Removing Carbon Dioxide from the Atmosphere: Scientific, Technological and Societal Challenges

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School of Chemical & Biomolecular Engineering

Presentation Overview:

1. **Why alternative energy technologies will not solve the climate problem.**

2. Carbon dioxide capture and utilization/storage.

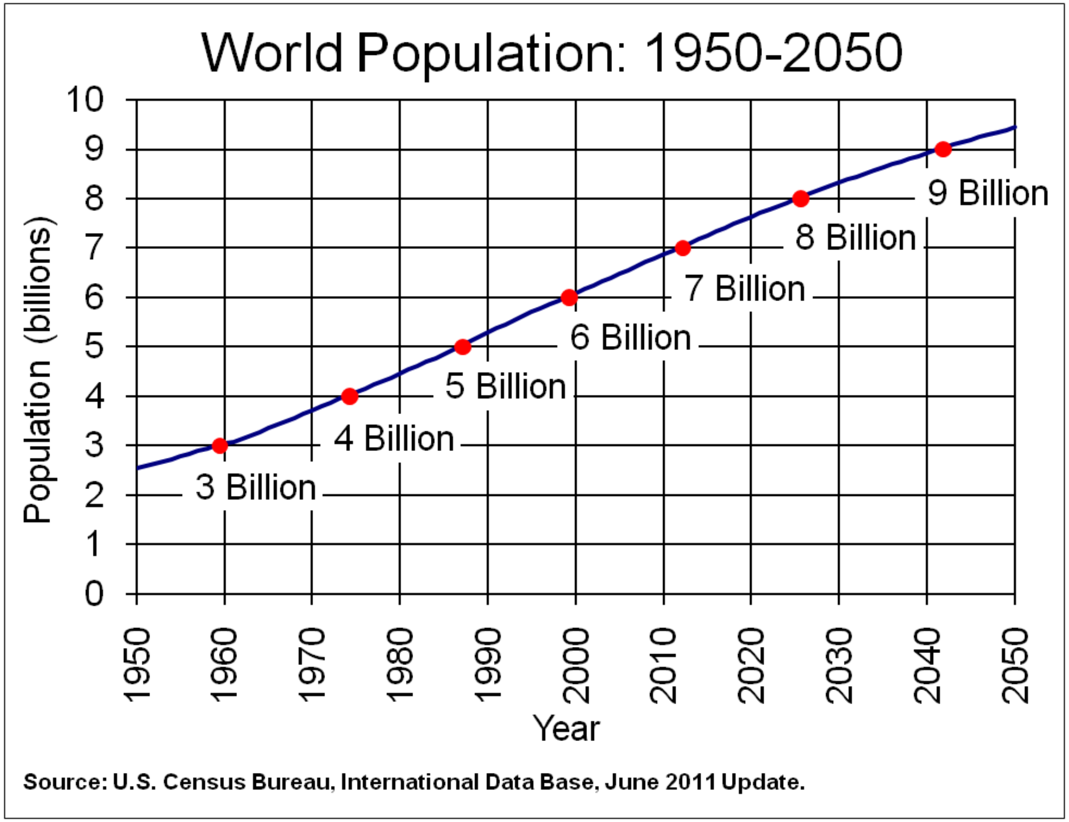
3. Direct capture of carbon dioxide from the atmosphere.
   "Air Capture"

4. Technical, political, societal challenges facing air capture.

Alternative Energy Technologies:

- Alternate (green) energy technologies are needed.
- These technologies will not supplant use of fossil energy in our lifetime.
- Why?

Energy Problem = Population Problem

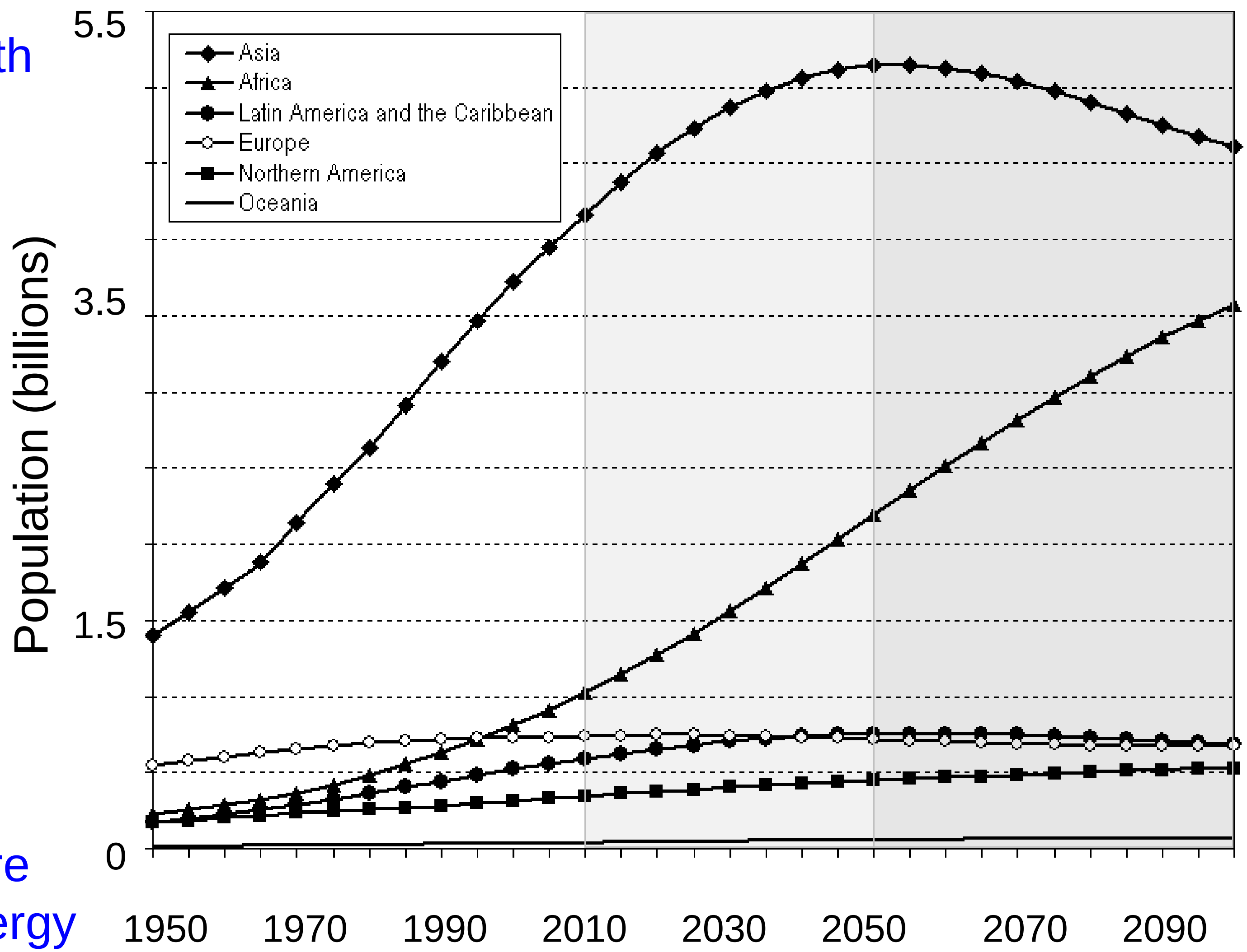


Year	Population
1650	0.5 Billion
1900	1.6 Billion
2011	7.0 Billion

http://www.census.gov/population/international/data/idb/worldpopgraph.php

Energy Problem = Population Problem

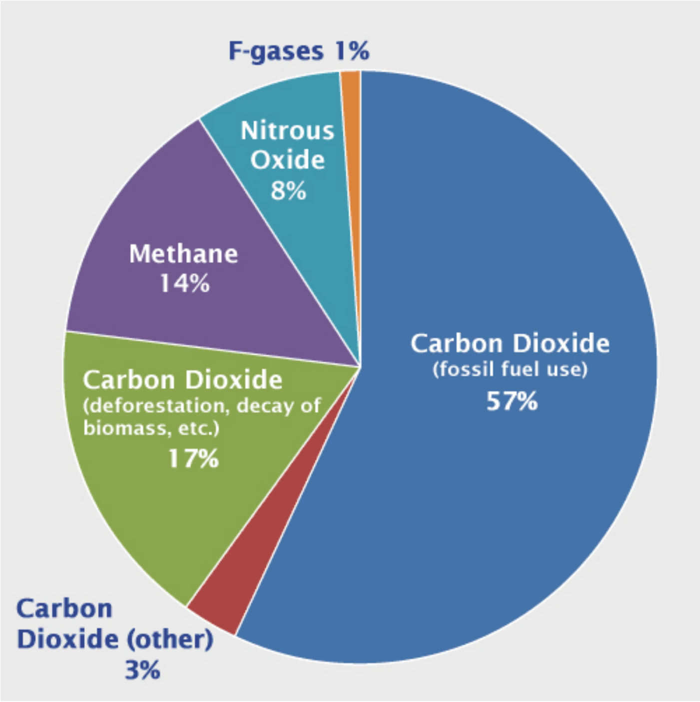
- Population growth in developing regions
- Low cost energy will be used
- Growth of demand will largely negate growth of green energy use
- Future will require MORE fossil energy



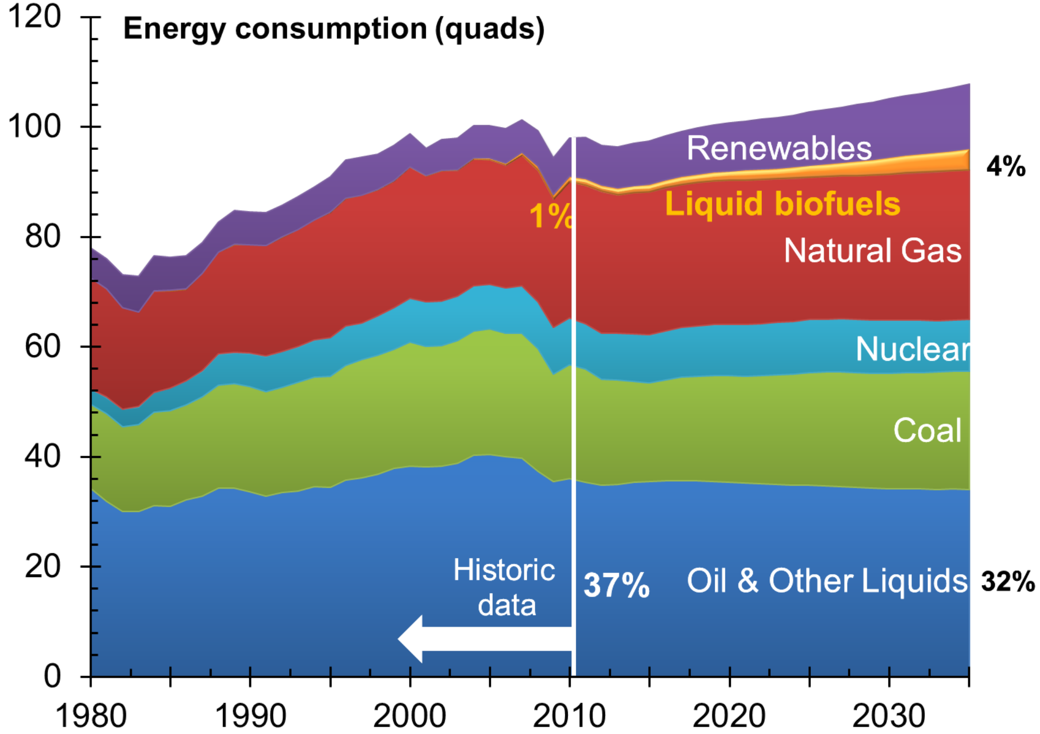
http://esa.un.org/wpp/Analytical-Figures/htm/fig_2.htm

Projected Energy Consumption

- Fossil energy will continue to play a dominant role.



Source: US EPA, 2012



Source: IPCC, 2007

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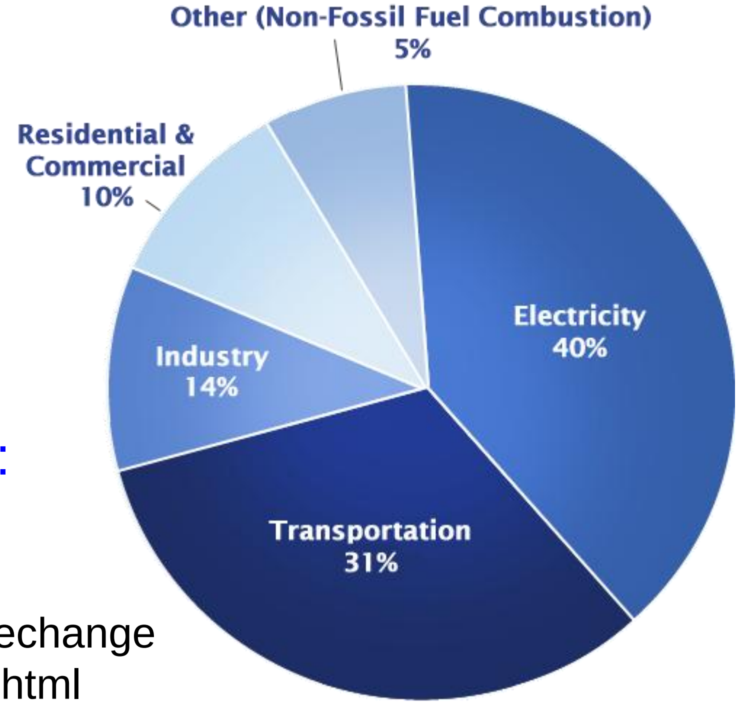
CO_2 Capture & Sequestration:

- Carbon capture and sequestration (CCS) as a climate change mitigation strategy.

- CCS is (i) the capture of CO_2 when released from combustion
  (ii) compression and transport by pipeline, and
  (iii) storage in geological formations.

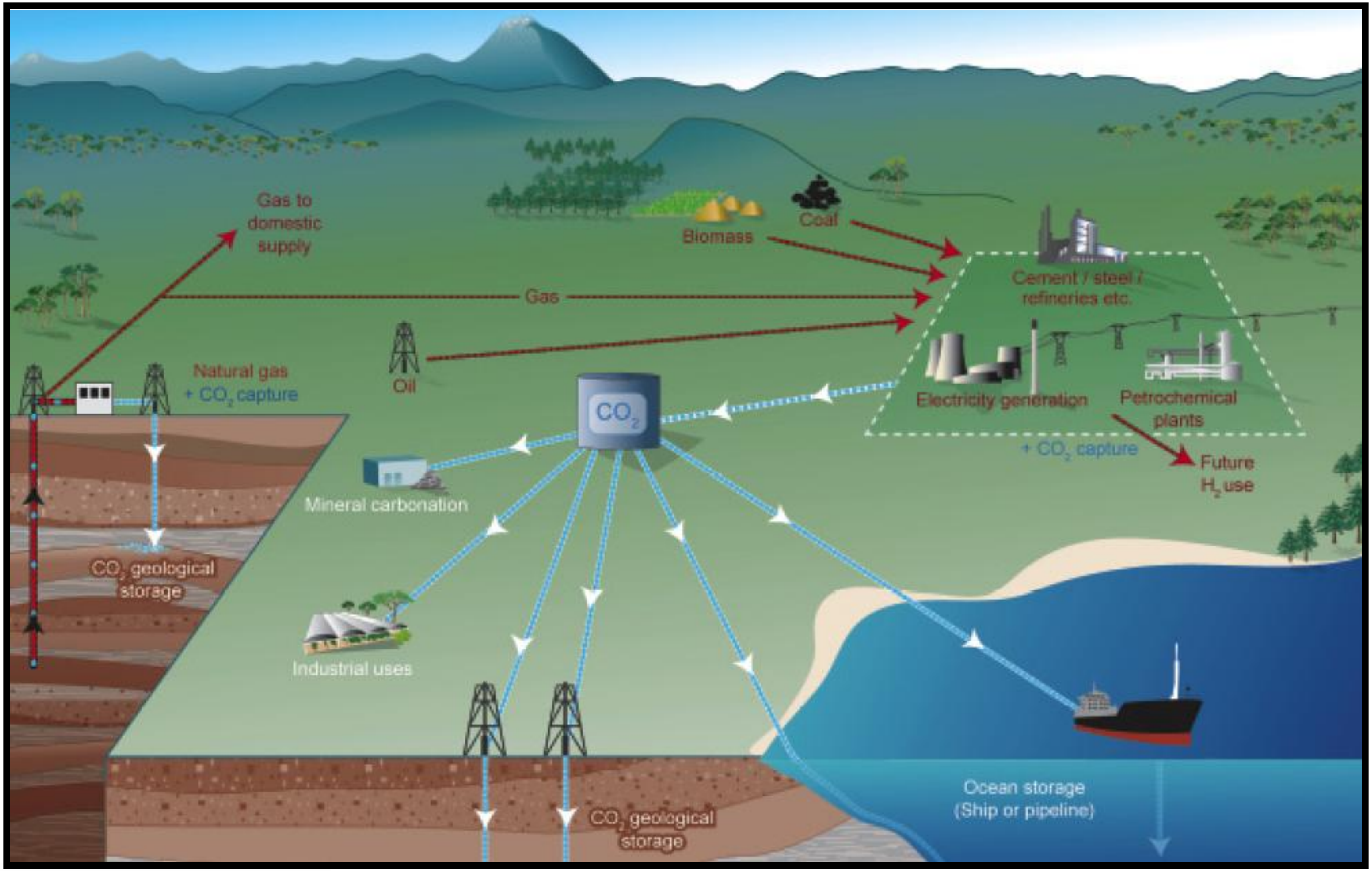
- Traditional CCS can be adapted to large, fixed sources, called "point sources."

US CO_2 emissions by source:



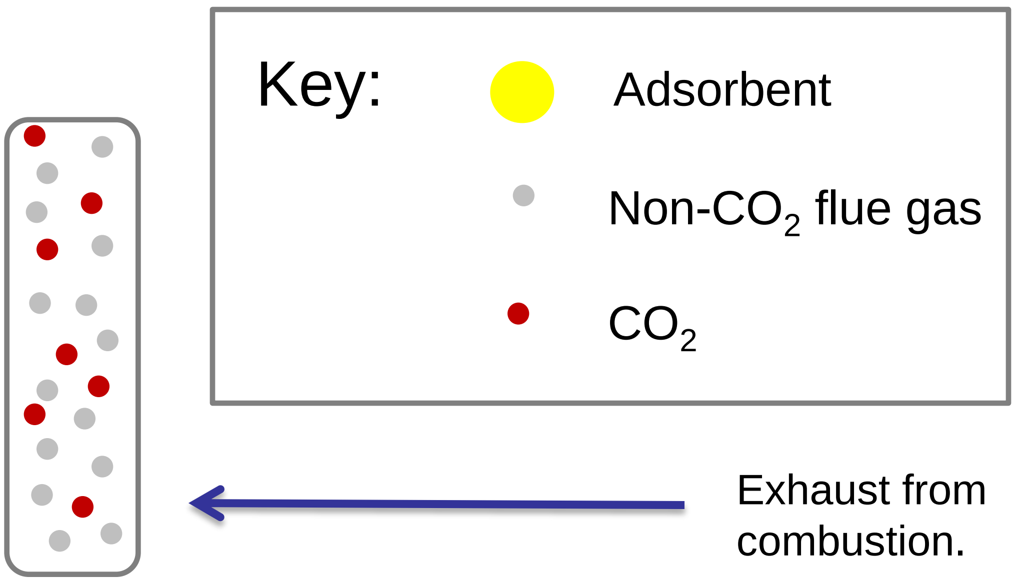
http://www.epa.gov/climatechange/ghgemissions/gases/co2.html

Envisioning Widespread Carbon Capture and Sequestration:



Source: IPCC, 2005

Schematic of a CO_2 Capture Process



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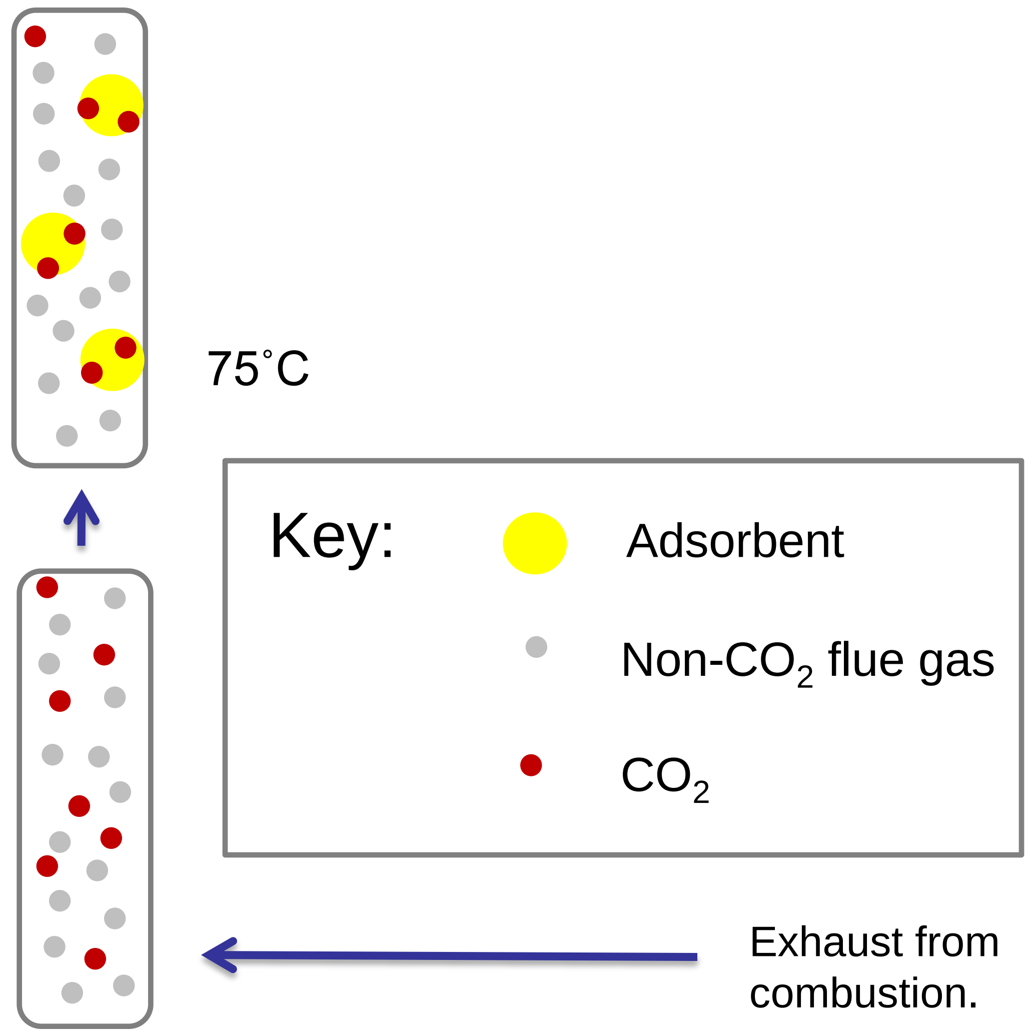

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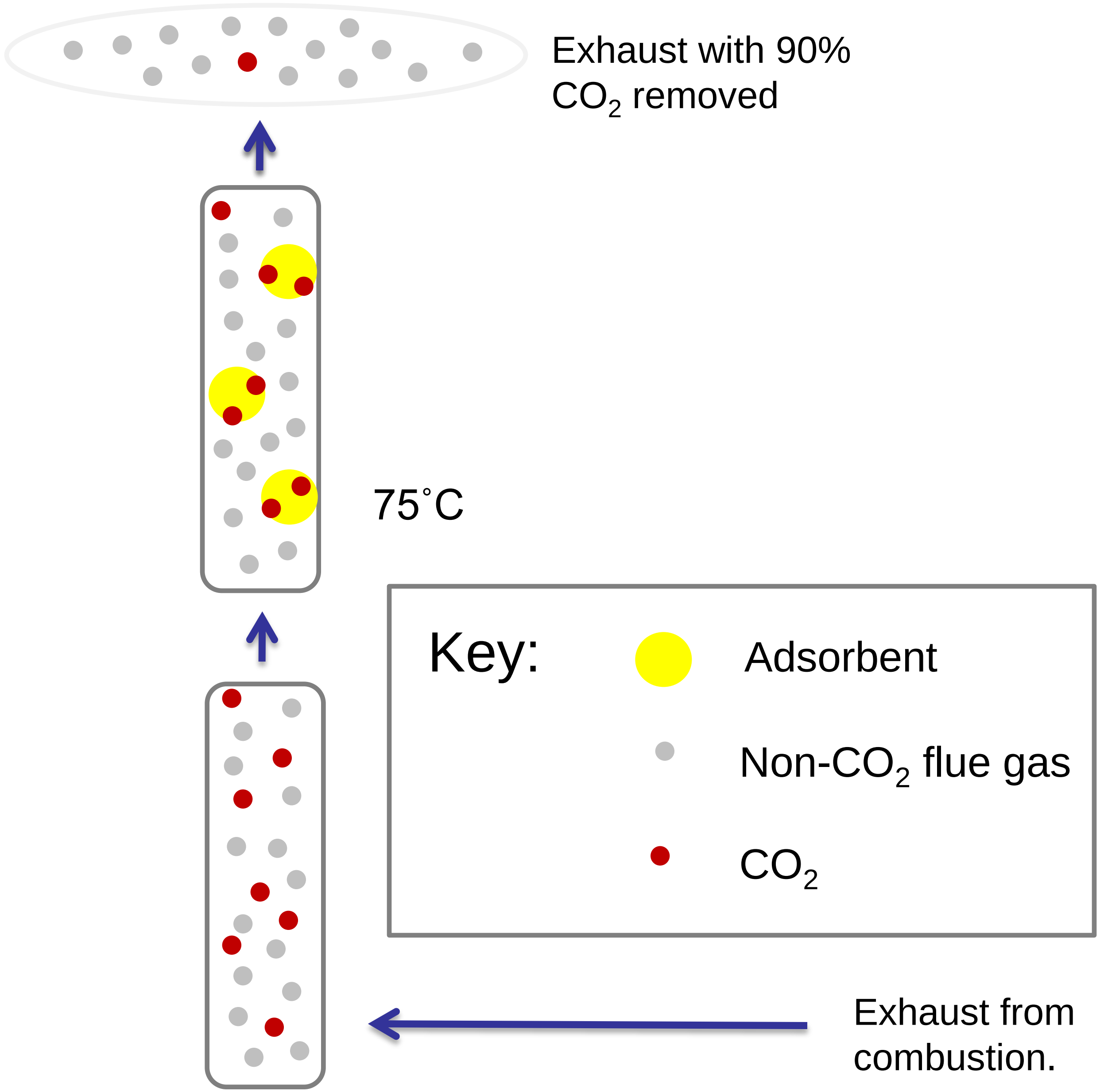

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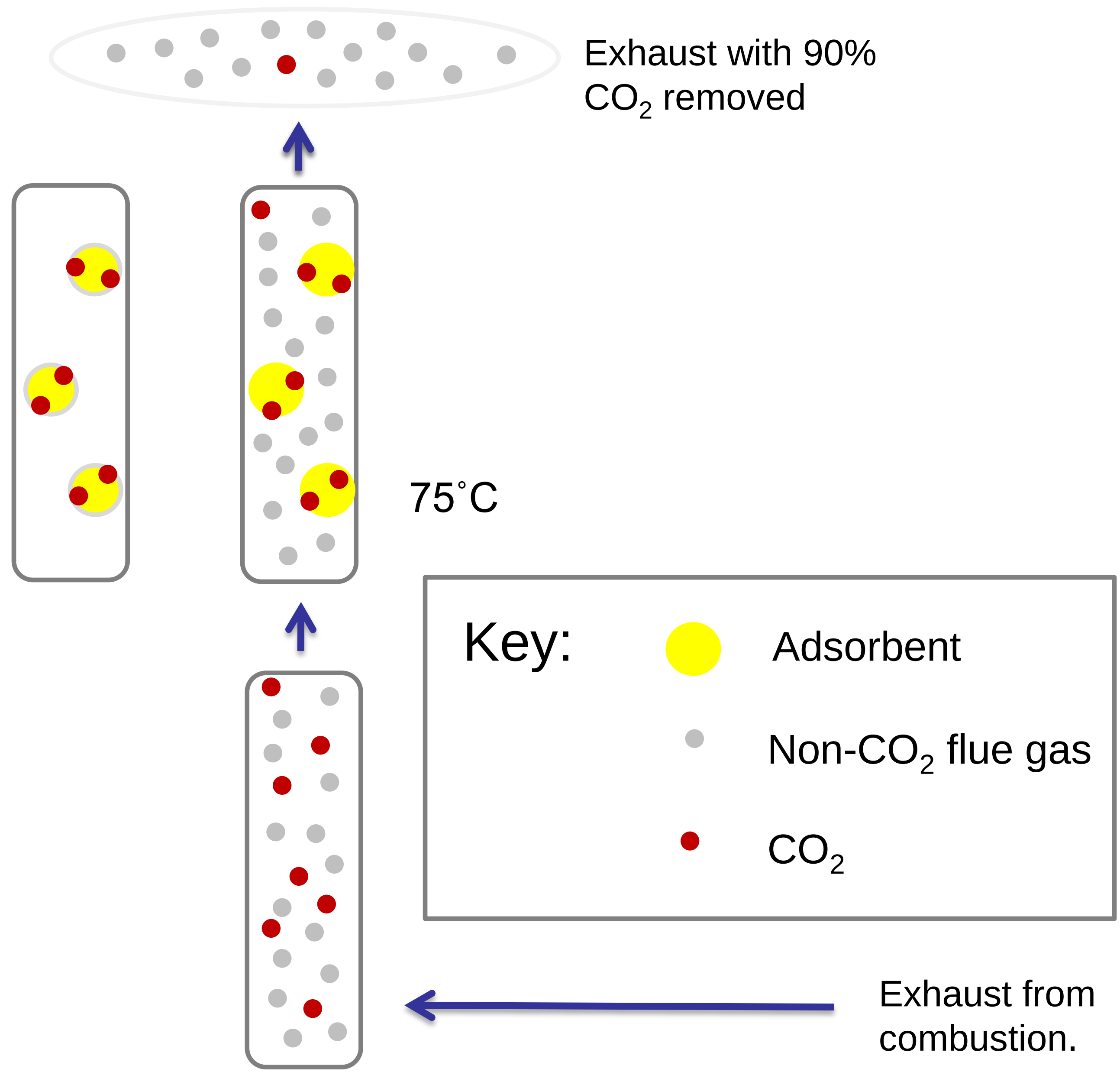

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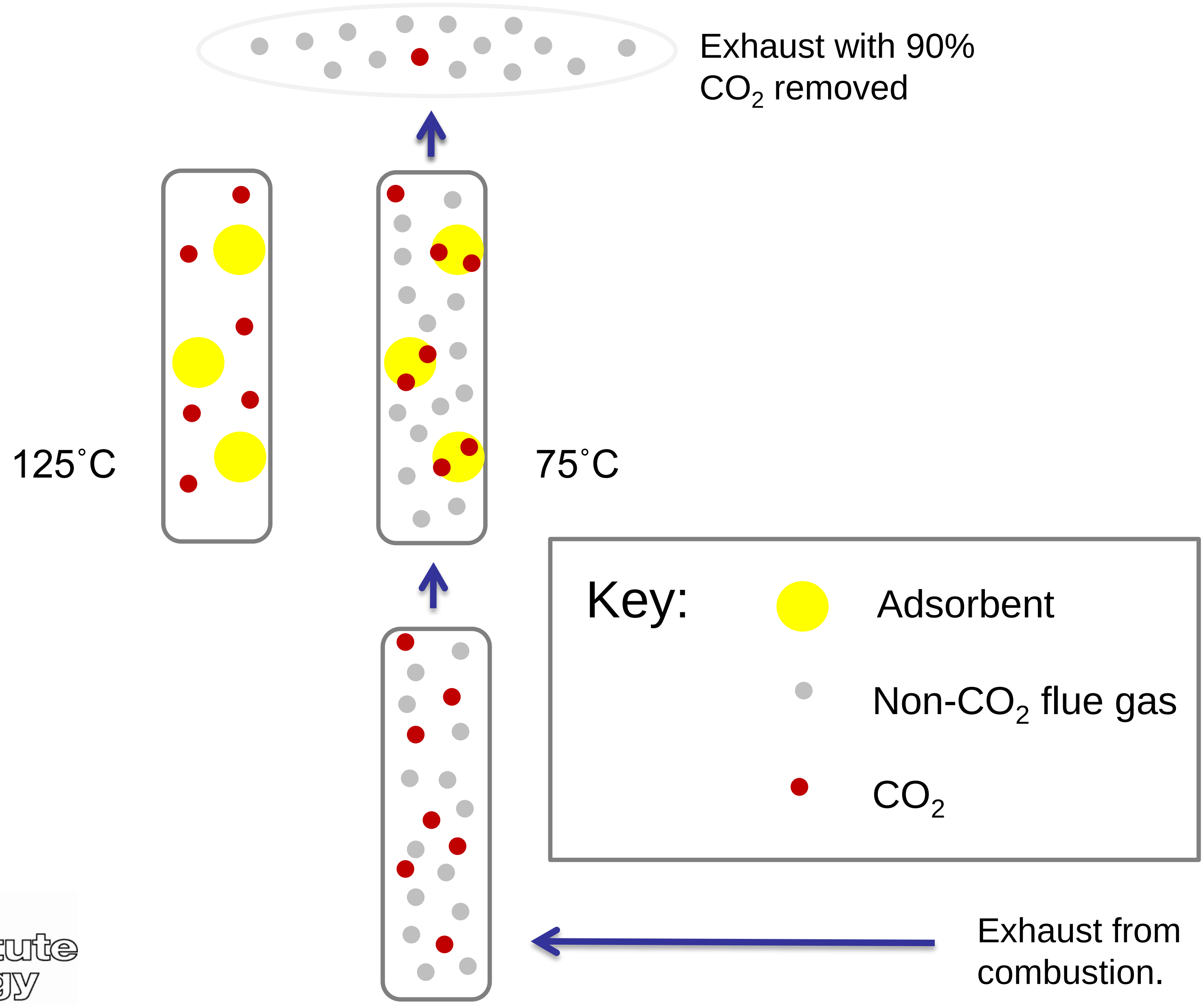

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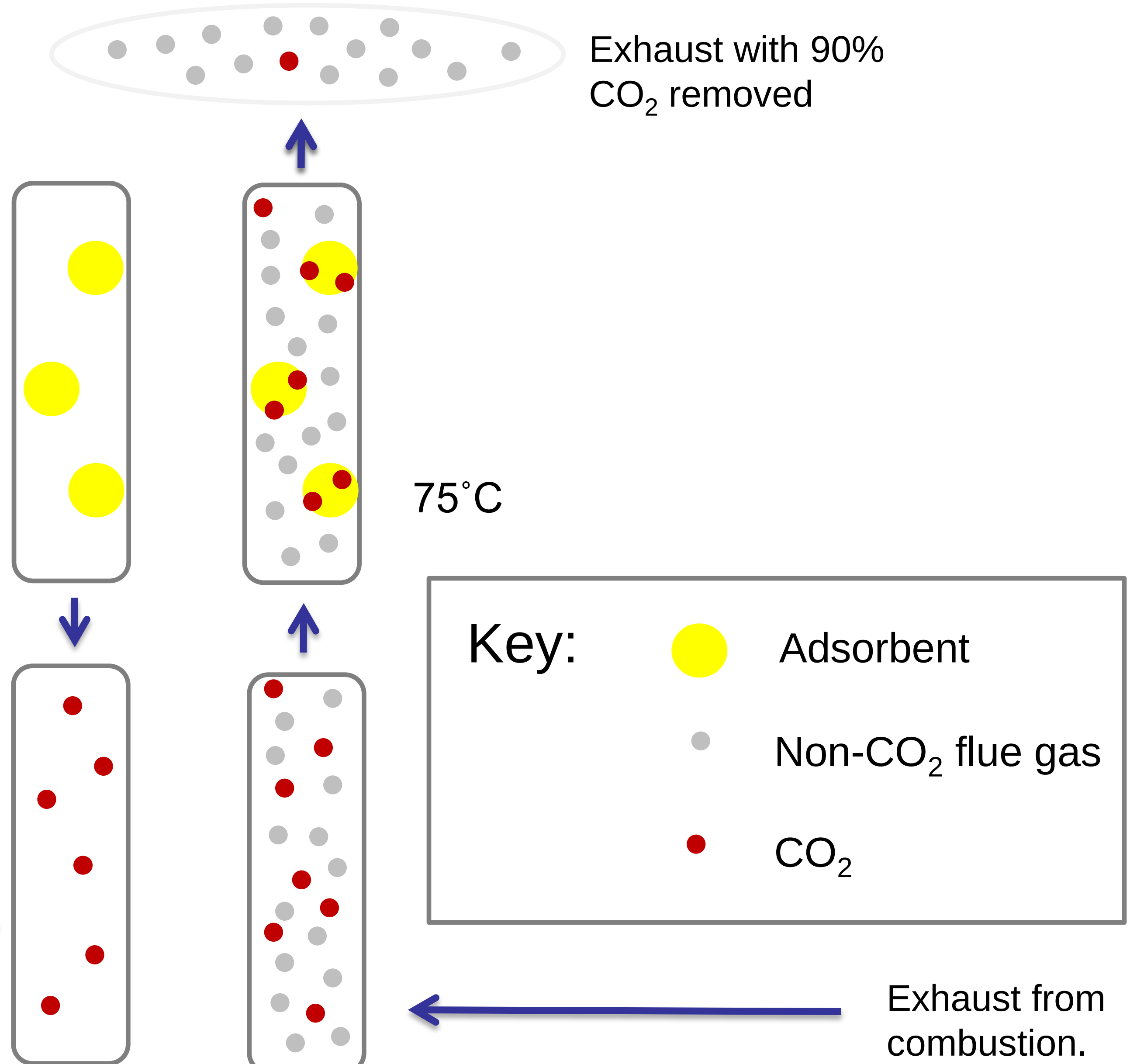

CCS Today:

- Many CCS installations operating globally at pilot scale.

- Why are we not doing this on a large scale today?

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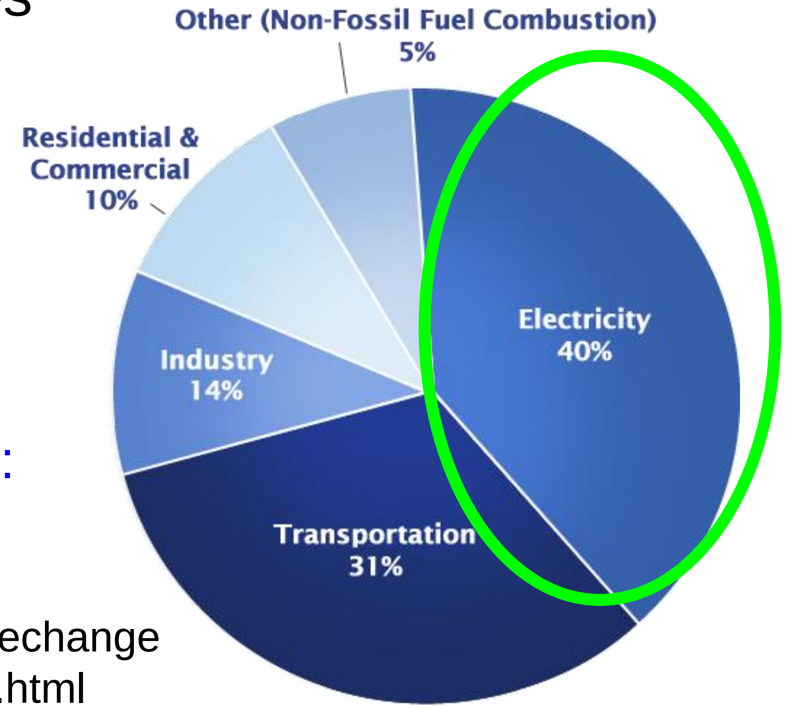
- Why are we not doing this on a large scale today?
- Cost-benefit analysis:
  - (i) only addresses 40% of sources
  - (ii) skeptical public in USA
  - (iii) projected cost: \$60B/yr in USA (~2% of GDP)

US CO_2 emissions by source:



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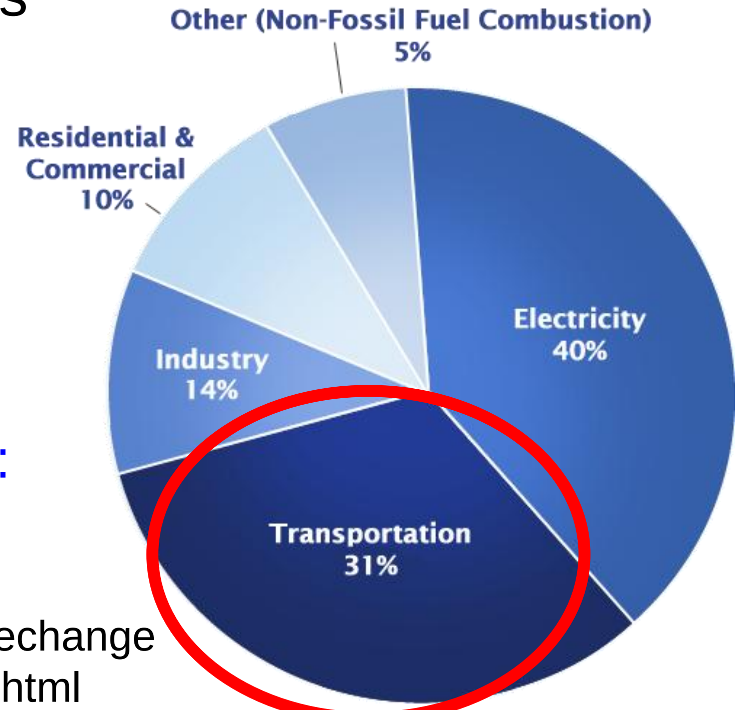

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CO_2 Capture from Air or "Air Capture:"

Best Way: Preserve forests

Prevent deforestation

Plants are our lowest cost atmospheric CO_2 removal option.

CO_2 Capture from the Atmosphere:

- Mobile sources (planes, ships, cars, trucks) cannot be addressed by traditional CCS.

- Direct extraction of CO_2 from the atmosphere can, in principle, account for all emission sources.

  -- *unlike other climate engineering approaches, CO_2 capture from air fits the traditional pollution clean-up paradigm.*

Extraction of CO_2 from ambient air as an environmental technology pioneered by Lackner and coworkers (now Columbia University):

Lackner KS, Grimes, P., Ziock, H.-J. 1999. Carbon dioxide extraction from air? Los Alamos National Laboratory, LAUR-99-5113, Los Alamos, NM, 1999

- Will air capture be expensive or technically challenging?

Point Source Capture vs. "Air Capture":

CO_2 Source Properties: Air/Point Source Exhaust

Property	Air	Flue (Point Source)
Amount of CO_2	3 teratonnes (3 x 10^{12} tonnes)	20 gigatonnes/yr (20 x 10^{9} tonnes)
Distribution	**400 ppm** - "infinite" mostly uniform source	5-15% point sources 10% - 250x more conc. vs. air
Movement	wind, fans	fans

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Low CO_2 concentration poses a major challenge.

Base Case Scenario of Energy Cost:

- What is the best we can do? The thermodynamic limit.

Post-Combustion Capture from Coal-fired Power Plant Flue Gas:

Dilute CO_2 mixed in N_2 → Separated CO_2 at 1 atm → Pressurized CO_2 at 140 atm Pipeline ready → Pumping underground and water displacement

~9kJ/mol ~5% of the output	~13kJ/mol ~7% of the output	~2kJ/mol ~1% of the output

House et al., *Energy Env. Sci*. **2009**, 2, 193.

CO_2 Capture from Ambient Air:

-- only first step different

Base Case Scenario of Energy Cost:

- Traditional CCS from point sources is expensive.

  24 kJ/mol CO_2 minimum energy

- Air capture only differs in the first step.

  ~40 kJ/mol CO_2 minimum energy

- Air capture is thermodynamically feasible.

- Is air capture technically feasible and might it be a complimentary or alternate technology to traditional CCS?

Needs for a Practical "Air Capture" Process:

1. Low Pressure Drop, High Surface Area Contactor:
   - must move 125-375 X more gas through process vs. flue gas

2. Adsorbent with strong binding energies with CO_2 (thermodynamics)
   - must adsorb a large amount of CO_2 at low P_{CO2}.

3. Adsorbent and process design that allows for rapid adsorption/desorption rates (kinetics)
   - need to remove massive amounts of CO_2.

4. Low cost source of energy for adsorbent regeneration by temperature-swing.
   - adsorption is exothermic, desorption is endothermic

5. Acceptable capital costs and ultra-long process/material lifetime
   - sorbent degradation and lifetime is a critical element.

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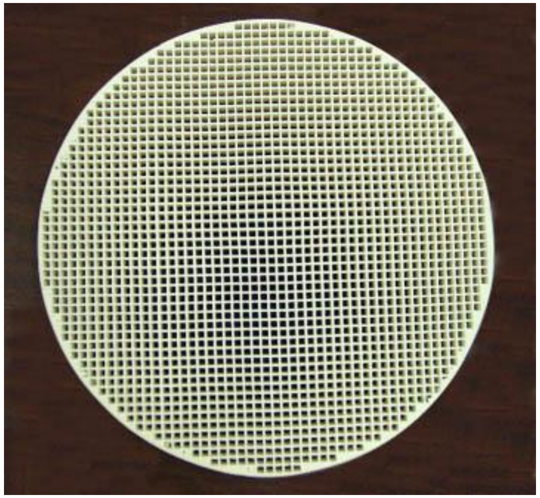

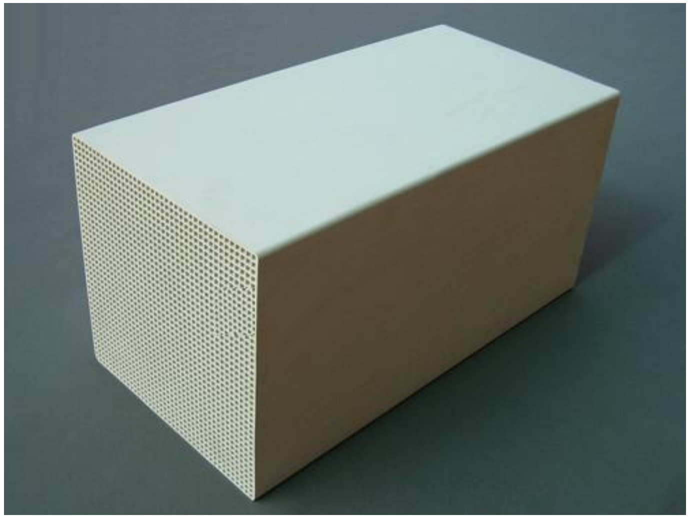

Ceramic monoliths:

(i) commercially available (Corning)
(ii) low cost
(iii) low pressure drop [100-200 Pa or 0.15-0.3 psi]
(iv) easily coated with adsorbent materials
(v) high surface area

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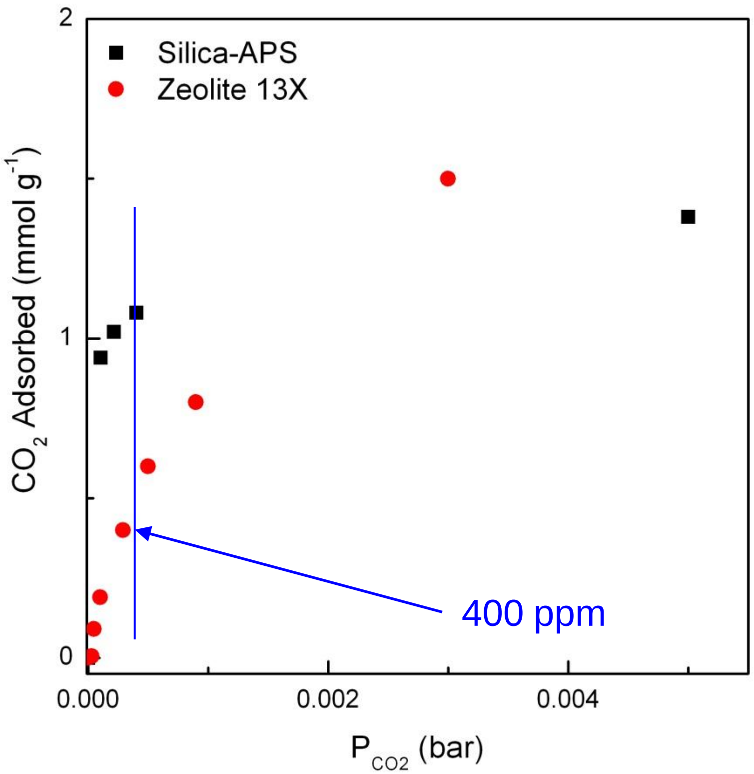
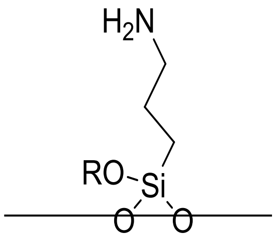


Zeolite 13X

-- physisorbant
(low ΔH_{ads} ca. 36 kJ/mol)

Silica-Amine



-- **chemisorbant (high ΔH_{ads} ca. 85 kJ/mol)**

-- highest capacities ca. 2.2 mol CO_2 / kg sorbent (10 wt%)

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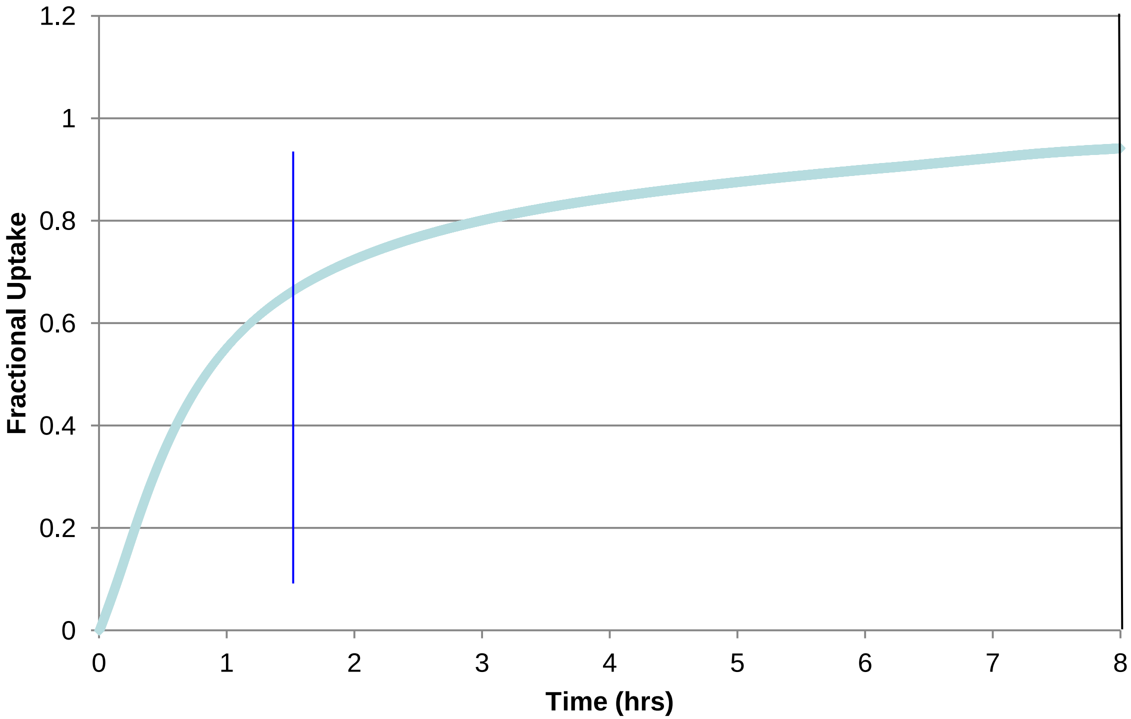


-- rapid initial uptake
to 70+% total capacity
= “working capacity”

-- lab conditions,
equilibrium, ~ 1 day
working capacity, ~1.5 h

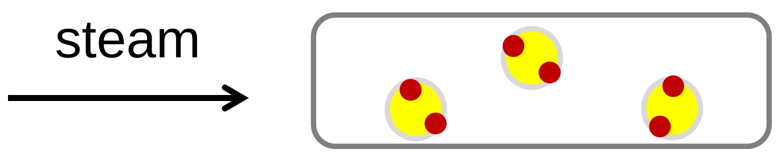
-- practical conditions,
gas velocity 2-5 m/s
working capacity, ~0.5 h

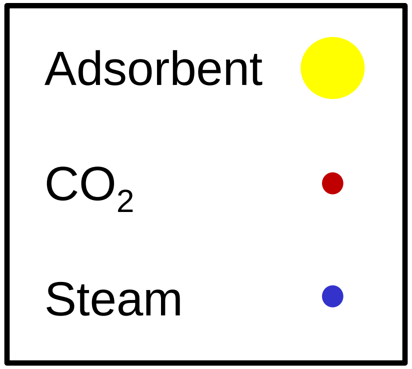
- Monolith contactor yields good kinetics

Needs for a Practical “Air Capture” Process:

4. Low cost source of energy for adsorbent regeneration by temperature-swing; Adsorption is exothermic, desorption is endothermic

- Amine adsorption occurs at ambient temperatures (0-35 ˚ C)
- Only low grade heat for regeneration (80-110 ˚ C) = waste heat.
- Steam-stripping gives pure CO_2 upon compression = highly efficient





- Low grade waste heat from:
  (i) Manufacturing processes
  (ii) Solar-thermal heating = minimal costs in short term

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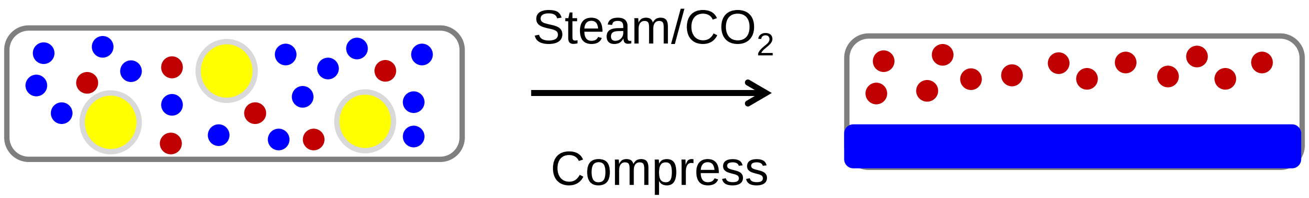

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Needs for a Practical "Air Capture" Process:

5. Acceptable capital costs and ultra-long process/material lifetime
   - sorbent degradation and lifetime is a critical element.

- Capital costs significant, installations big ($0.01\ m^2$ / tonne CO_2-yr)
- Capital costs for large scale equipment can be estimated.
- Largest cost unknown = lifetime of adsorption media.


-- studies underway Georgia Tech and elsewhere

-- amine degradation (thermal, oxidative)
-- sorbent blocking (dust, sand, etc.)

Practical "Air Capture" Processes:

***Global Thermostat*, NY/Palo Alto**, Georgia Tech - designed sorbents in a pilot-scale air capture process, http://globalthermostat.com/

-- Peter Eisenberger, Graciela Chichilnisky

Three other significant efforts also underway:

Carbon Engineering, Calgary; http://www.carbonengineering.com/

-- basic liquid solutions (absorption)

-- David Keith

Kilimanjaro Energy, NY/SF; http://www.kilimanjaroenergy.com/

-- humidity swing with ammonium resins (absorption/adsorption)

-- Klaus Lackner

Climeworks, Zurich; http://www.climeworks.com/

-- adsorption with amines (alternate gas contactor and regeneration methods from Global)

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Technical, Political and Societal Challenges:

- Technically, air capture is feasible.

- If power comes from fossil energy, is there net CO_2 removal from the atmosphere?

-- first generation NaOH process (American Physical Society study), perhaps not

-- for monolith/amine/steam-stripping design, energy needs are very promising:

-- low T process/waste heat = 80% of energy
-- electrical energy (draft fans) = 20% of energy

-- if steam from waste heat / solar thermal (natural gas), 1 CO_2 released for every 20 (2) CO_2 captured.

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Kulkarni and Sholl, *Ind. Eng. Chem. Res*. **2012**, 51, 8631.

Technical, Political and Societal Challenges:

- Technically, air capture is feasible. Net CO_2 removal from atmosphere.

- Economics are not well-established. Estimates vary widely:

  -- No published economic estimates exist from the core businesses themselves.

  -- Public, 3rd party cost estimates: ca. \$100 - \$1000+ / ton CO_2

- **Long-term pilot data are needed to allow for accurate projections of capital and operating costs**

How do we get these data?

Technical, Political and Societal Challenges:

- Funding challenges:

  -- total federal funding for traditional CCS[1]: $6B+

  -- total federal funding for air capture: <$300K (20,000x)

  -- thus, essentially all investment is private.

- Private investment requires a profit motive.

  -- greenhouses/algae farms (small scale, small payoff / significant risk, long time horizon)

  -- CO_2 as carbon source for fuels/chemicals (fuel = VERY long term, chemicals = VERY small scale)

1. CRS Report for Congress, Carbon Capture and Sequestration: Research, Development, and Demonstration at the U.S. Department of Energy, April, 2012.

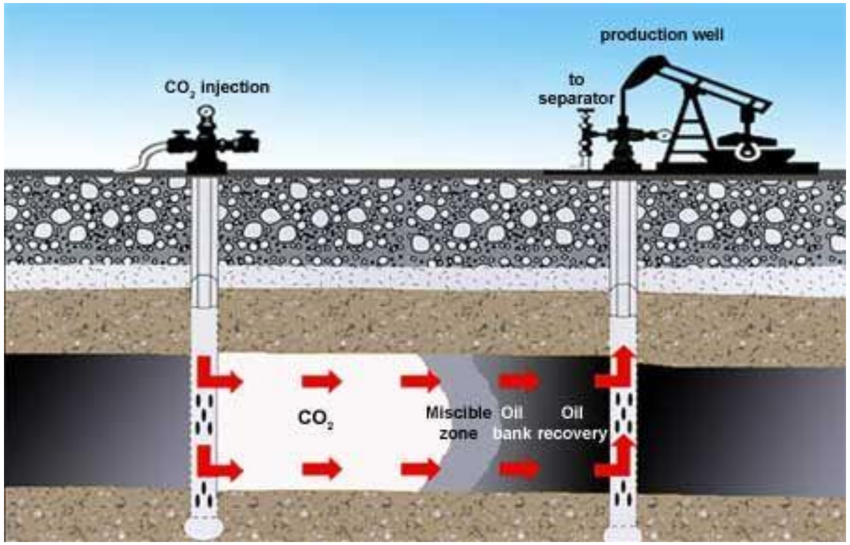
Technical, Political and Societal Challenges:

- Private investment requires a profit motive.

-- enhanced oil recovery (EOR)

-- inject compressed CO_2 to allow for removal of additional oil

-- initial demonstration projects likely here (in parallel with traditional CCS)



-- may cause a fundamental shift in air capture proponents and detractors

Climate protection (original intent of technology) = environmentalists

Oil extraction (most-likely demonstration mode) = fossil energy interests

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Technical, Political and Societal Challenges:

Path forward for air capture:

Short term (2012-2015)

1. Operate pilot processes; obtain data needed for accurate cost projections – private financing

2. Implement processes, likely for EOR, generating additional anthropogenic CO_2

3. Use experience to move along learning curve, refine process, reduce costs

Medium term (2020+)

4. Couple with conventional CCS to reduce CO_2 emissions and possibly remove CO_2 from atmosphere on a large scale.

Summary:

- Direct capture of CO_2 from air is technically feasible.
- Very early in technology development = major advances still possible/probable.
- Long-term sorbent stability is key to clarifying economics.
- Lack of federal investment, initial implementations likely for EOR – will actually produce MORE CO_2.
- Medium term: implementation along with traditional CCS for climate change mitigation.

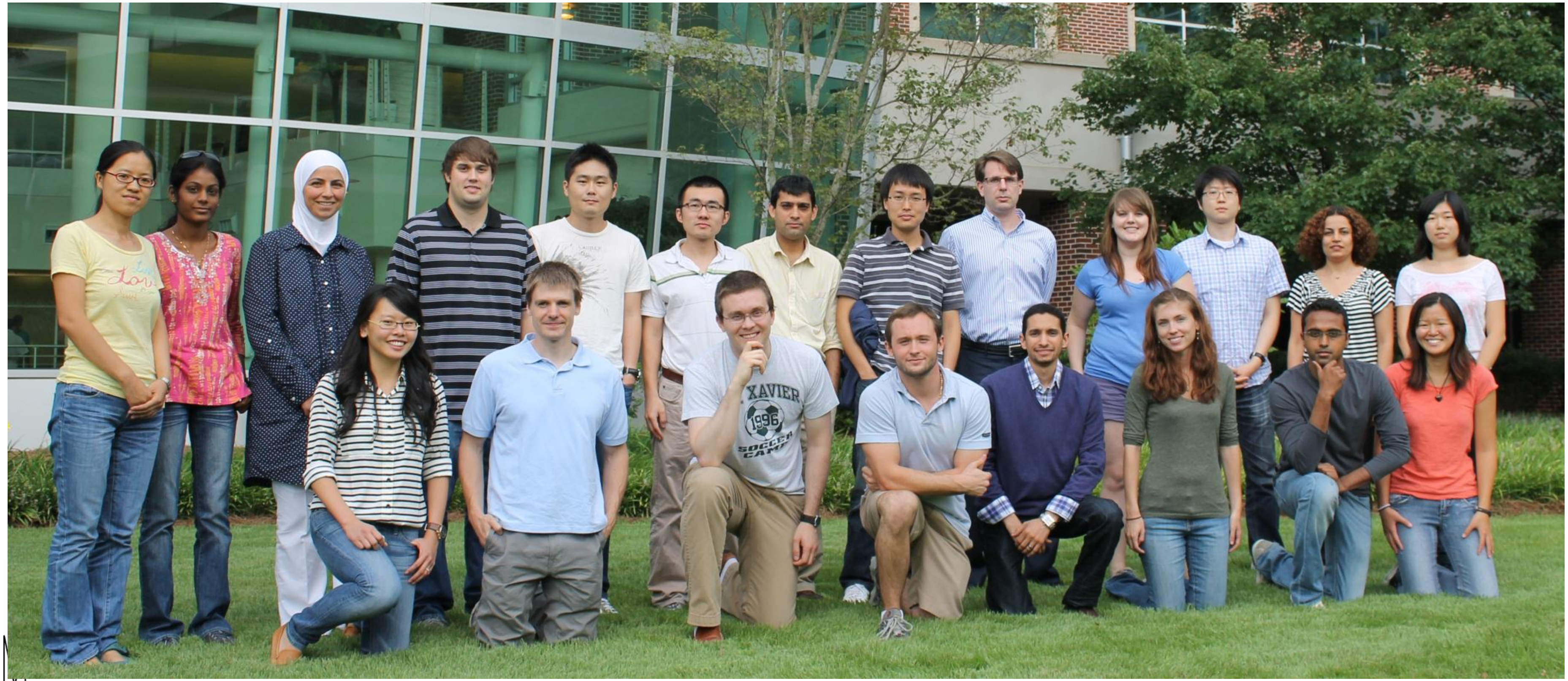
Thanks to:

CO$_2$ Separation Collaborators

Prof. Bill Koros (GT)
Dr. Ron Chance (GT)
Mac Gray (NETL)
Prof. David Sholl (GT)

Dr. Ryan Lively (GT)
Dr. Peter Eisenberger (Global Thermostat)
Dr. William Addiego (Corning)
Prof. Matthew Realff (GT)

Note: Jones has a financial interest in Global Thermostat, LLC



Research Support: CO_2 Capture

CORNING

global thermostat
a carbon negative solution

NETL

GE Energy

The Camille & Henry Dreyfus Foundation, Inc.

Also thanked for financial support:

Dow

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Q & A

Why Not On-Board CO_2 Capture from Cars?

Two Cars:	2012 Cadillac CTS-V Wagon		2013 Chevrolet Cruze Eco
MPG:	19 mpg		42 mpg
Curb Weight:	4396 lbs		3011 lbs
Fuel:	18 gal	(gasoline w/10% ethanol)	12.6 gal
CO_2/tank:	318 lbs		223 lbs

Large capacity sorbent (CaO): 0.79 lbs CO_2 / lb sorbent

Sorbent required*:	402 lbs sorbent 9% wt. car	282 lbs sorbent 9% wt. car

* if sorbent "canister" changed at every fill-up

Land Area for Air Capture

- One commercial GT unit captures 2000 ton / yr and covers an area of 5 m x 2 m.
- Increase by a factor of two for additional piping, etc.:
  $0.01\ m^2$ / ton – yr large coal plant (50K ton/day) = $0.18\ km^2$
- Installation would be long and thin:

Carbon Engineering

Global Thermostat

Literature Review:

• Choi et al. *ChemSusChem* **2009**, 2, 796.

Chemisorbants

-High ΔH_{ads}

-Steep isotherm

-Strong binding

-- *amines*

-- *CaO*

--*hydrotalcites*

Physisorbants

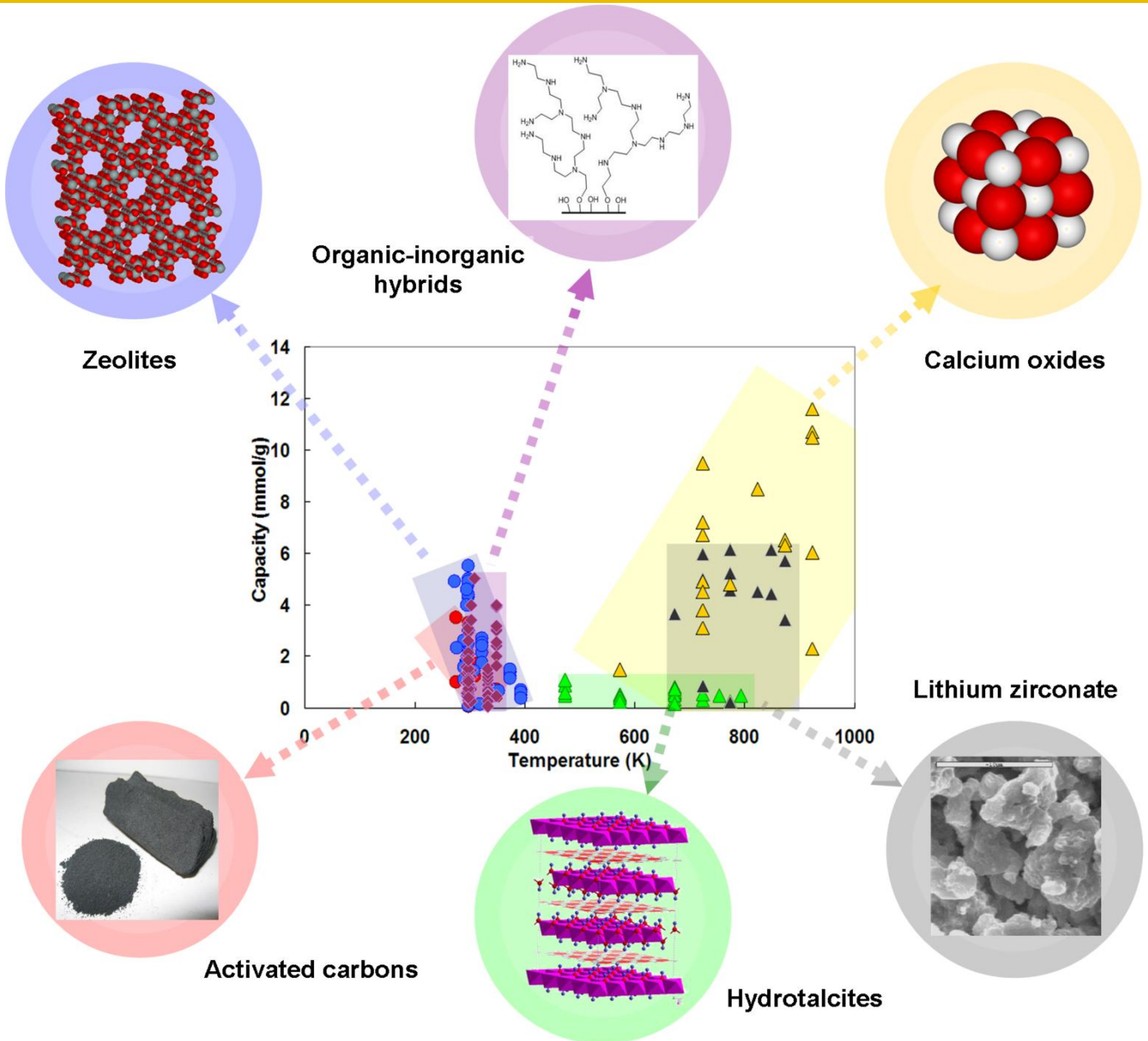
-Low ΔH_{ads}

-Shallow isotherm

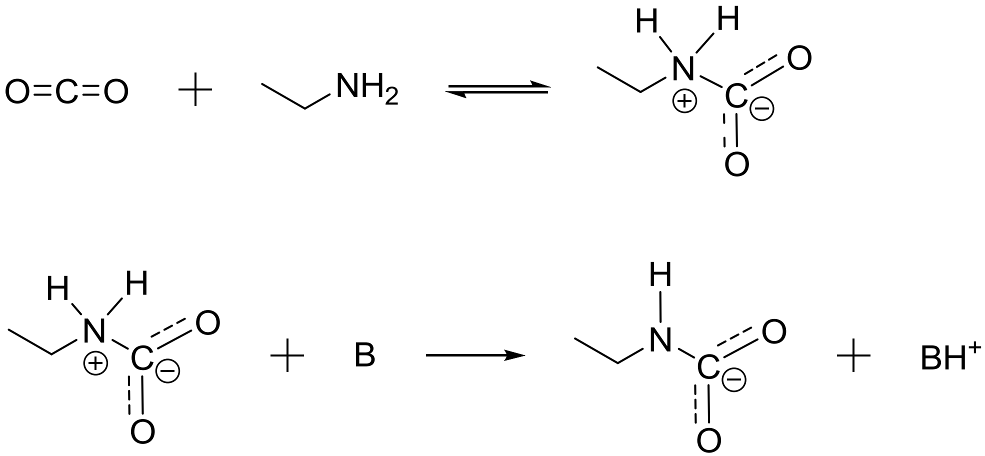
-Weak binding

--*zeolites*

--*carbons*



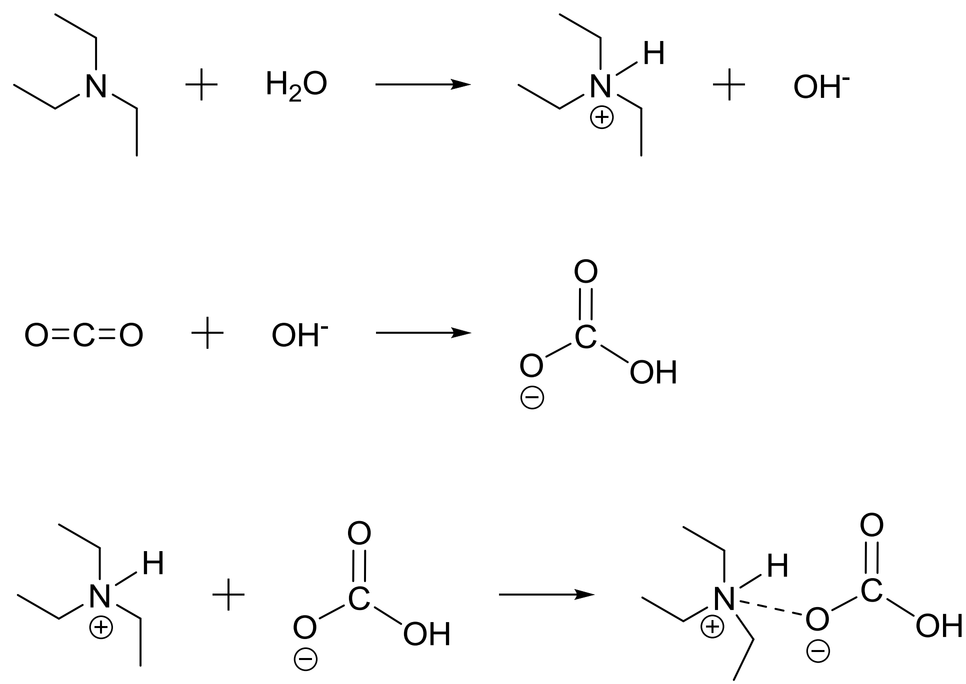
CO_2 Capture with Amines:



Reaction scheme for carbamate formation by reaction of CO_2 with primary or secondary amines.

-- capture with tertiary amines:
  wet – 1:1 N:CO_2 possible
  dry – does not occur

Mechanism for the reaction of CO_2 with tertiary amines, forming bicarbonate.



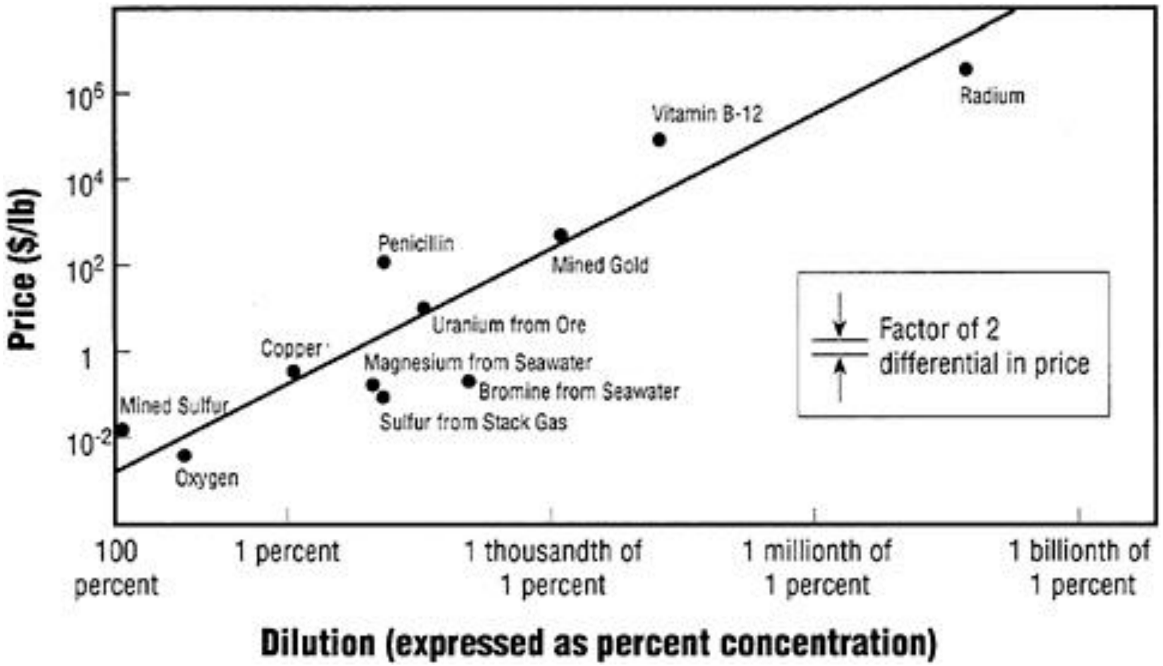
-- capture with primary or secondary amines:
  wet – 1:1 N:CO_2 possible
  dry – 2:1 N:CO_2 possible

Air Capture Conclusions:

- Economic viability of large scale air capture still under evaluation. Depends on application: environmental protection vs. CO_2 utilization.
- *American Physical Society* study concluded air capture is too expensive for environmental protection applications, but report only considers one (poorly designed) process.

http://www.aps.org/policy/reports/popa-reports/loader.cfm?csModule=security/getfile&PageID=244407

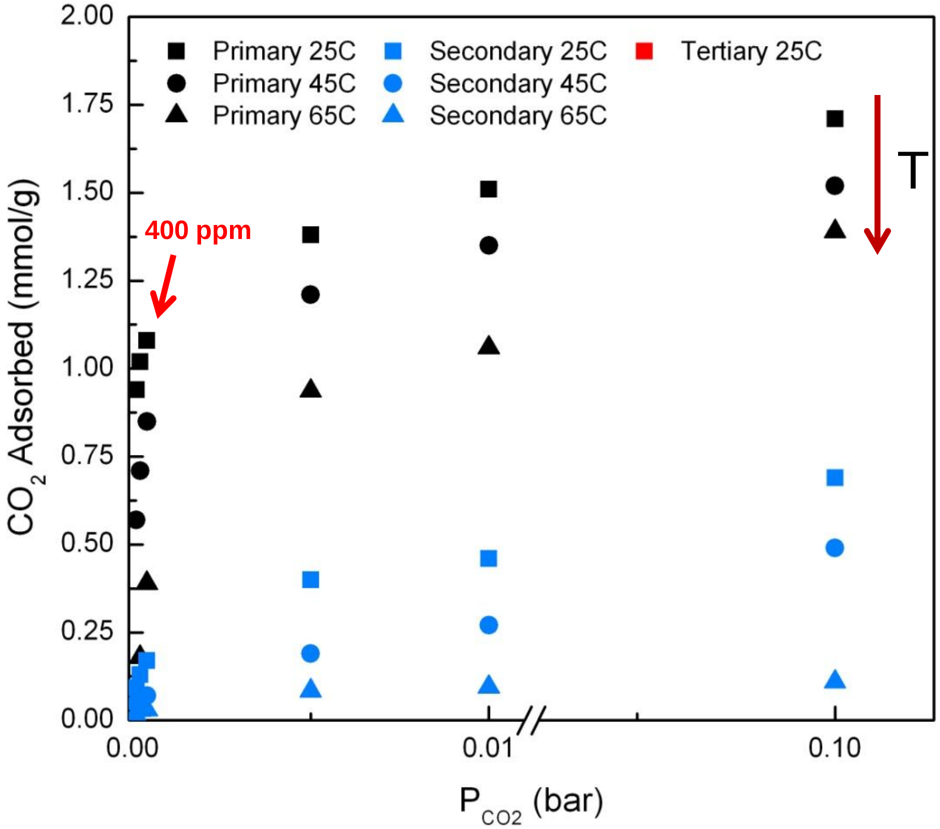
The Greening of Industrial Ecosystems
(1994)
National Academy of Engineering (NAE)

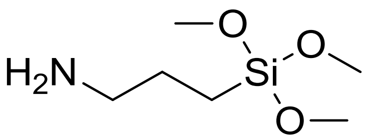


Effect of Amine Type - Air Capture:

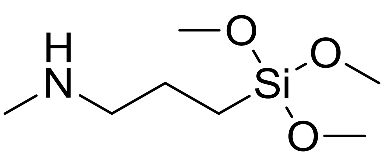
Can supported amine materials be effective “air capture” sorbents?

Yes! If based on primary amines.

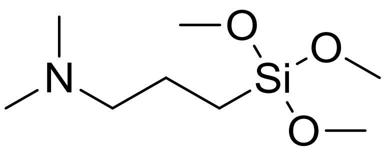




Primary



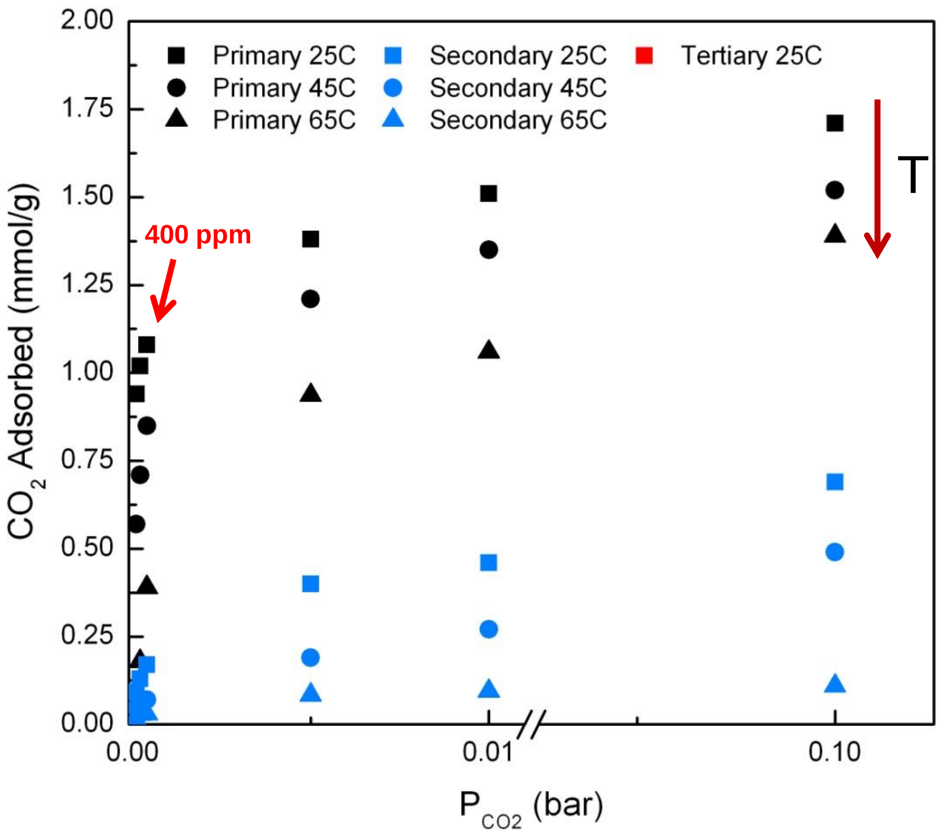
Secondary



Tertiary

Effect of Amine Type - Air Capture:

Competitive Amine Efficiencies



Amine Efficiency at 25 °C

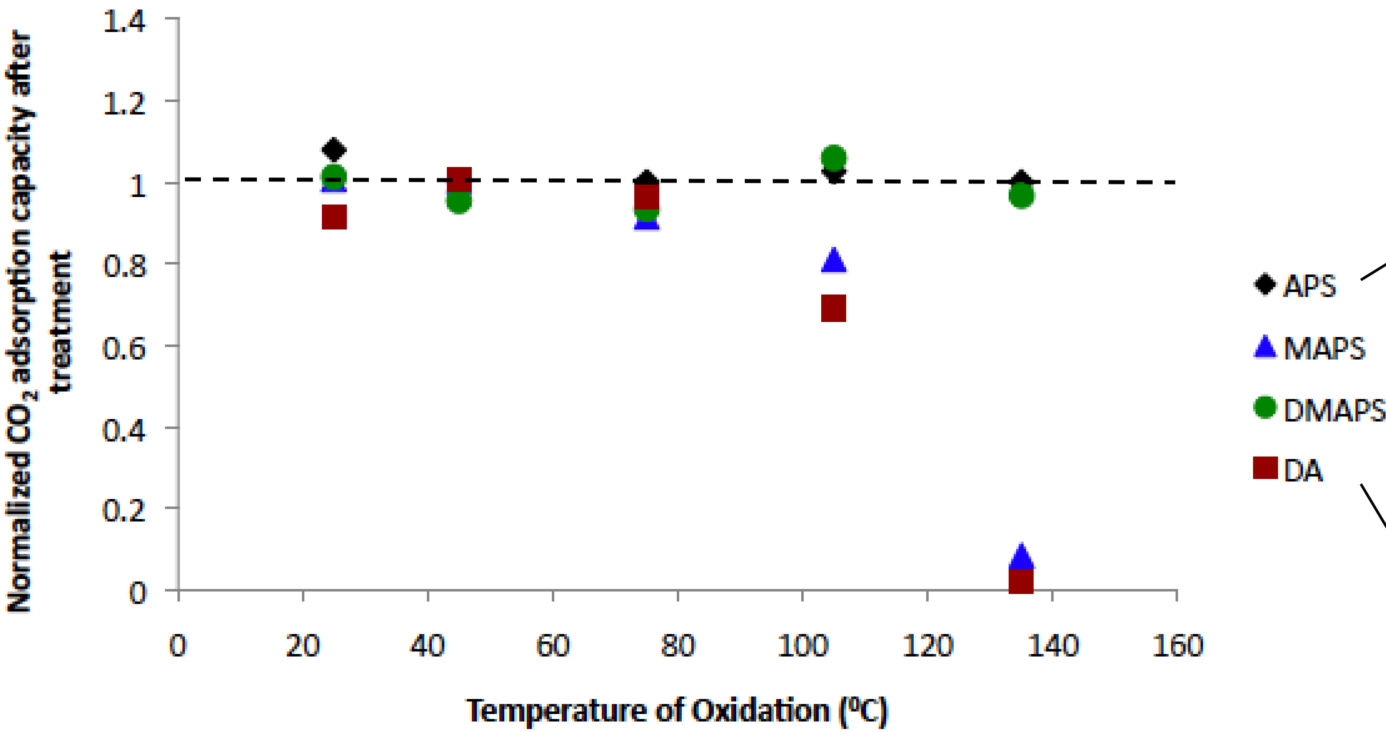
P_{CO2} (bar)	Amine efficiency ($mmol\ CO_2/mmol\ N$) Primary	Secondary
1.1×10^{-4}	0.25	0.04
2.2×10^{-4}	0.27	0.05
4×10^{-4}	0.29	0.07
0.005	0.37	0.17
0.01	0.4	0.19
0.1	0.46	0.29

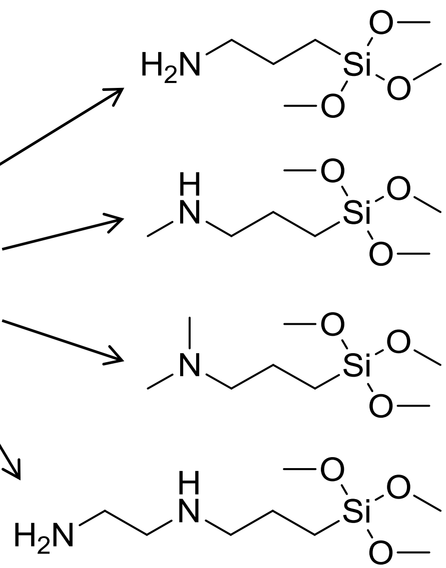
Heat of adsorption: Toth isotherm fit

Amine Type	$-\Delta H_{ads}$ (kJ/mol)
Primary	72
Secondary	56

Georgia Institute of Technology
School of Chemical & Biomolecular Engineering

Amine Adsorbents Stability to Oxidation:





- Measure CO_2 capacity
- Exposure to 100% O_2 for 24 hr.
- Measure CO_2 capacity again

-- all sorbents oxidation resistant below ca. 80 ˚C

-- primary aminopropyl groups (primary amines are best for air capture) stable at all temperatures!

Air Capture Conclusions:

- Air capture may allow for feeding CO_2 to biomass for biofuel production (low concentration) or eventually, CO_2 production for sale or sequestration.

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Algae-based Biofuels:

-- algae use CO_2 as a nutrient via photosynthesis

-- algae are being engineered to produce hydrocarbons suitable for *<u>Diesel fuel</u>* use as well as *<u>ethanol</u>*.

Photo from Popular Mechanics: http://www.popularmechanics.com/science/earth/4213775.html

The Bruce Mansfield Power Plant:

- 2360 MW electric power generation capacity.
- 7 million tons coal burned/year.
- ~41% efficiency.
- 17.5 million tonnes CO_2 generated per year.
- 47,800 tonnes/day CO_2 formed (at ~15% vol concentration).
- 220,000 tonnes flue gas processed per day.

• The yearly output fits in a 400m cube at sequestration pressures (140 atm).

Slide courtesy of Prof. John Kitchin, Carnegie Mellon University.

Post-Combustion Capture Conditions Separation of CO_2:

- Flue gas composition after sulfur scrubbing
  - 13-16% CO_2
  - 4-5% O_2
  - 6-7% H_2O
  - Minor impurities
  - Balance N_2
- Flue gas conditions
  - 60-80°C
  - 10-15 psi
- Flue gas production rate
  - A 2500 MW coal plant produces **~550 kg CO_2/s**
  - ~240,000 tons/day of flue gas must be treated
- Capture goal
  - 1200-2000 psi, dry CO_2 for pipeline ready transport

Point Source Capture vs. "Air Capture":

CO_2 Source Properties: Air/Point Source Exhaust

Property	Air	Flue
Amount of CO_2	3 teratonnes	20 gigatonnes/yr
Distribution	400 ppm - "infinite" mostly uniform source	5-15% point sources 10% - 250x more conc. vs. air
Temperature	10-30 °C	45-65 °C
Contaminants	Low levels of contaminants	High levels of SOx NOx , particulates
Movement	wind, fans	fans

Technical, Political and Societal Challenges:

- Technically, air capture is feasible. Net CO_2 removal from atmosphere.
- Economics are not well-established. Estimates vary widely:

-- American Physical Society report: http://www.aps.org

-- studied first generation process (known not to work)
-- estimated cost, \$600/ton CO_2

-- House et al. *Proc. Nat. Acad. Sci*. **2011**, 108, 20428.

-- estimate air capture costs by extrapolating costs of other trace component purification processes.
-- >\$1000/ton CO_2

-- Kulkarni and Sholl, *Ind. Eng. Chem. Res*. **2012**, 51, 8631.

-- estimated air capture operating costs for amine-monolith-steam process
-- ca. \$100/ton CO_2, depending on location