Regenerable polyamine based solid adsorbents for CO_2 capture from the air

Alain Goeppert

Loker Hydrocarbon Research Institute
and
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661

Air Capture and its Application in Closing the Carbon Cycle
Lenfest Center for Sustainable Energy
Earth Institute, Columbia University
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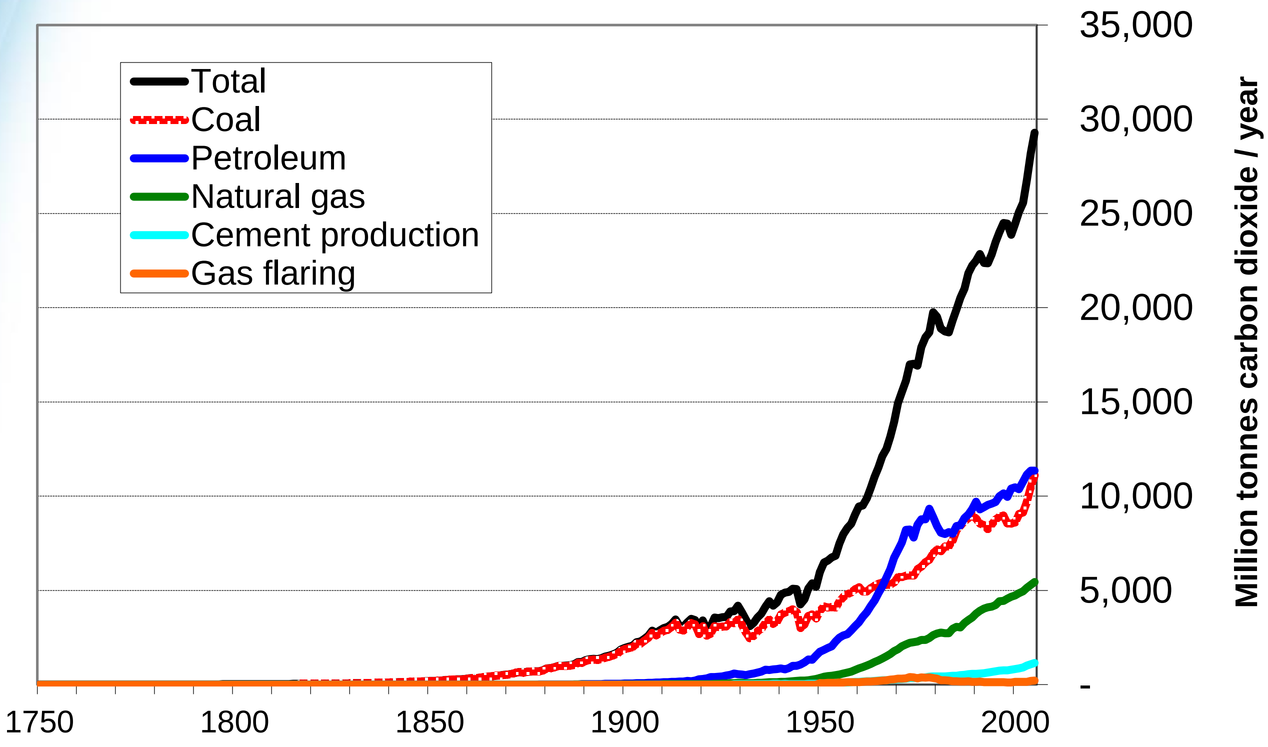
Annual Global CO_2 Emissions- 1750-2005

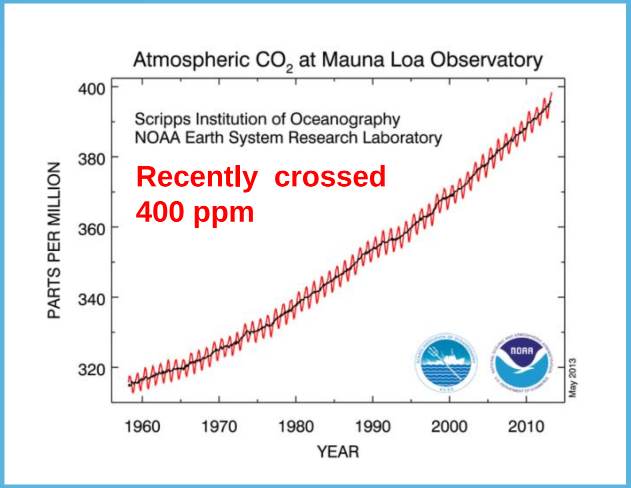


More than 30 billion tonnes of CO_2 per year released into the atmosphere!

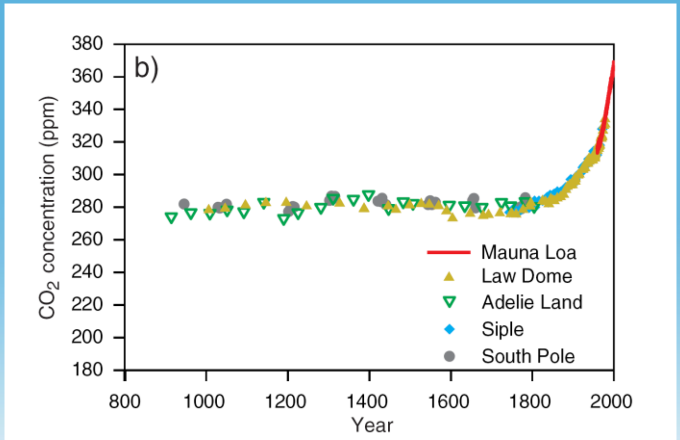
About half the CO_2 emissions accumulate in the atmosphere

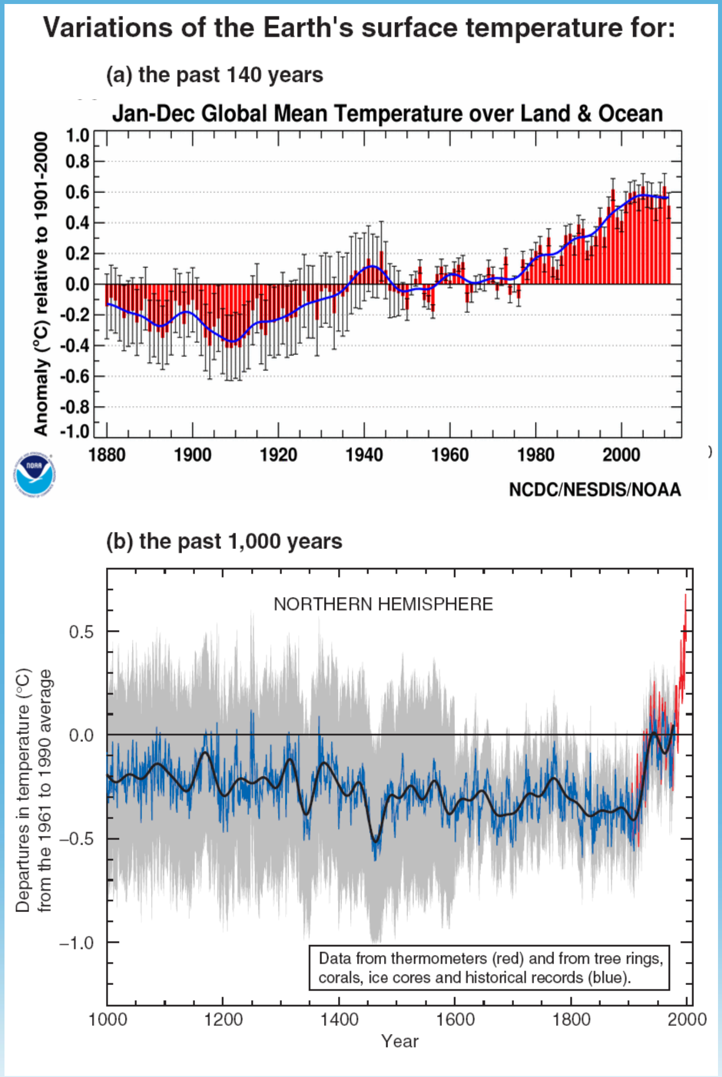
Presently around 15 billion tonnes per year

CO_2 concentration in the atmosphere and climate change



Atmospheric CO_2 concentration measured at Mauna Loa, Hawaii
Keeling Curve





Source: IPCC

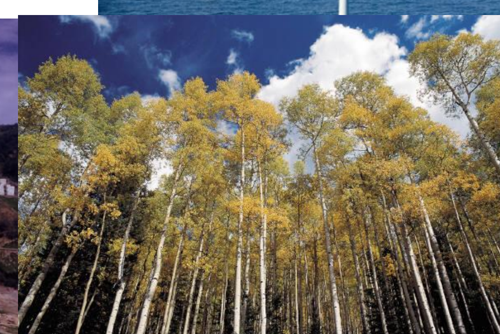
Alternative Energies?

Hydropower
Geothermal energy
Wind energy
Solar energy
Biomass
Ocean energy (waves, tides, thermal)
Nuclear energy

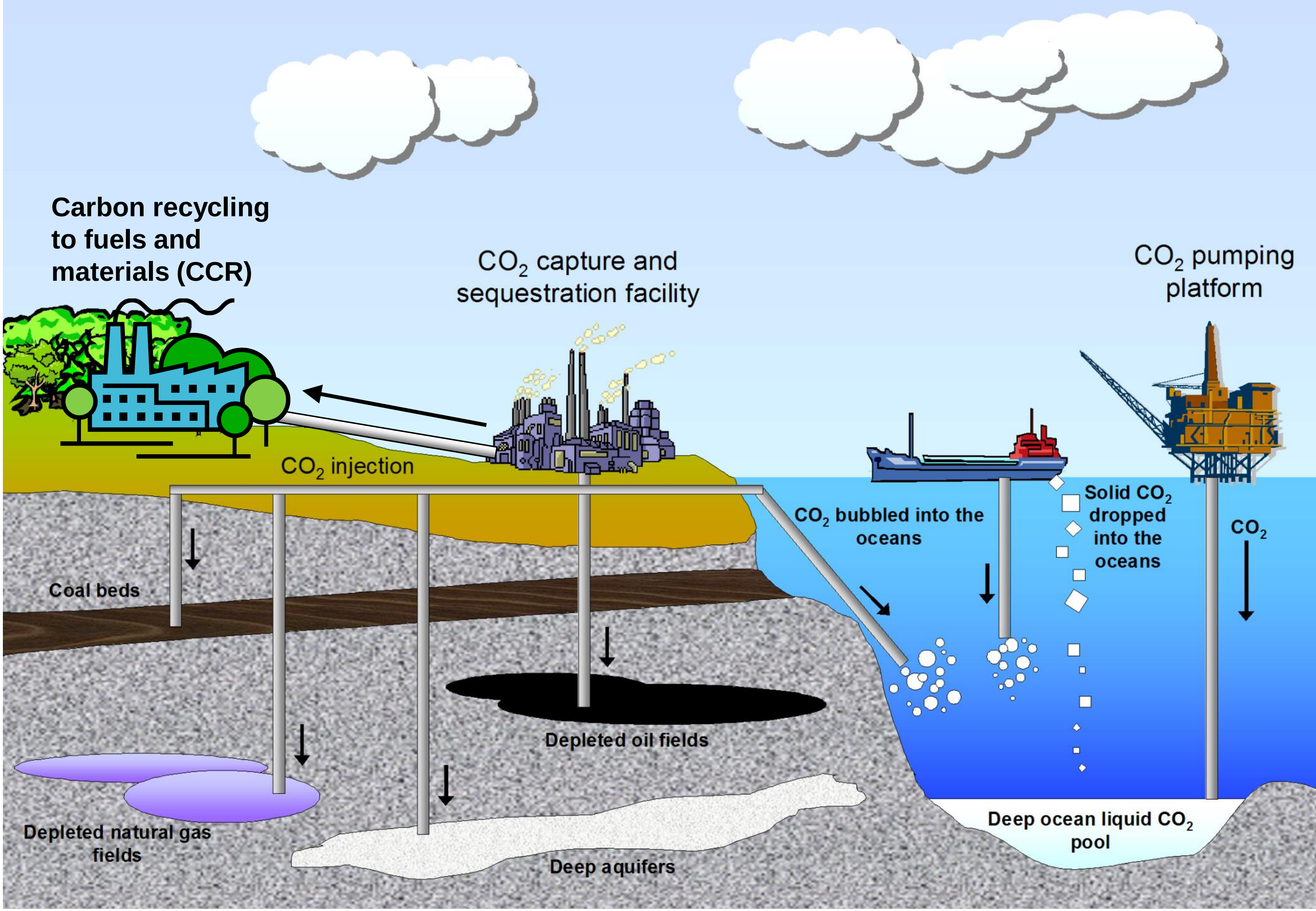



Why don’t we use more alternative energies?
- Mainly a problem of cost
- Fossil fuels are still the biggest bargain
- Most renewable energies are intermittent
-They produce mostly electricity
- Difficult to store
(storage in the form of Hydrogen, methanol, etc)





Carbon capture and sequestration (CCS)



Sources of CO_2

- Geothermal Vents
- Fermentation Processes
- Natural Gas Wells
- Cement Plants
- Fossil Fuel Burning Power Plants
- Aluminum Plants
- Air Itself

CO_2 separation and Capture technologies

- Absorption
  - Chemical
    - MEA, DEA
    - KOH, NaOH, MgO
    - Etc.
  - Physical
    - Solexol
    - Rectisol
    - Etc.
- Adsorption
  - Alumina
  - Zeolite
  - Activated carbon
- Cryogenics
  - Dry ice formation at low temperature
- Membranes
  - Polymer based
    - Poly(phenylene oxide)
    - Poly(ethylene oxide)
    - Poly(ionic liquid)
  - Inorganic membranes
    - Ceramic based
    - Zeolite based
- Algal and microbial systems

Regeneration method

- Pressure swing
- Temperature swing
- Moisture swing
- And combination thereof

Not well suited for CO_2 capture from the air

Efficient capture from the air is considered challenging

Why capture CO_2 from the air?




Important to address ~ 50% of anthropogenic CO_2 emissions from small distributed sources such as home and office heating and cooling and the transportation sector

Collection of CO_2 from billions of small fossil fuel burning units at the source is difficult and not practical and/or economical

Direct air capture (DAC) of CO_2 would allow the collection of CO_2 from any source, small or large, static or mobile.

Independence from CO_2 point source means the capture unit could be placed anywhere, offering considerable flexibility

Lower concentration of contaminants such as NO_x, SO_x and particulates in air compared to flue gases

Eventually, DAC could even be used to lower atmospheric CO_2 concentrations

Nature does it. Why not us?

CO_2 fixation by photosynthesis (carbon neutral)

$$nCO_2 + nH_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} n(CH_2O) + nO_2$$

Biofuels – ethanol, butanol, vegetable oils (biodiesel) – a small % of the energy mix

→ Biomass will be able to fulfill at most 10-15% of energy needs in a sustainable way

- Land availability and use
- Water resources - Irrigation
- Food security vs Energy security
- Fertilizer use (nitrogen fertilizers from NH_3 (synthetic N_2 + H_2, Haber Bosch process)
- Processing technologies, energy use
- Overall energy balance (life cycle analysis)

Sun is the source of most energy on Earth- **past, present and future**
~130,000 TW continuous- A reliable nuclear fusion reactor 150 million km away!

Thermodynamics of CO_2 capture from the air

Minimum thermodynamic energy to extract CO_2 from the air is relatively low at ~ 20 kJ/mol (1.6 GJ/tCO_2) at RT

$$RT \ln (P/P_0)$$

P_0: partial pressure in air 0.0004 Atm
P: final pressure of CO_2 in the enriched gas (ideally 1 Atm or higher)
R is the ideal gas constant (8.3 $J.mol^{-1}.K^{-1}$)

Energy required grows only logarithmically with dilution

CO_2 concentration in air 0.04%
CO_2 concentration in flue gas ~10%

~ 250 x lower

Theoretically CO_2 capture from air would require only 2 to 4 times energy as capture from flue gases

Actual energy needed for the entire system is of course much higher

From a thermodynamic point of view DAC should not be a problem

CO_2 capture from the air

Current and future applications:

- Removal of CO_2 in closed environment such as submarines and spacecrafts
- Production of CO_2 free air for alkaline fuel cells and batteries
- Capture of CO_2 for sequestration and recycling to fuels and materials

Unit for CO_2 removal in the space station currently undergoing tests (source: NASA)

Technologies for CO_2 capture from the air

Based on chemisorbents

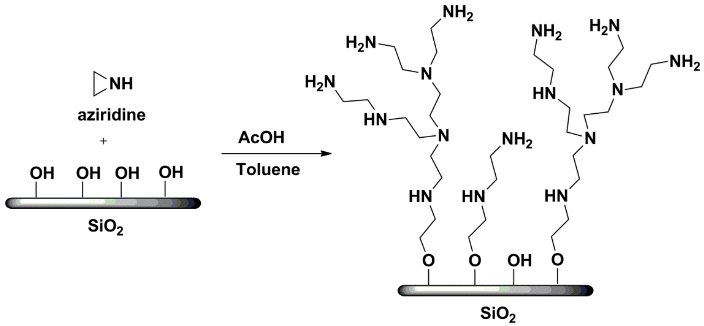
- **Inorganic chemisorbents**

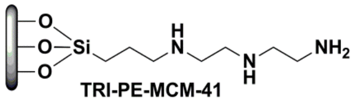
NaOH, LiOH, KOH, $Ca(OH)_2$, K_2CO_3

$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$$

- **Organic or hybrid chemisorbent materials**

Physically adsorbed amines and polyamines, immobilized amine and polyamines, Hyperbranched aminosilicas, anionic exchange resins



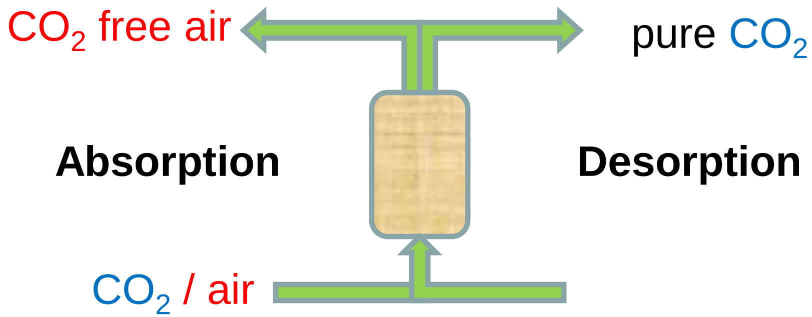


PEI impregnated on polymethylmethacrylate, SBA-15, alumina, silica, carbon fibers, etc…

Adsorption/desorption cycle of the absorbents

Absorption/desorption of CO_2 are two mirror reactions

Absorption	$A + CO_2 \rightarrow ACO_2$	exothermic (releases energy)
Desorption	$ACO_2 \rightarrow A + CO_2$	endothermic (needs energy)



Heat, vacuum, other means of desorption

Regeneration of the sorbents is the energy demanding step

Inorganic sorbents bind CO_2 strongly
In most cases they require high temperatures for the regeneration step (700-900 °C) but are relatively stable over numerous absorption/desorption cycles

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)} \qquad \triangle H^0 = +179.2 \text{ kJ/mol}$$

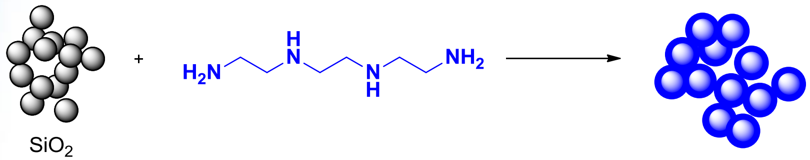
⇒ High energy demand for the regeneration step

Supported organoamine hybrid adsorbents

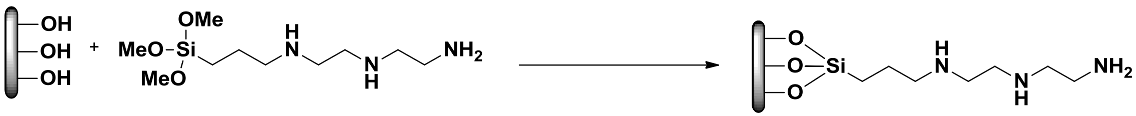
Bind CO_2 less strongly and require less harsh conditions for regeneration, such as lower temperatures (80-200 °C)

Can be divided in 3 main categories depending on the type of interaction between support and active sorbent and mode of preparation

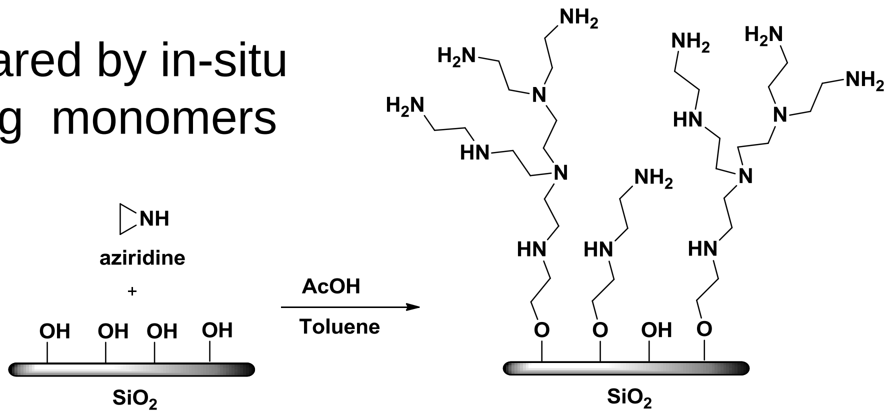
Class 1: Amine or polymeric amine physically adsorbed on the support material



Class 2: Amines immobilized (anchored) on the support



Class 3: Grafted Polyamine prepared by in-situ polymerization of amine containing monomers



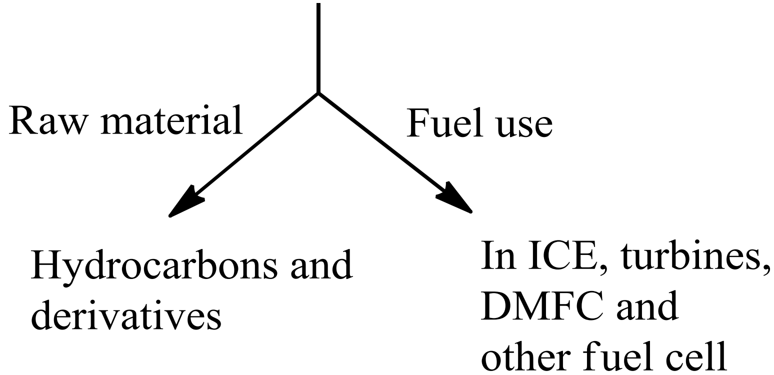
Work on CO_2 capture from the air at the Loker Hydrocarbon Research Institute

We decided to focus our effort on finding an easy to prepare, inexpensive but at the same time efficient adsorbent based on a Class 1 hybrid material

Interest for various reasons:

- Capture of CO_2 for recycling to fuels and materials such as methanol, DME, hydrocarbons (methanol economy)

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

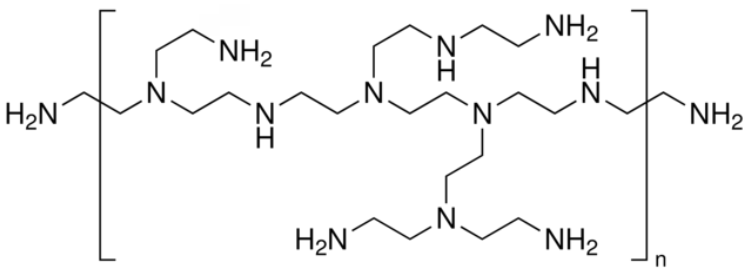


- Capture of CO_2 to produce CO_2 free air for use in iron/air batteries with an alkaline electrolyte (ARPA-e)

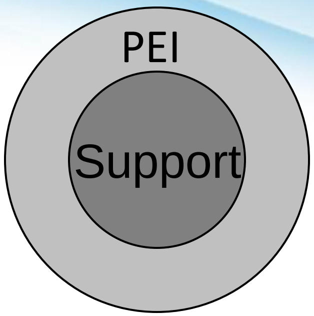
- Indoor air quality (reduce the amount of CO_2 in enclosed spaces)

Solid hybrid adsorbent preparation

Structure of branched polyethylenimine (PEI)



PEI (HMW)
Mw ca. 25000



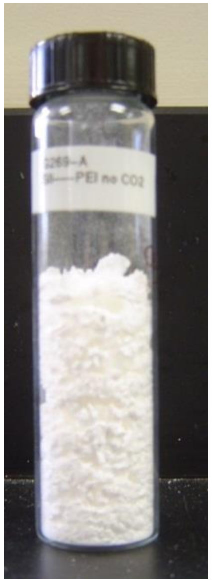
Solid support: fumed silica (300-380 m^2/g)

Prepared easily by

- Dissolving the polyamine in methanol and mixing the solution into a suspension of support in methanol.
- Evaporation of the solvent and drying.

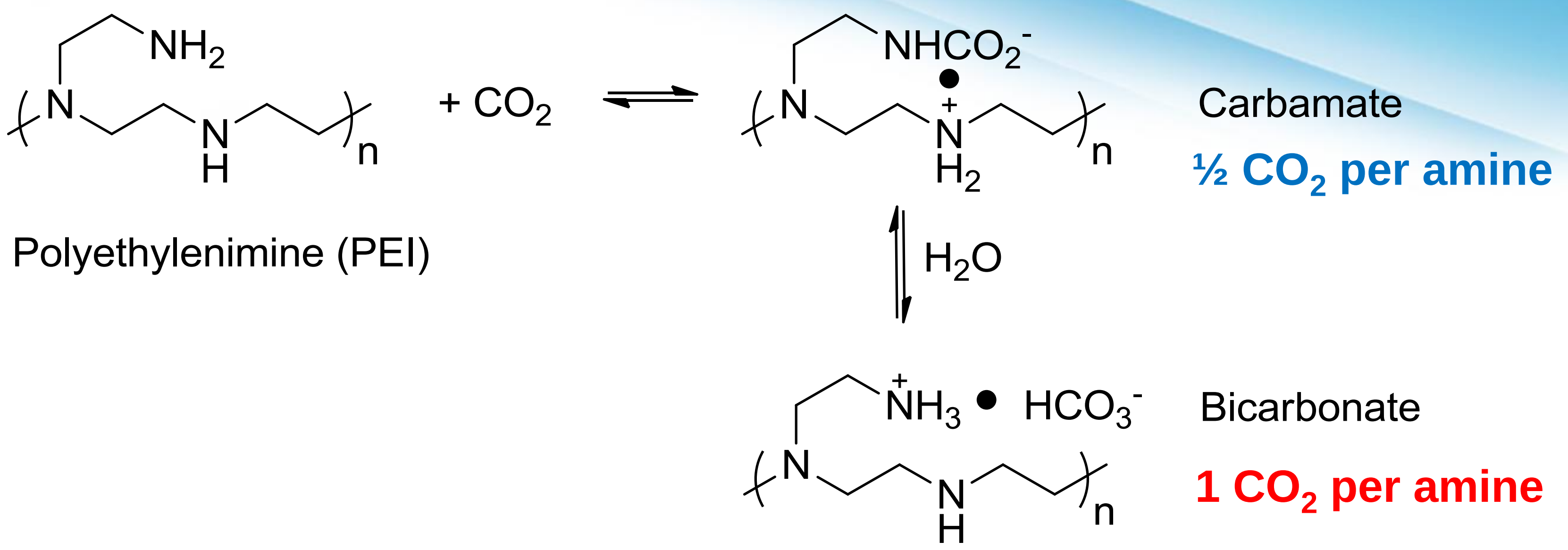
Adsorbent	PEI content
FS-PEI-50	50%
FS-PEI-33	33%
FS-PEI-25	25%
FS-PEI-20	20%

Can be prepared in very short time



Goeppert, A.; Meth, S.; Prakash, G. K. S.; Olah, G. A. *Energy Environ. Sci.* **2010**, *3*, 1949

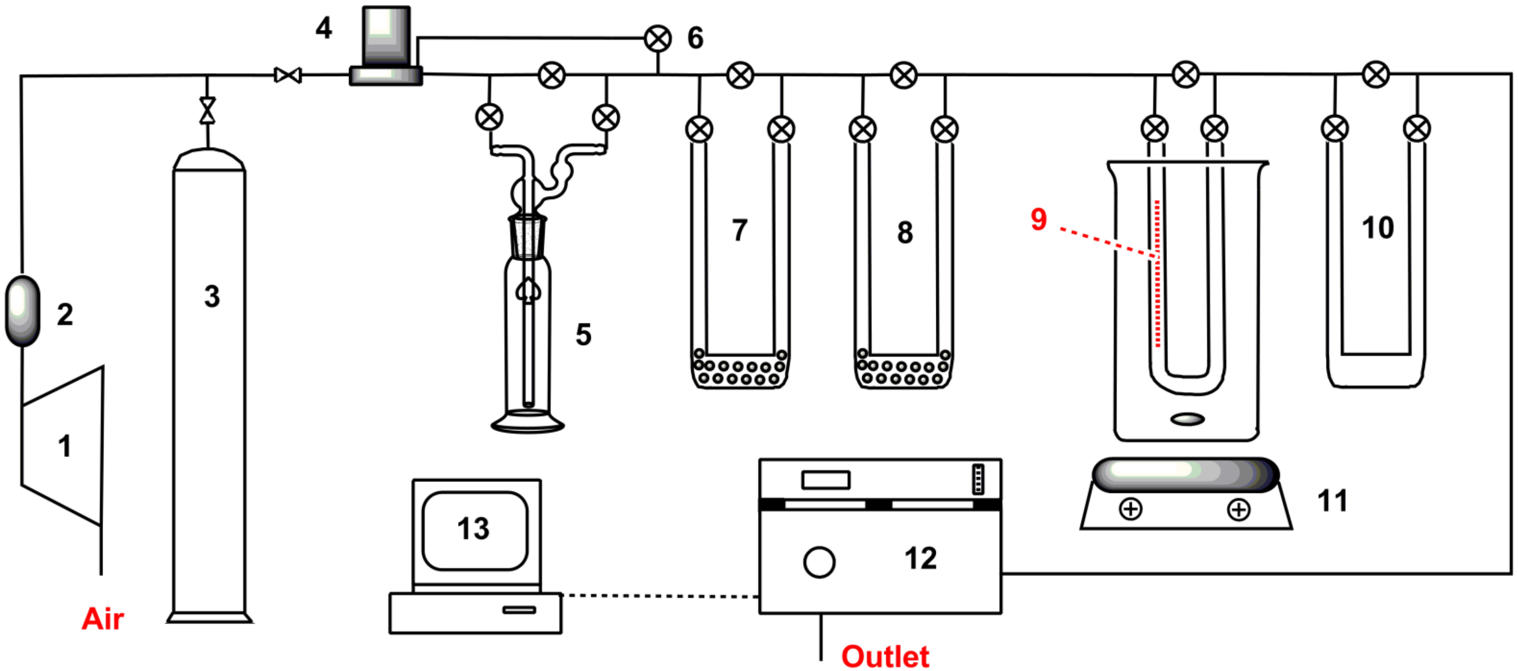
Reaction of polyethylenimine (PEI) with CO_2



Under dry conditions: carbamate formation. Two amino groups needed for each CO_2 molecule

Under humid conditions: bicarbonate formation. In theory only one amino group needed for each molecule of CO_2

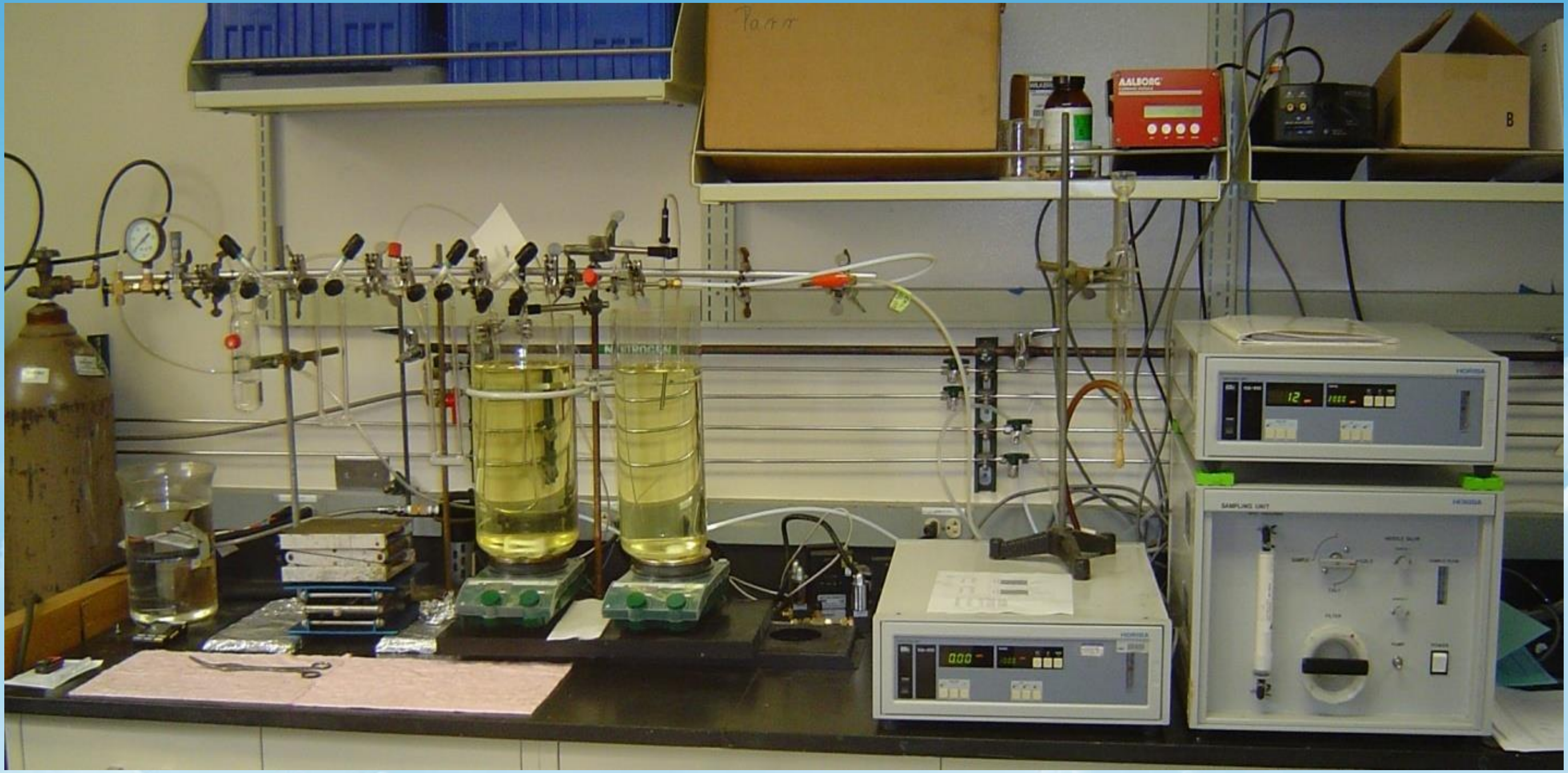
Setup and experimental procedure for CO_2 capture from the air



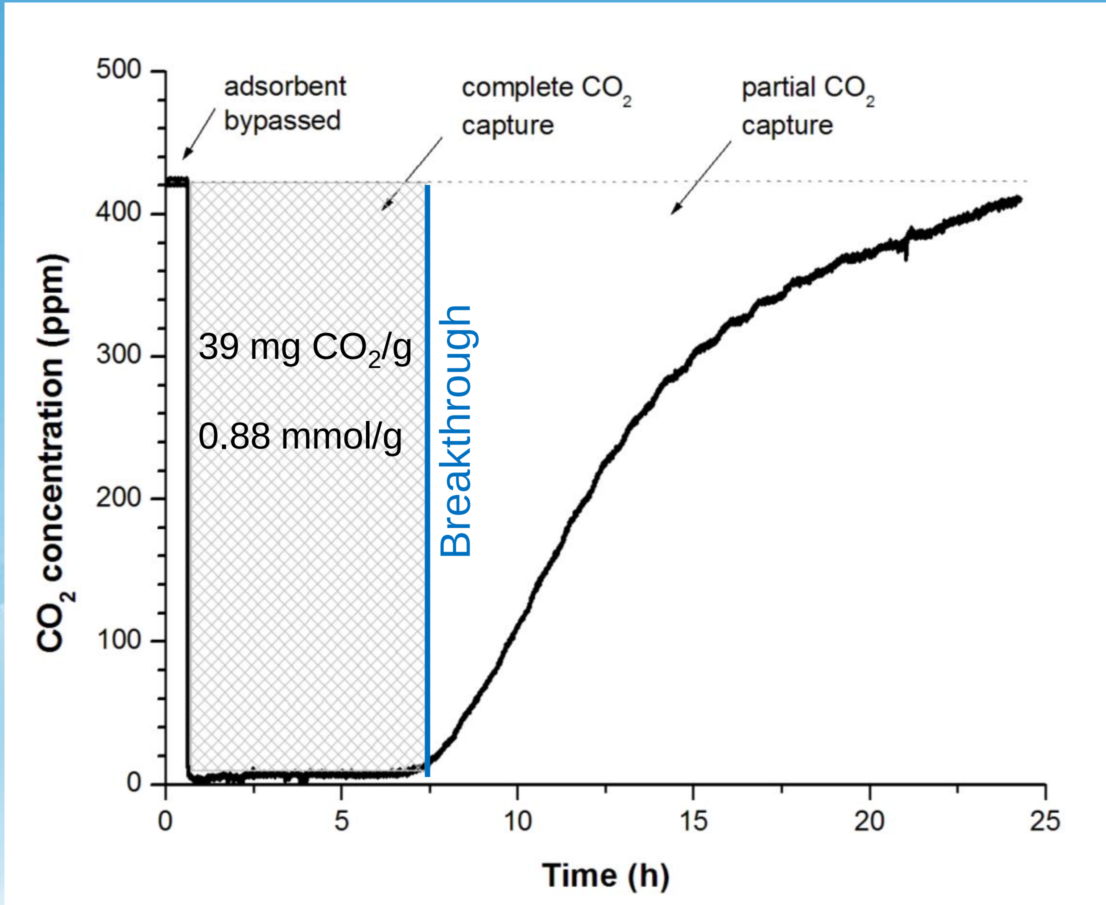
1	Compressor	8	Water droplet separator II
2	Air dryer (silica gel)	9	Adsorbent
3	Reservoir	10	Particle separator
4	Mass flow controller	11	Stirrer and oil bath
5	Humidifier	12	Horiba CO_2 analyzer
6	Dry air inlet	13	Computer
7	Water droplet separator I.		

CO_2 analyzer calibrated prior to each measurement

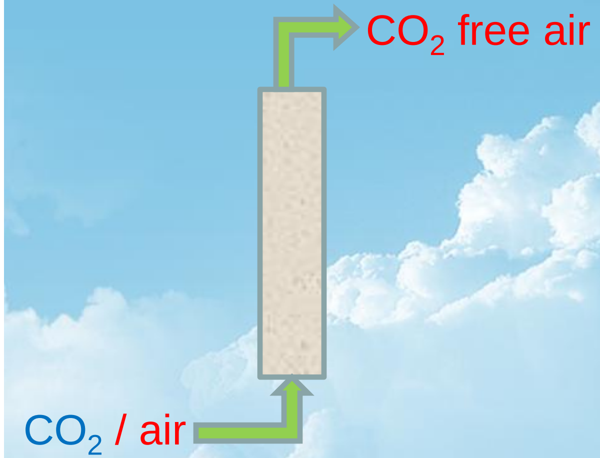
Bench-top test system for CO_2 adsorption experiments



Adsorption of CO_2 from the air at 25 ° C on FS-PEI-50



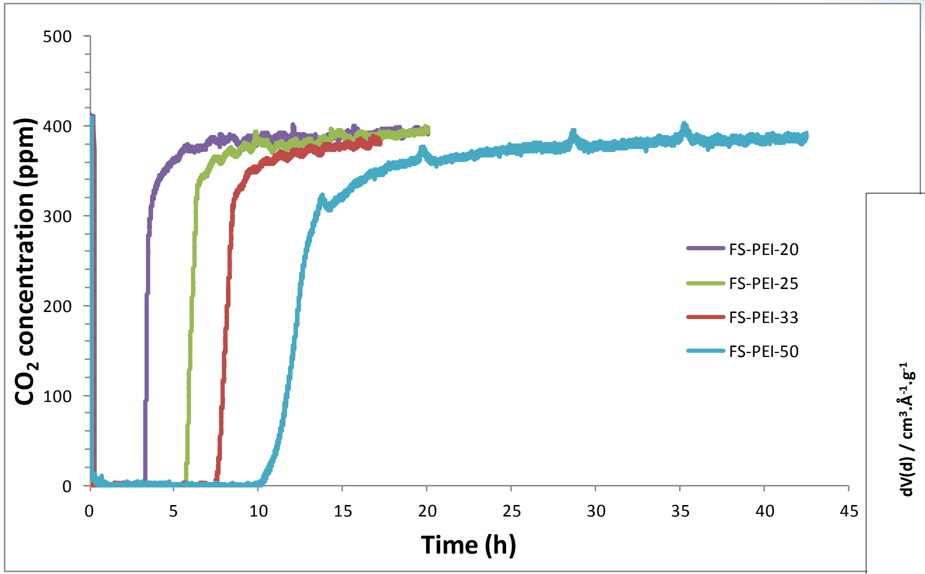
Total CO_2 adsorption:
75 mg/g
1.71 mmol/g

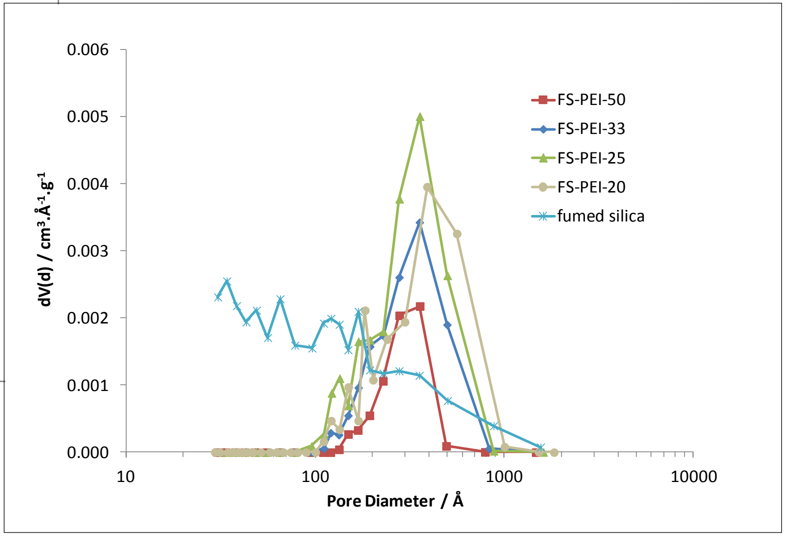


Amount of catalyst : 2.72 g
Flow rate: 335 mL/min air

Goeppert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. *J. Am. Chem. Soc*. **2011**, *133*, 20164

CO_2 Adsorption from the air on FS-PEI as a function of PEI loading

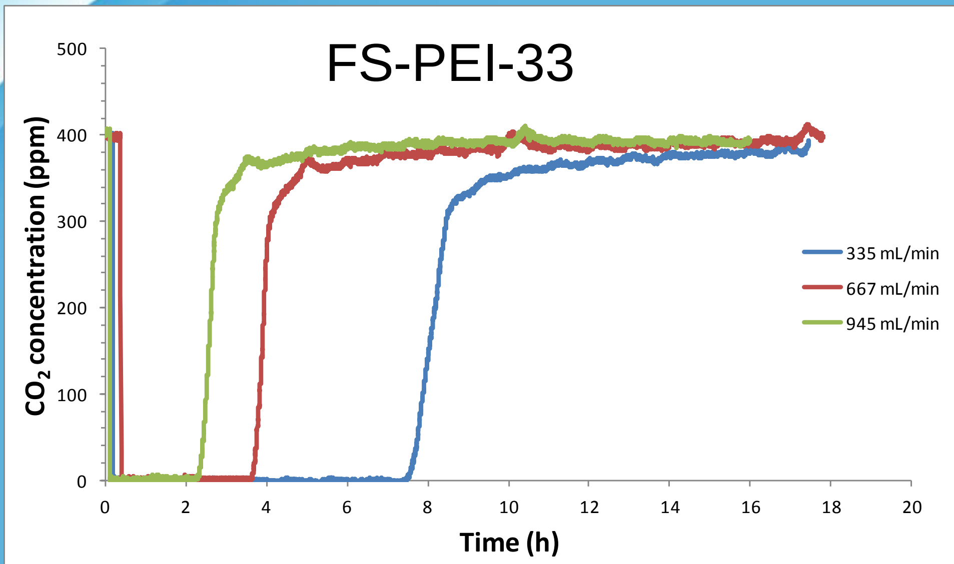




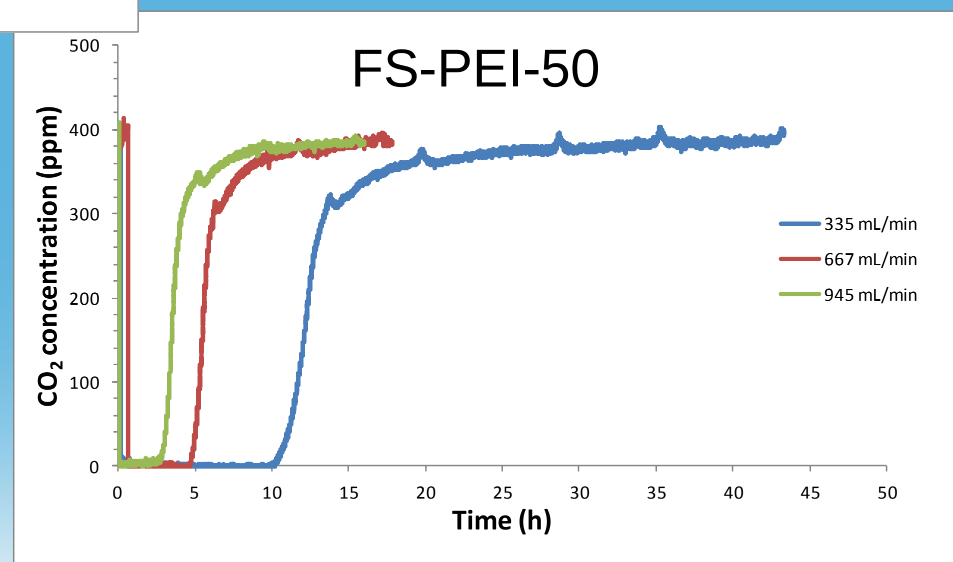
Better distribution of PEI and easier access to amino sites at lower PEI loadings

Adsorbent	Surface area (m^2/g)	Volume of pores (cm^3/g)	Total CO_2 adsorption from air (mg/g)	CO_2 adsorption from air under 10 ppm (mg/g)	Ratio adsorption under 10 ppm/total adsorption
FS-PEI-50	27.2	0.40	73.7	51.8	0.70
FS-PEI-33	79.9	1.06	50.0	40.8	0.82
FS-PEI-25	108	1.42	34.5	29.4	0.85
FS-PEI-20	114	1.49	16.8	15.8	0.94

CO_2 Adsorption from the air as a function of flow rate

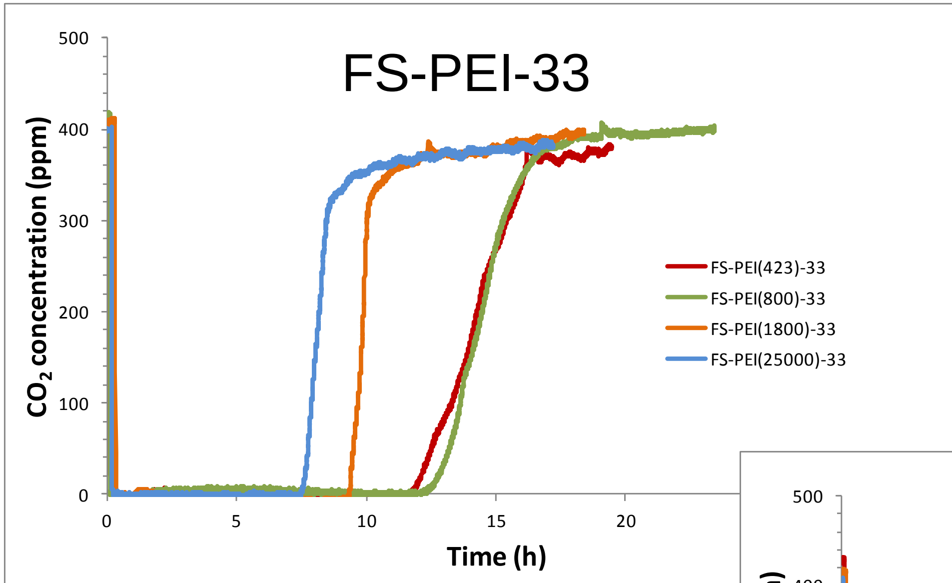


Flow rate (mL/min)	total CO_2 adsorption from air (mg/g)	CO_2 adsorption from air under 10 ppm(mg/g)	Ratio adsorption under 10 ppm/total adsorption
335	50	41	0.82
667	47	38.7	0.82
945	47	37.1	0.79



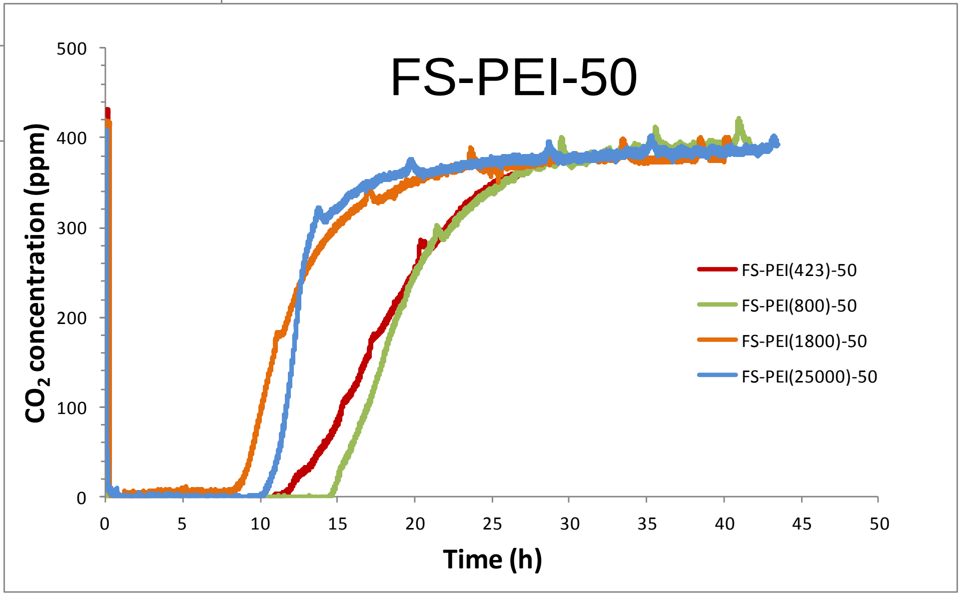
Flow rate (mL/min)	total CO_2 adsorption from air (mg/g)	CO_2 adsorption from air under 10 ppm(mg/g)	Ratio adsorption under 10 ppm/total adsorption
335	67.8	51.7	0.76
667	59.2	40.8	0.69
945	57.4	37.1	0.65

CO_2 Adsorption from the air as a function of the molecular weight of PEI



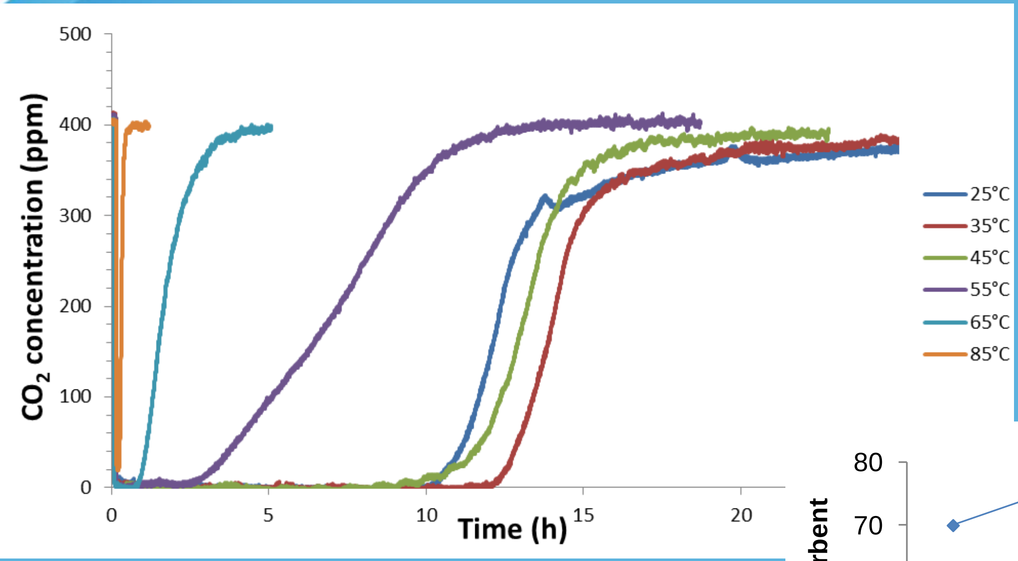
Adsorbent	total CO_2 adsorption from air (mg/g)	CO_2 adsorption from air under 10 ppm(mg/g)
FS-PEI(423)-33	71.9	59.8
FS-PEI(800)-33	74.7	62.7
FS-PEI(1800)-33	56	48
FS-PEI(25000)-33	50	40.8

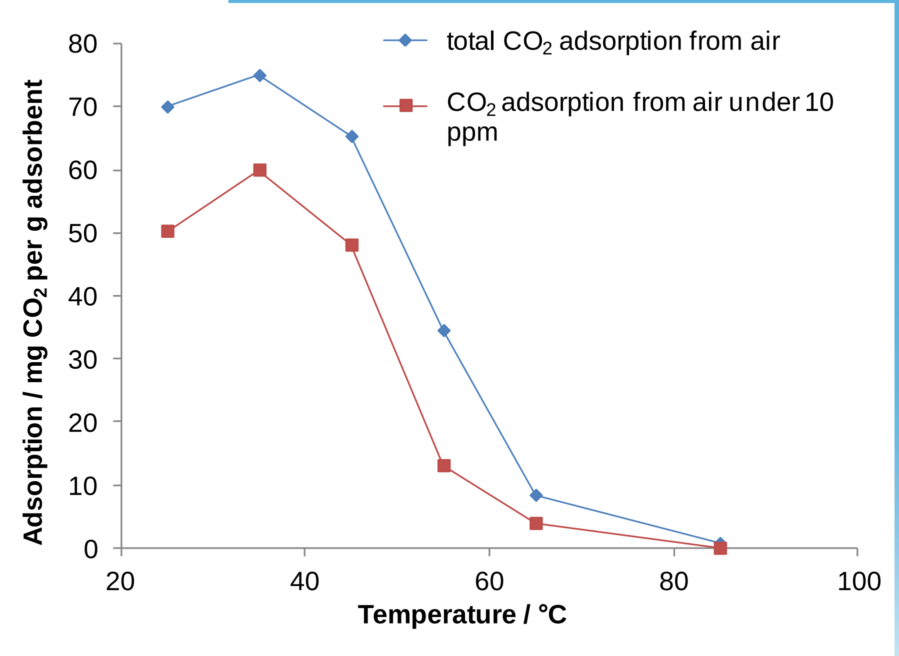
Adsorbent	total CO_2 adsorption from air (mg/g)	CO_2 adsorption from air under 10 ppm(mg/g)
FS-PEI(423)-50	103	64.1
FS-PEI(800)-50	107.3	75.9
FS-PEI(1800)-50	74.6	42.5
FS-PEI(25000)-50	74.7	51



Goeppert, A.; Zhang, H.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R. *ChemSusChem*, in press

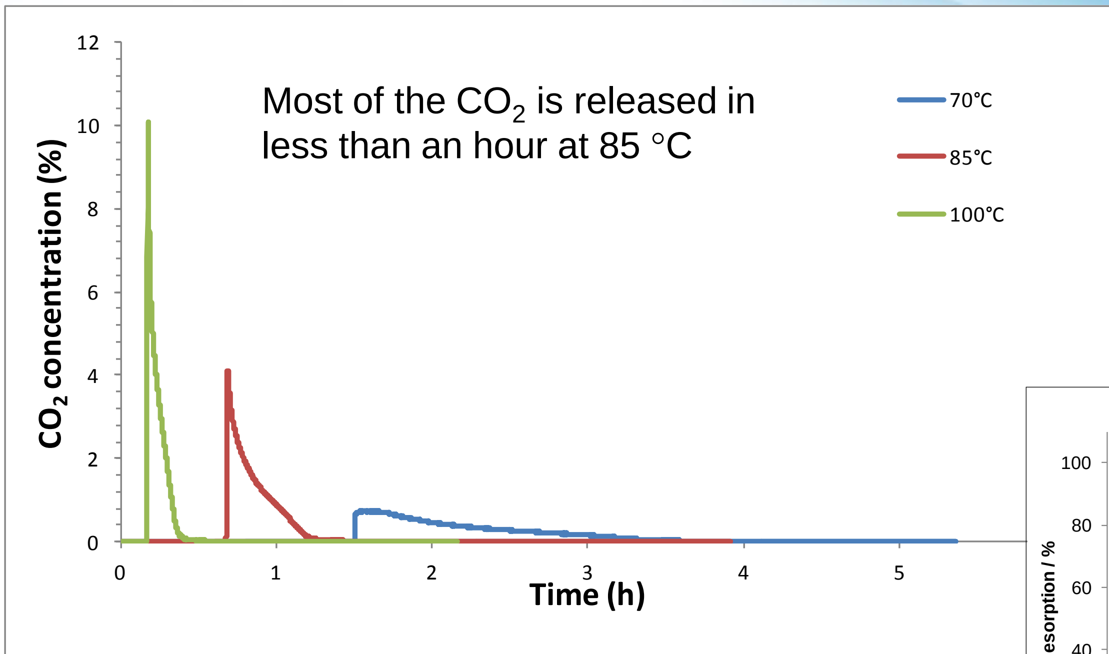
CO_2 Adsorption from the air on FS-PEI-50 as a function of temperature





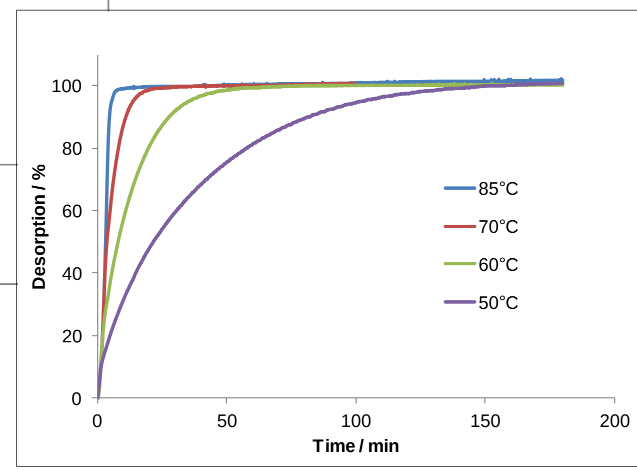
No adsorption observed above 85 °C

Effect of the temperature on the desorption on FS-PEI-50



CO_2 Desorption (measured in the flow system)

Amount of adsorbent : 3 g
Flow rate: 335 mL/min air



CO_2 Desorption (measured by TGA)

- Adsorbent is regenerable under mild conditions

- The higher the desorption temperature, the faster the desorption kinetics

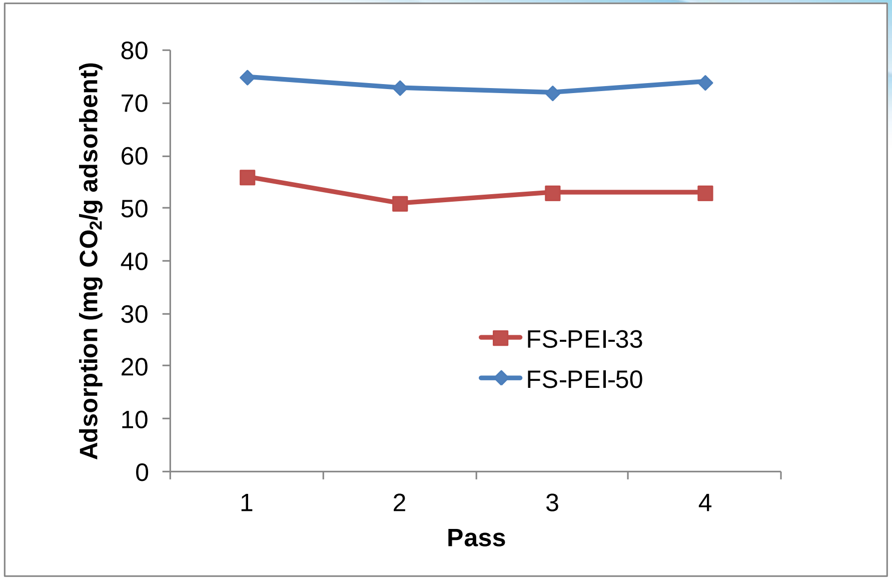
Regeneration of FS-PEI adsorbents in short term cycling tests

FS-PEI-33

Pass	CO_2 adsorption before breakthrough (mg/g)	Total CO_2 adsorption (mg/g)
1	42	56
2	39	51
3	40	53
4	40	53

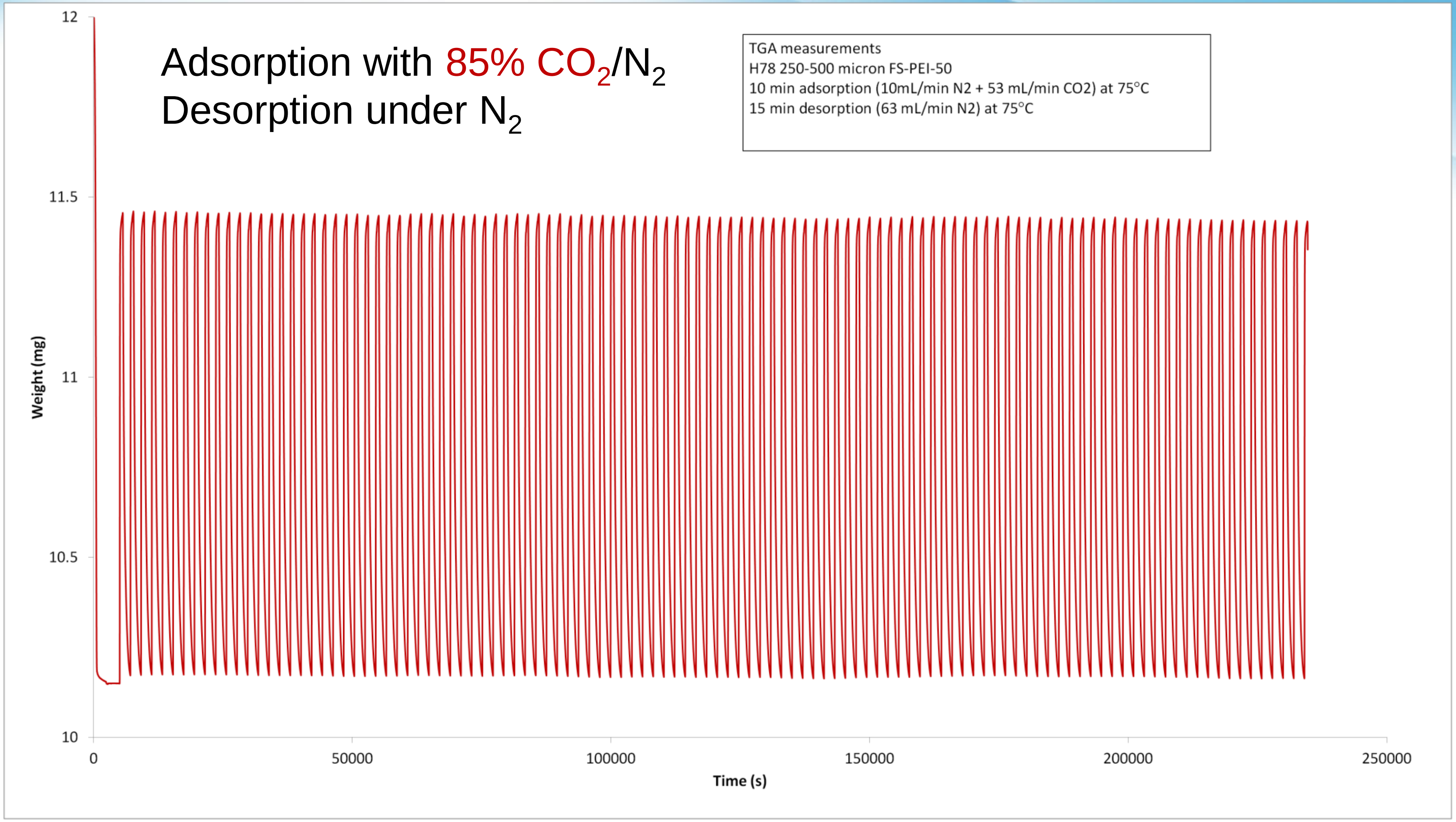
FS-PEI-50

Pass	CO_2 adsorption before breakthrough (mg/g)	Total CO_2 adsorption (mg/g)
1	39	75
2	38	73
3	35	72
4	36	74



Regeneration at 85 °C under vacuum

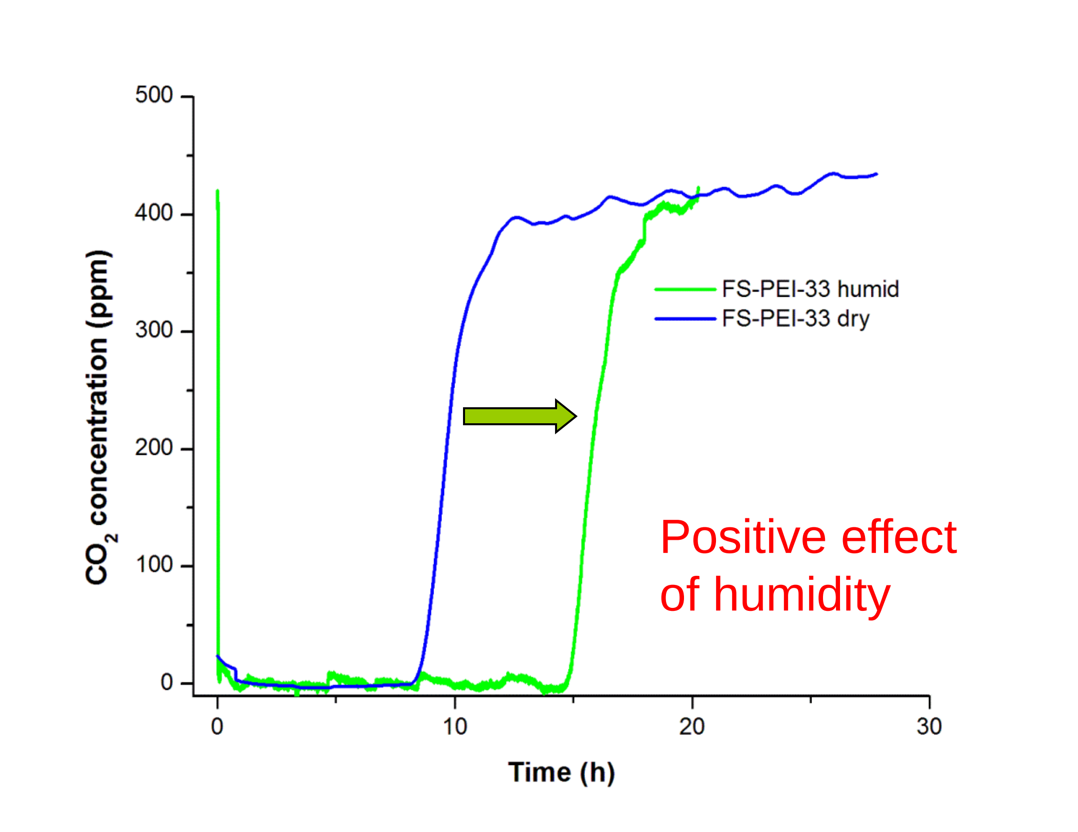
110 cycles adsorption/desorption at 75° C on FS-PEI-50

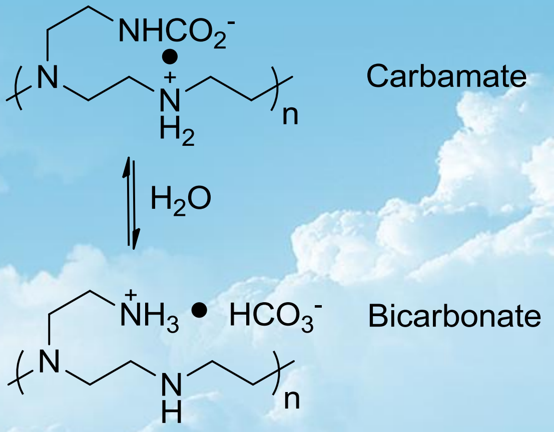


➡ No significant loss in adsorption capacity under CO_2/N_2

Adsorption of CO_2 from the air at 25 ° C on FS-PEI-33. Effect of humidity

Conditions	mg/g adsorbent	mmol/g adsorbent	mg/g PEI	mmol/g PEI
Dry	52	1.18	156	3.55
Humid	78	1.77	234	5.32





Consistent with the formation of bicarbonates

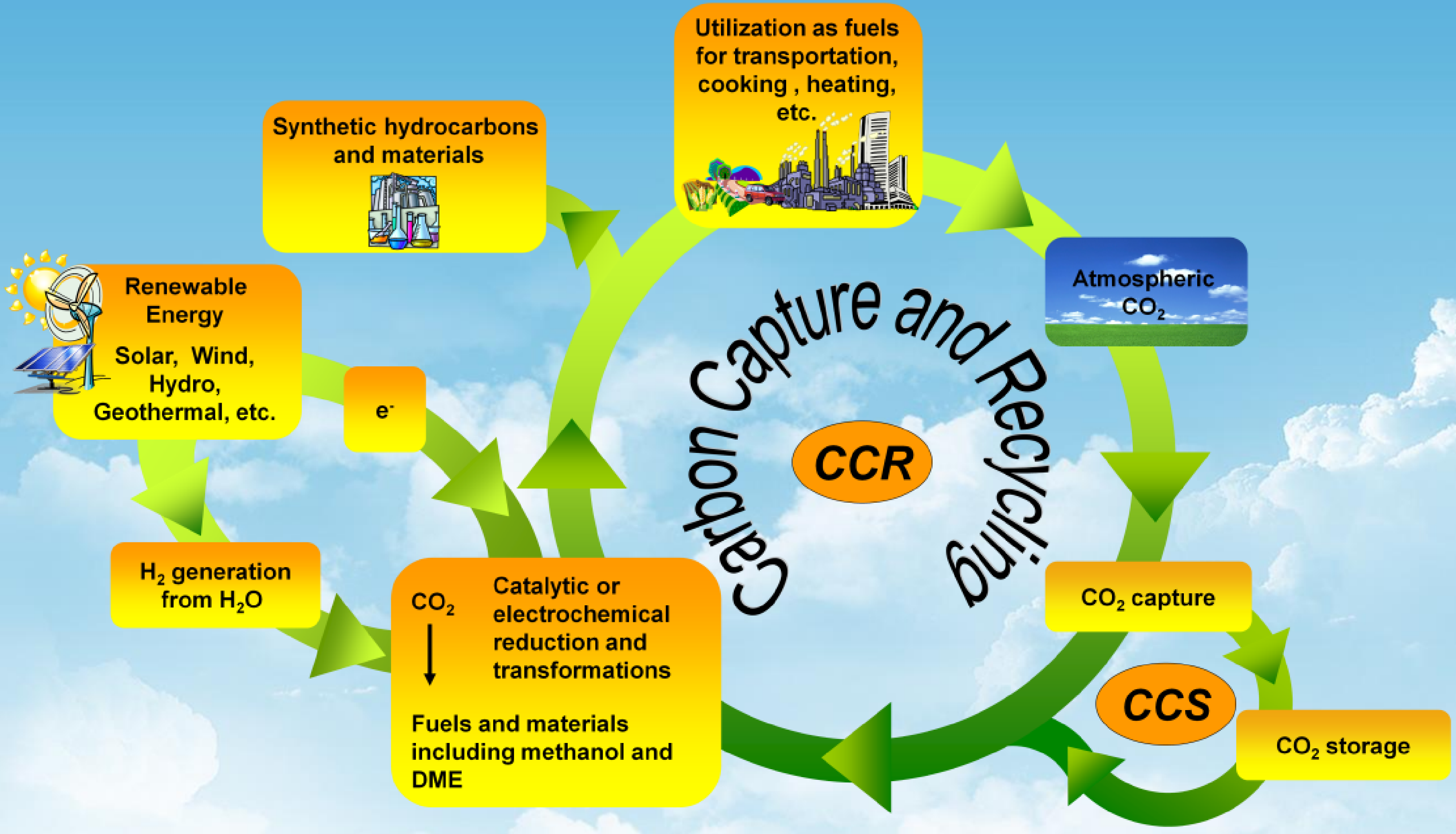
Humid conditions: 67% relative humidity at 25 °C

In the case of zeolites, humidity stops almost entirely the adsorption of CO_2

Conclusions on CO_2 adsorption from the air using fumed silica / PEI adsorbents

- Absorption of CO_2 from the air is technically feasible
- Amine based adsorbents show promises
  - relatively high adsorption capacity even under humid conditions
  - regeneration at low temperature (70-100 °C)
  - fast kinetics of reaction
  - easy to prepare using inexpensive starting materials
  - solids: does not require separation or heating of water
- Humidity improves the adsorption of CO_2 on amine based materials
- Promising adsorbent for air purification in closed environment or alkaline fuel cells

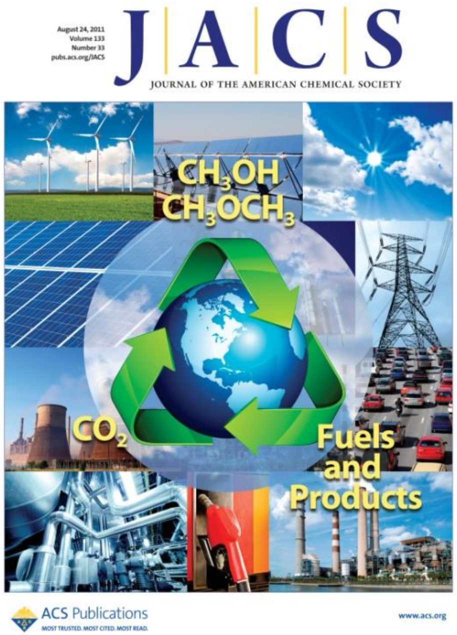
Utilization and recycling of CO_2 from the air
Anthropogenic carbon cycle
Mimic Nature's photosynthetic cycle

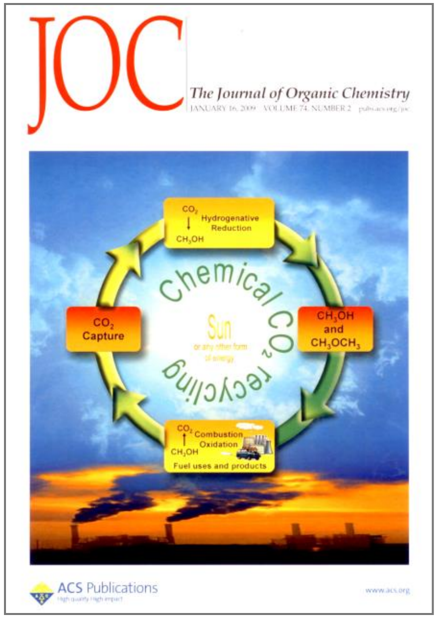


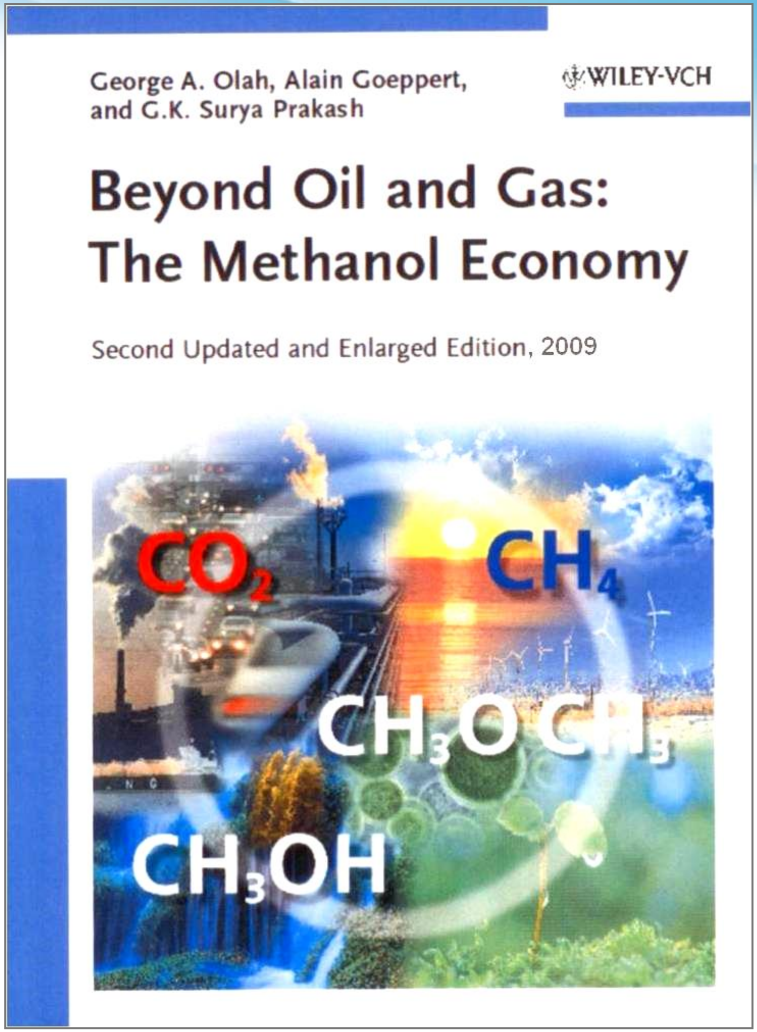
Sustainable recycling of atmospheric CO_2 to fuels and materials

Methanol economy

J. Am. Chem. Soc. **2011**, *133*, 12881







J. Org. Chem. **2009**, *74*, 487-498

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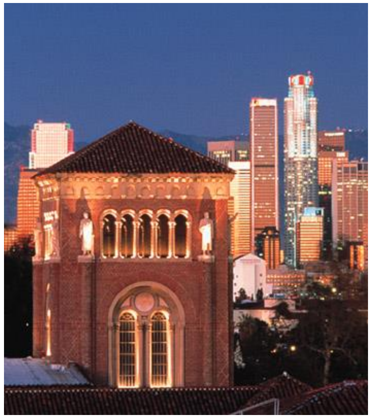

Thank you for your attention!

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arpa·e CHANGING WHAT'S POSSIBLE

U.S. DEPARTMENT OF ENERGY