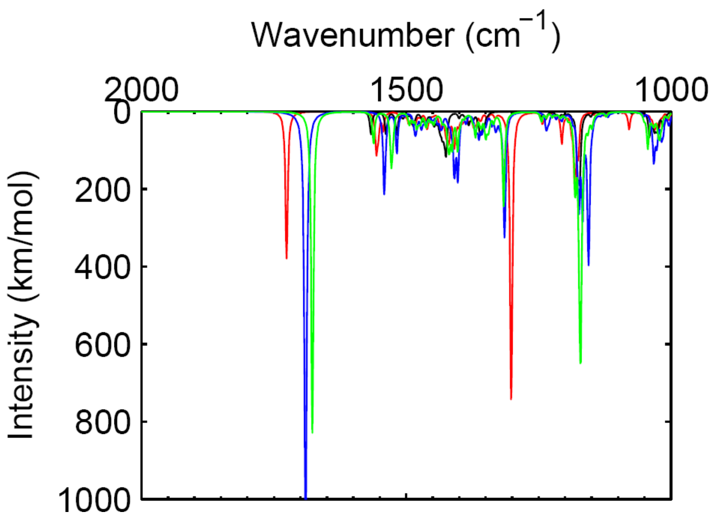
Stable molecule;
Fast reaction in NMR time scale

Synthetic Analogue Structure Analysis via Atomistic Modeling

DMol^3 model validated with experimental data

- Calculated structure predicts bond lengths & angles observed experimentally (XRD)
- Similar IR bicarbonate peaks observed in simulations and experiments
- Reasonable comparison between experimental and calculated analogue NMR



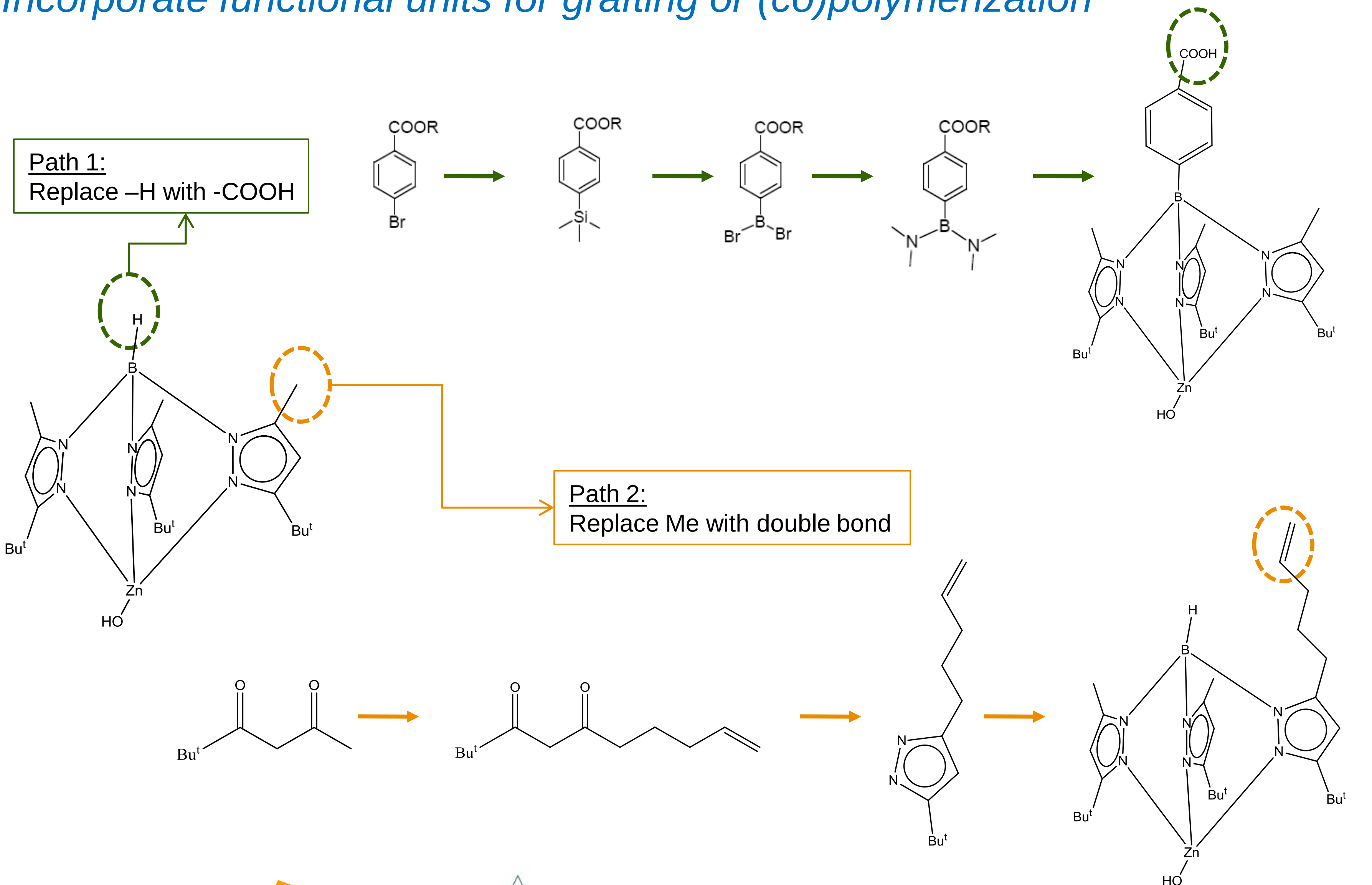


^1H

Atom	Vacuum	Chloroform	Benzene	Experimental
H1	-1.0	-0.7	-0.8	-0.3
H2	4.8	4.8	4.8	*
H(C2)	5.8	6.0	5.9	5.7
H(C4)	2.5	2.6	2.6	2.1
H(C6)	1.5	1.4	1.5	1.6

Synthetic Analogue Modification Example

Incorporate functional units for grafting or (co)polymerization



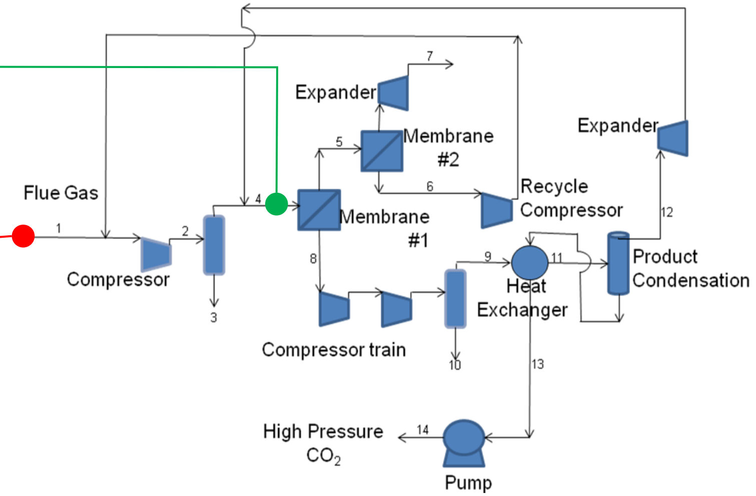
Resistance to Flue Gas Contaminants

No unrecoverable analogue poisoning (go/no go milestone)

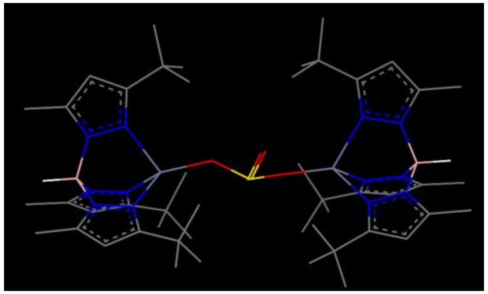
Concentrations over membrane calculated from HYSYS® model

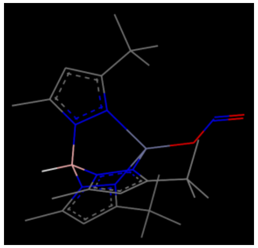
Max concentrations from WorleyParsons data (Sub-bituminus, bituminous A / B /C & lignite A / B

WorleyParsons resources & energy



Example possible structures (predicted by DMol[3])



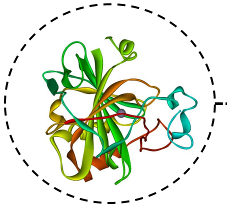


?

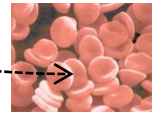
?

	mol %
Water	1.70
Oxygen	2.83
Nitrogen	78.61
Argon	0.94
CO_2	15.92
HCl	0.00115287
SO_2	0.00430116
SO_3	0.00004346
NO_2	0.00035149
HF	0.00005983

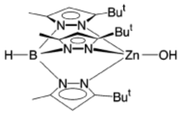
Program Summary



Carbonic anhydrase

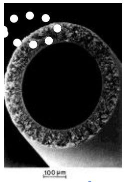


Erythrocytes
(red blood cells)



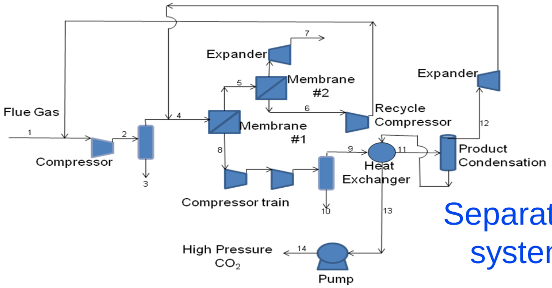
Carbonic anhydrase
Synthetic analogue

CO_2 -Selective film

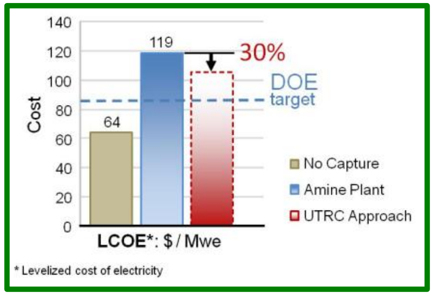


Porous substrate

Membrane
module



Separation
system



2010

Q1	Q2	Q3	Q4
Membrane prop. mapping ▲	Atomistic model verification ▲	≥3 paths to films ▲	**No unrecoverable poisoning** △ (Go / No go)

2011

Q1	Q2	Q3	Q4
Three model films prepared △	Selectivity improvement demonstration △	≥100 selectivity ≥ permeance △	≥200 hr durability test △; **30% cost reduction vs. amines** △ (Go / No go)

▲ : Accomplished   △ : Pending   △ : Go / No go