Shapeable Microporous Polymer Supercontactor/Sorbent for CO_2 Capture from Air

- ***Ali Sekizkardes***
  - *Research Scientist/LRTS 314-94*

- ***2022 NETL Carbon Management Meeting***
- ***08/16/2022***

Disclaimer

Authors and Contact Information

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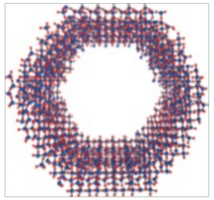
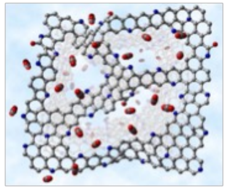
Research Objective

Adsorbent Portfolio

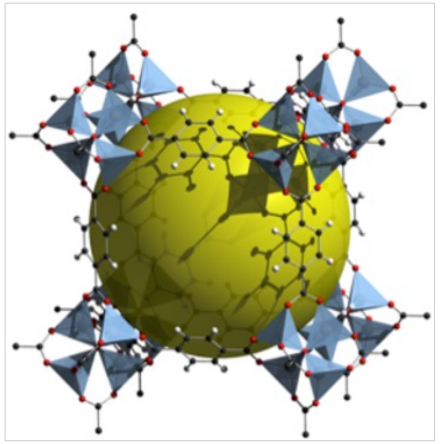
Zeolites



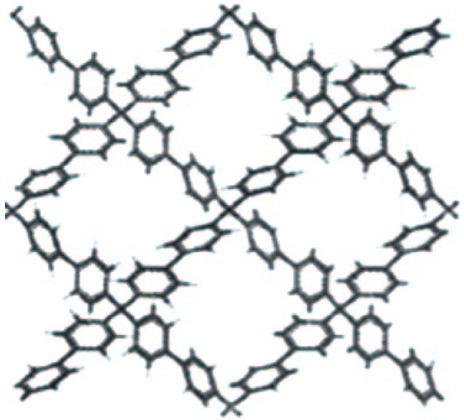
Silicates



Porous Carbon



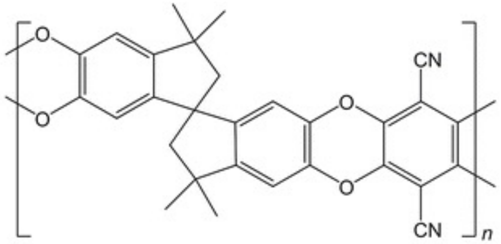
MOFs

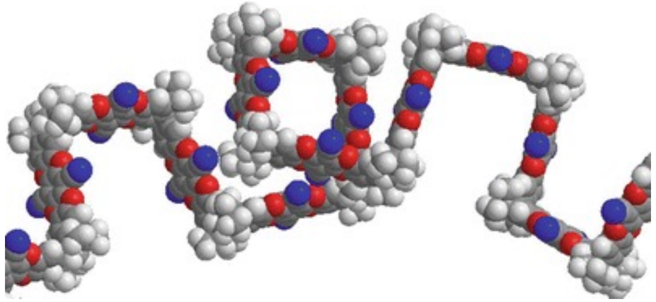


Porous Polymers

1990 **2000** **2010** **Timeline**

Chem. Rev. **2017**, 117, 1515−1563

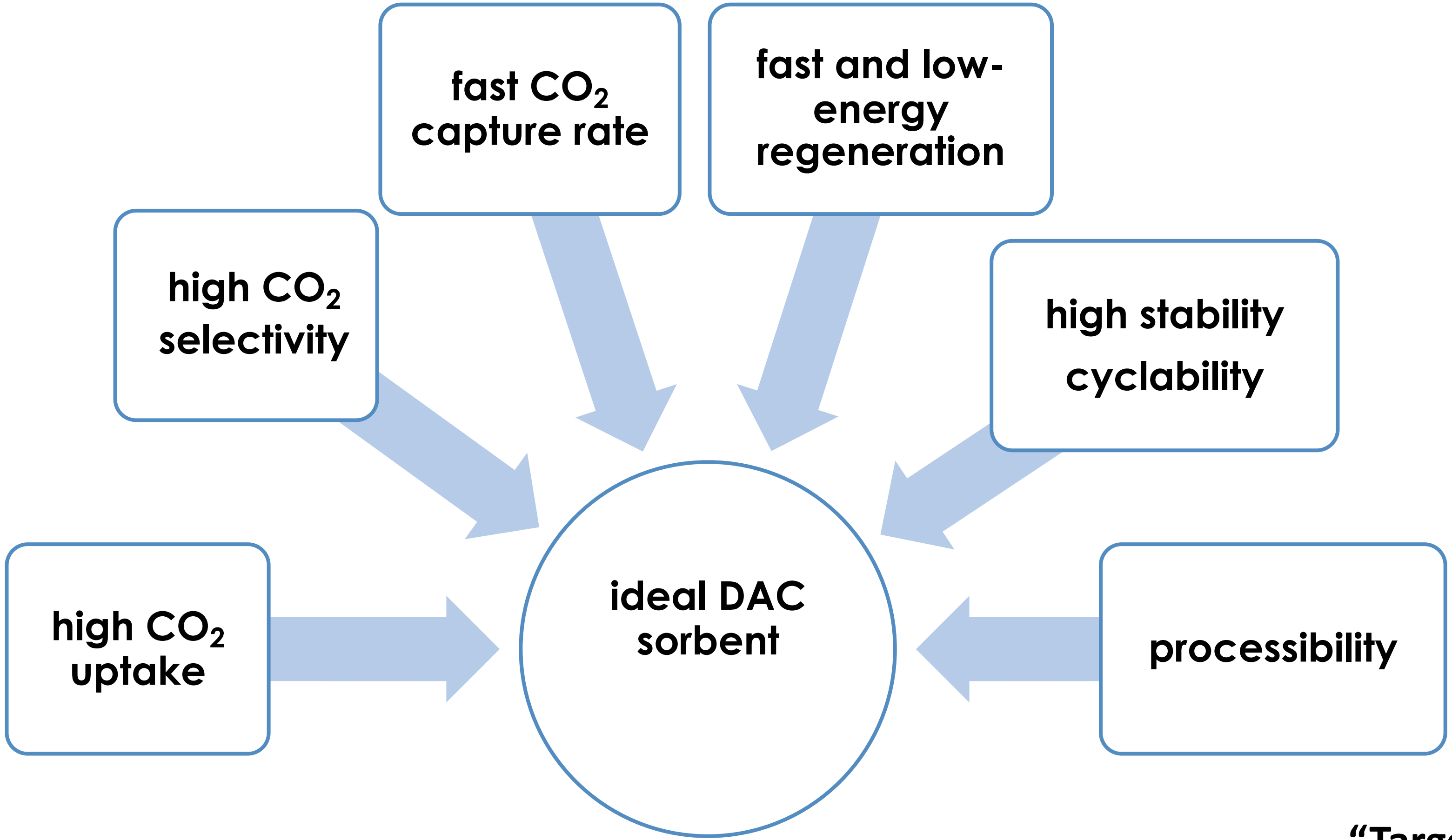




Polymers of Intrinsic Microporosity (PIM)

N. B. McKeown and P. M. Budd,
Chem. Soc. Rev., **2006**, 35, 675–683

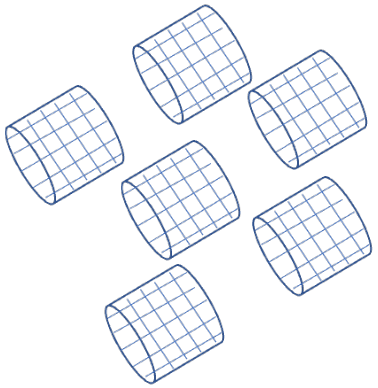
Technology Background



“Targeted geometries can have 10-20 times less pressure drop compared to packed reactors”

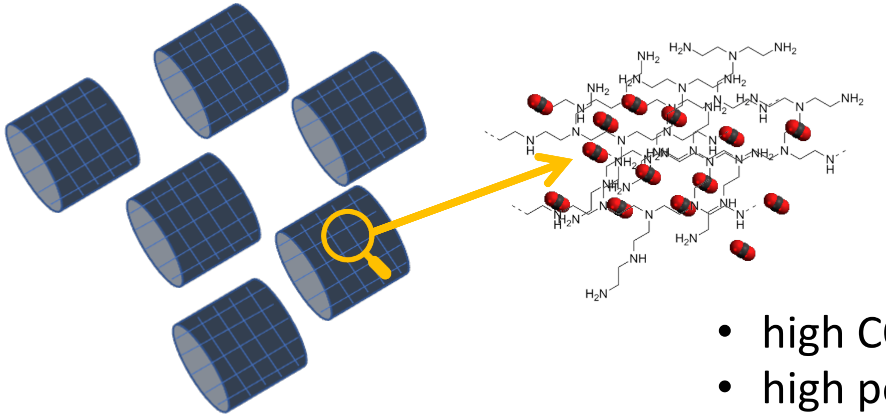
Chem. Mater. **2020**, 32, 17, 7081–7104

Technology Background: Aminated Sorbents



amine impregnation

polyamines



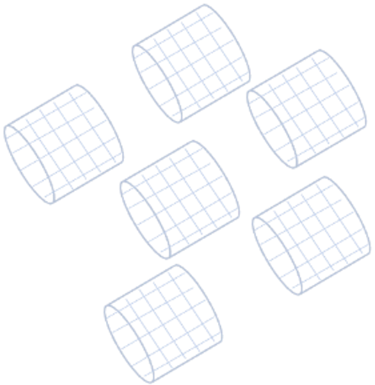
macro porous particle
(SA= 150 m^2/g)

amine impregnated sorbent

- high CO_2 uptake
- high polyamine loading (50%)
- slow CO_2 diffusion
- regeneration (>100 C)
- amine leaching
- oxidation problem

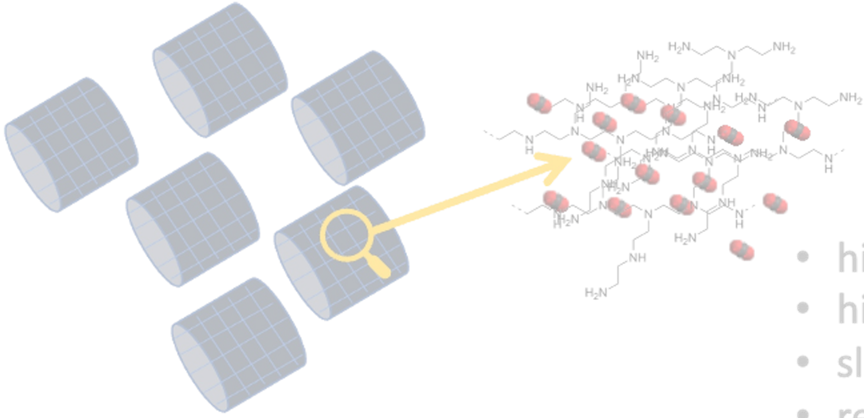
Energy Environ. Sci., 2022,**15**, 1360-1405

Technology Background: Aminated Sorbents



amine impregnation

polyamines



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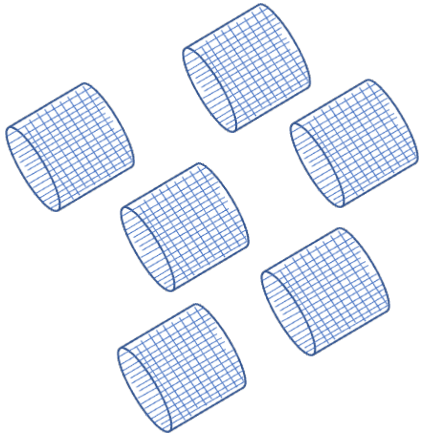
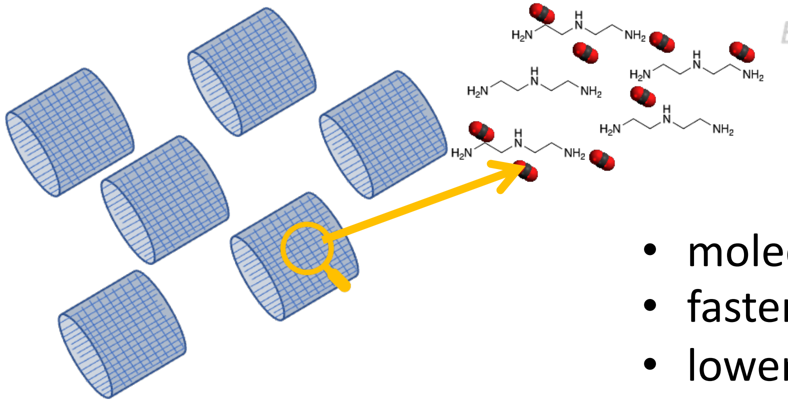
Energy Environ. Sci., 2022,**15**, 1360-1405



amine impregnation

molecular amines



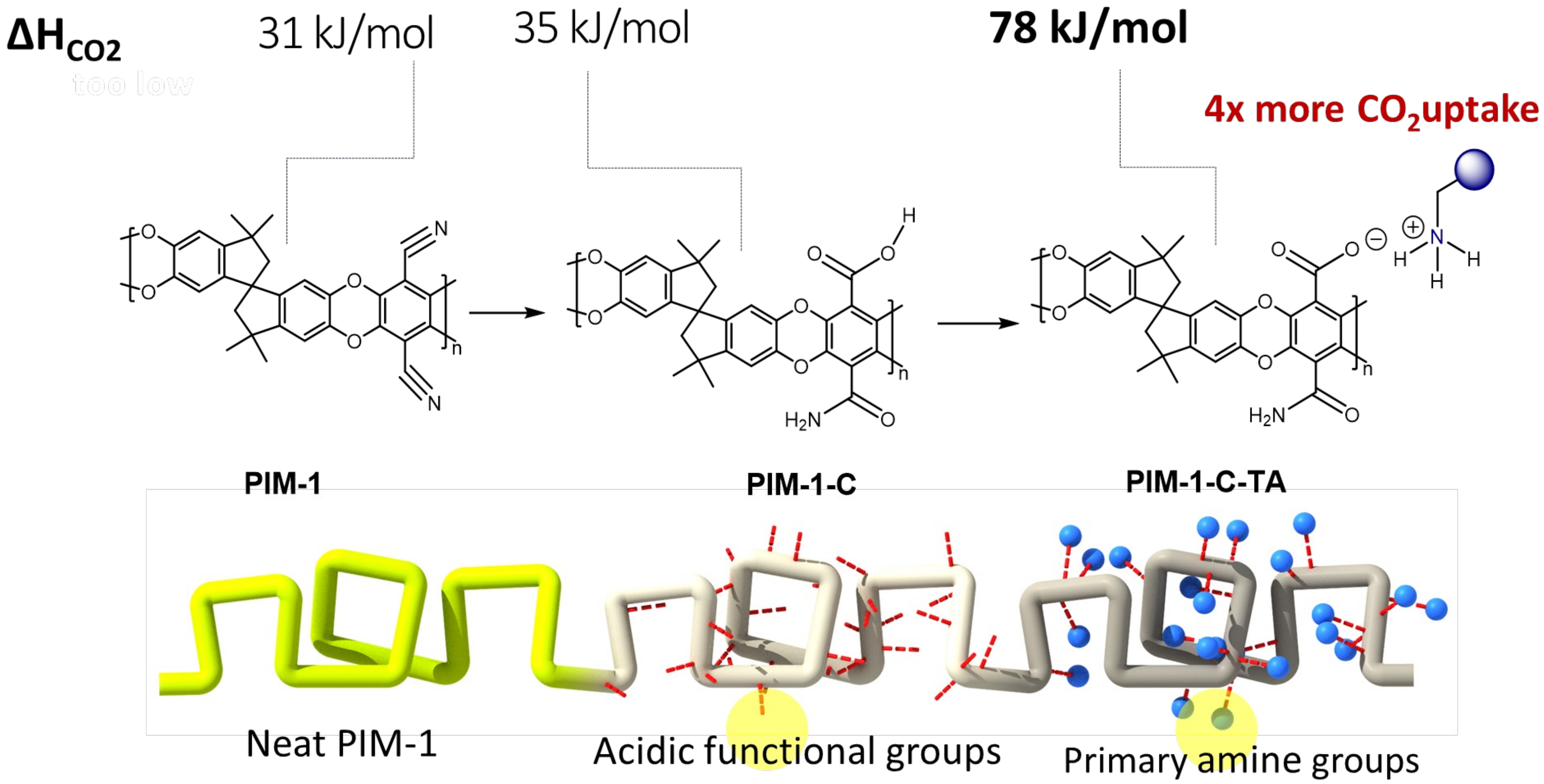
nano porous particle
(SA= 600 m²/g)

amine impregnated
sorbent

- molecular amine loading (20-50%)
- faster CO_2 diffusion
- lower temperature regeneration
- amine leaching
- less likely oxidation

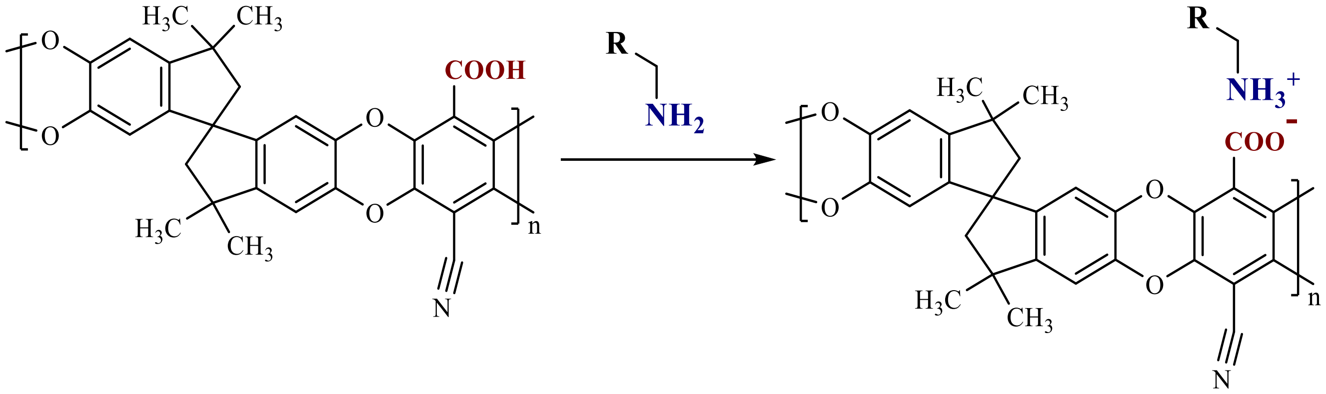
Mater. Adv., **2021**, *2*, 5843-5880

Processible Sorbent Concept



ACS Appl. Mater. Inter. **2019**, 11, 30987–30991

Processible Sorbent Concept

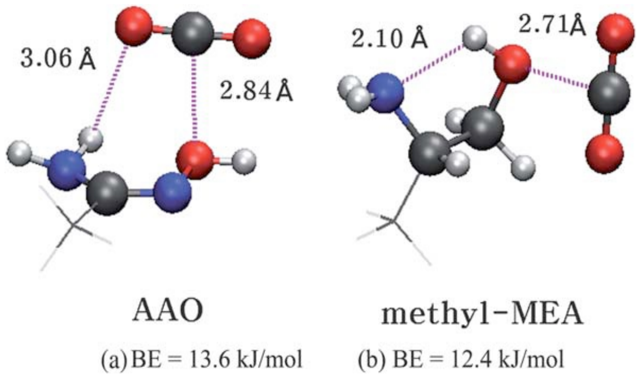


- Can be scaled up with cost efficient synthesis
- Soluble in common solvent and can be processed
- Tunable chemical structure
- High surface area and pore volume
- Library of different sorbents can be prepared

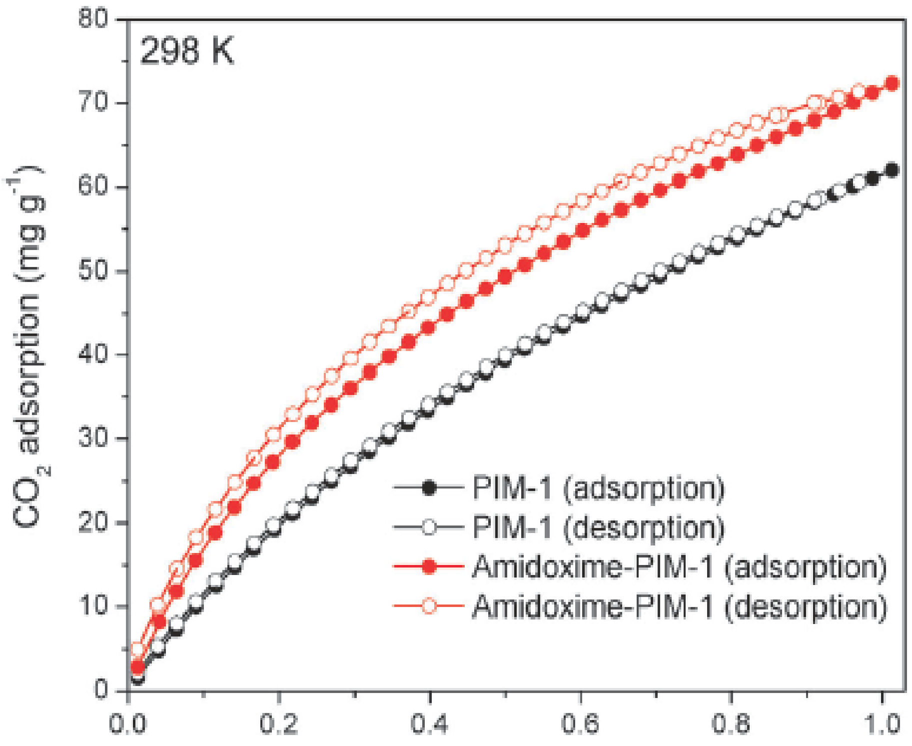
US Patent **2022**0032268A1

Amidoxime Functionality

- Amidoxime functionality for amine tethering

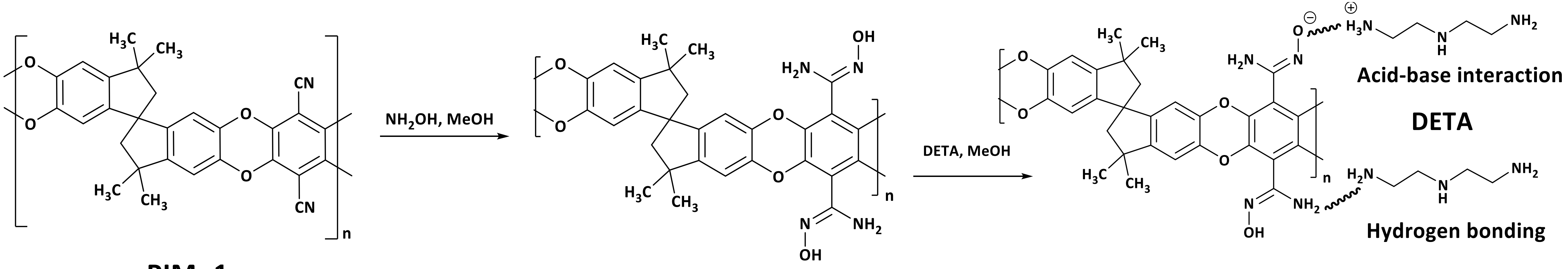


Energy Environ. Sci., **2011**, *4*, 4528–4531



Chem. Commun., **2012**, *48*, 9989-9991
by Yavuz group

Sorbent Preparation



PIM -1

PIM -1-AO

PIM -1-AO-DETA

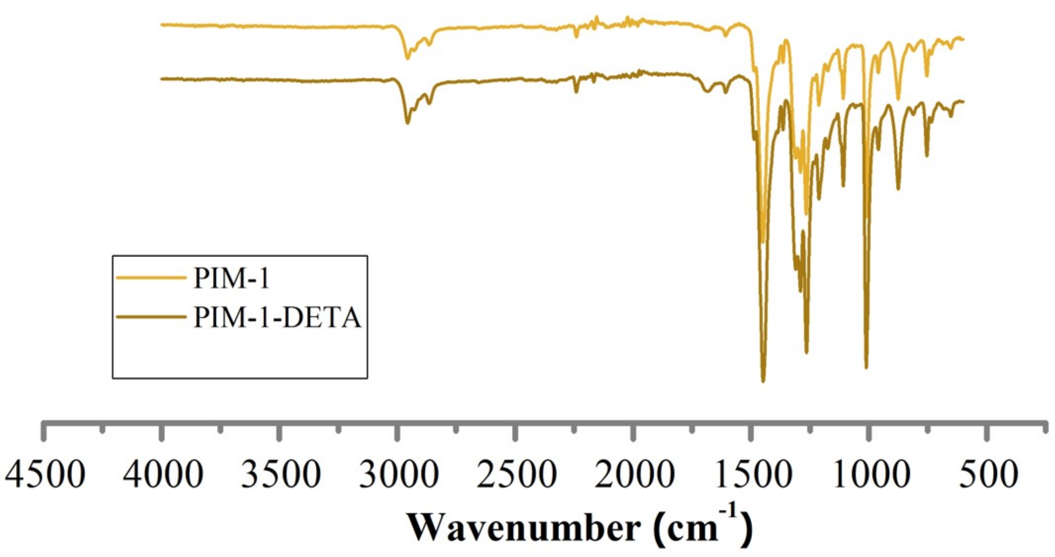
Amines considered:

- Diethylenetriamine (DETA)
- Tris(2 aminoethyl)amine (TAEA)
- Tetraethylenepentamine (TEPA)

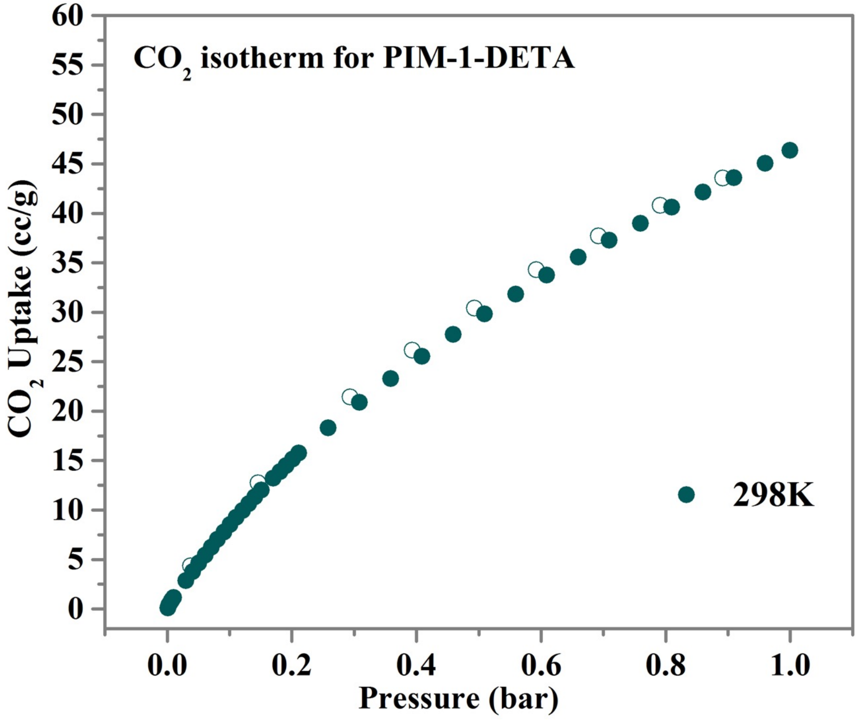
Energy Technology, **2020**, 8, 2000419

Sorbent Characterization

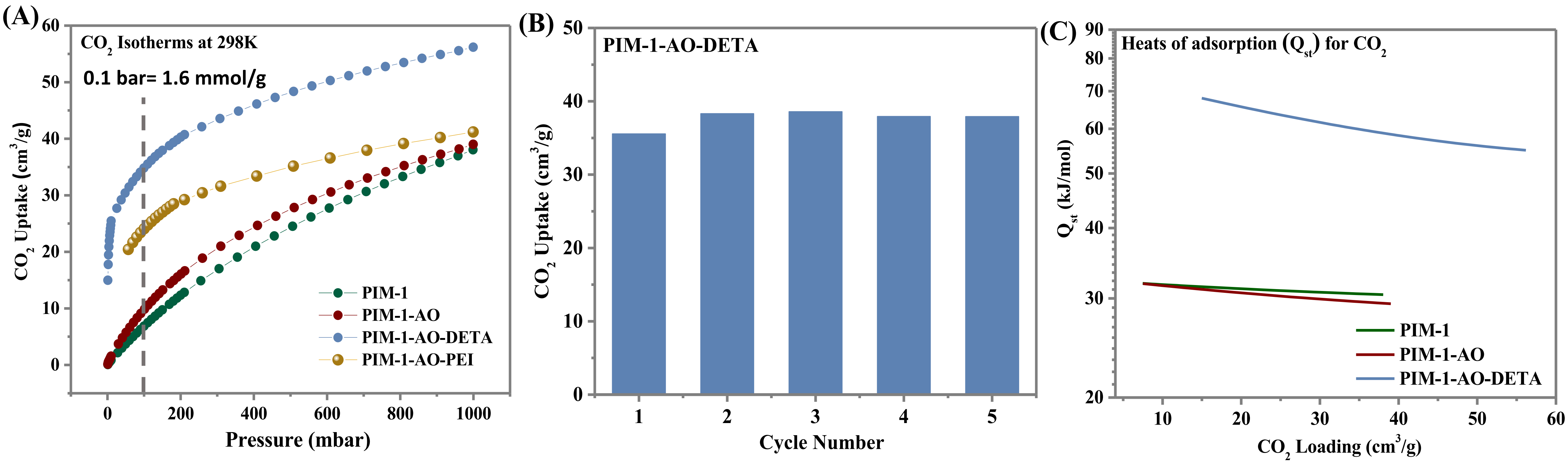
- Control study with neat PIM-1



FT-IR spectrum of neat PIM-1 and PIM-1 -DETA (control sample)

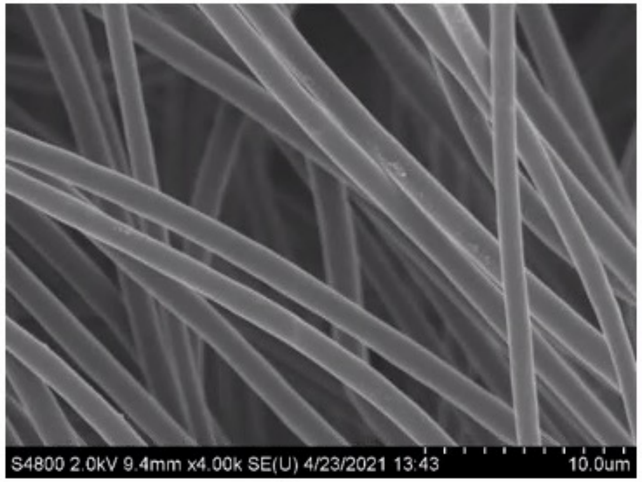


CO_2 uptake Performance of PIM-1-AO-DETA (powder)

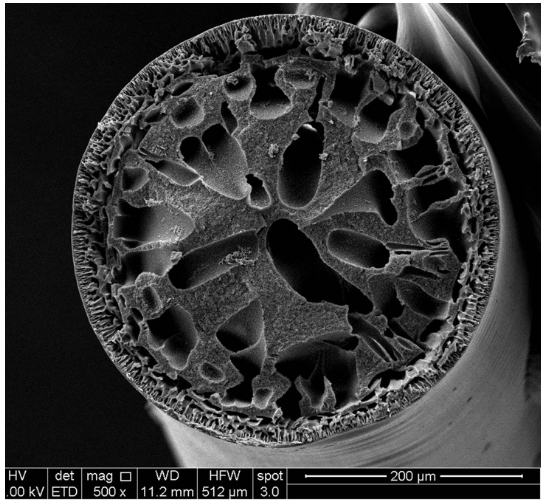


Sorbent processing

1. Electrospinning fibers



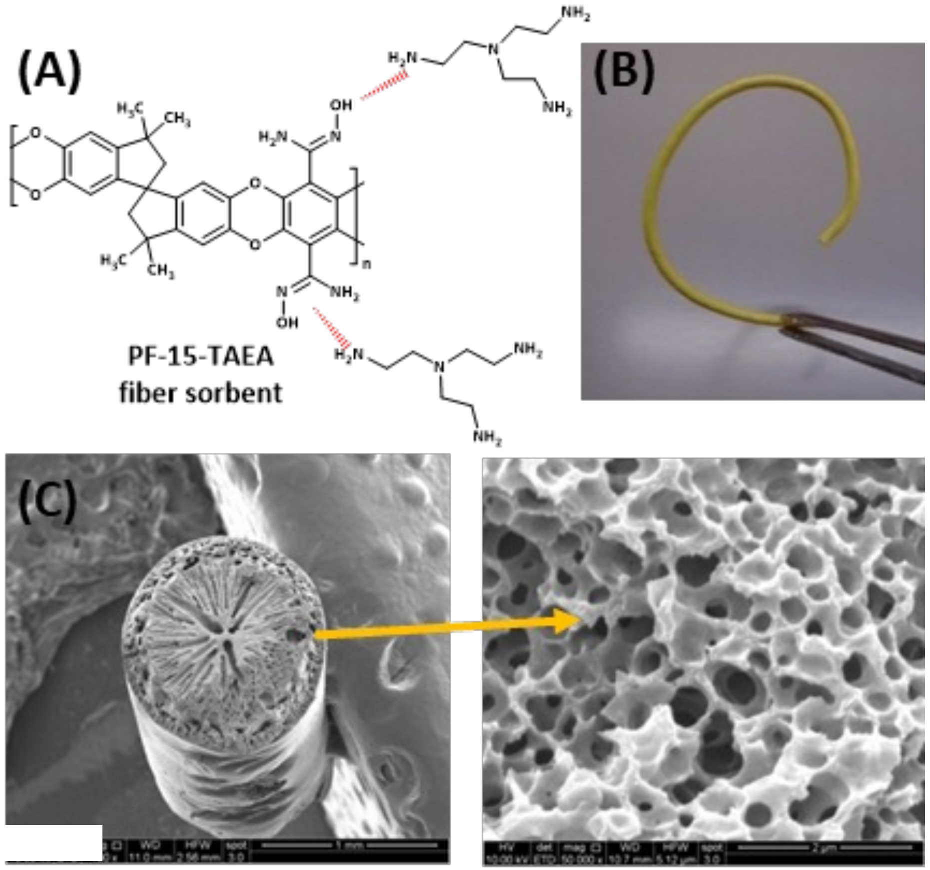
2. Porous Solid fibers



3. Hollow fibers

PIM-1-AO based fiber sorbent

PF-15-TAEA-fiber sorbent

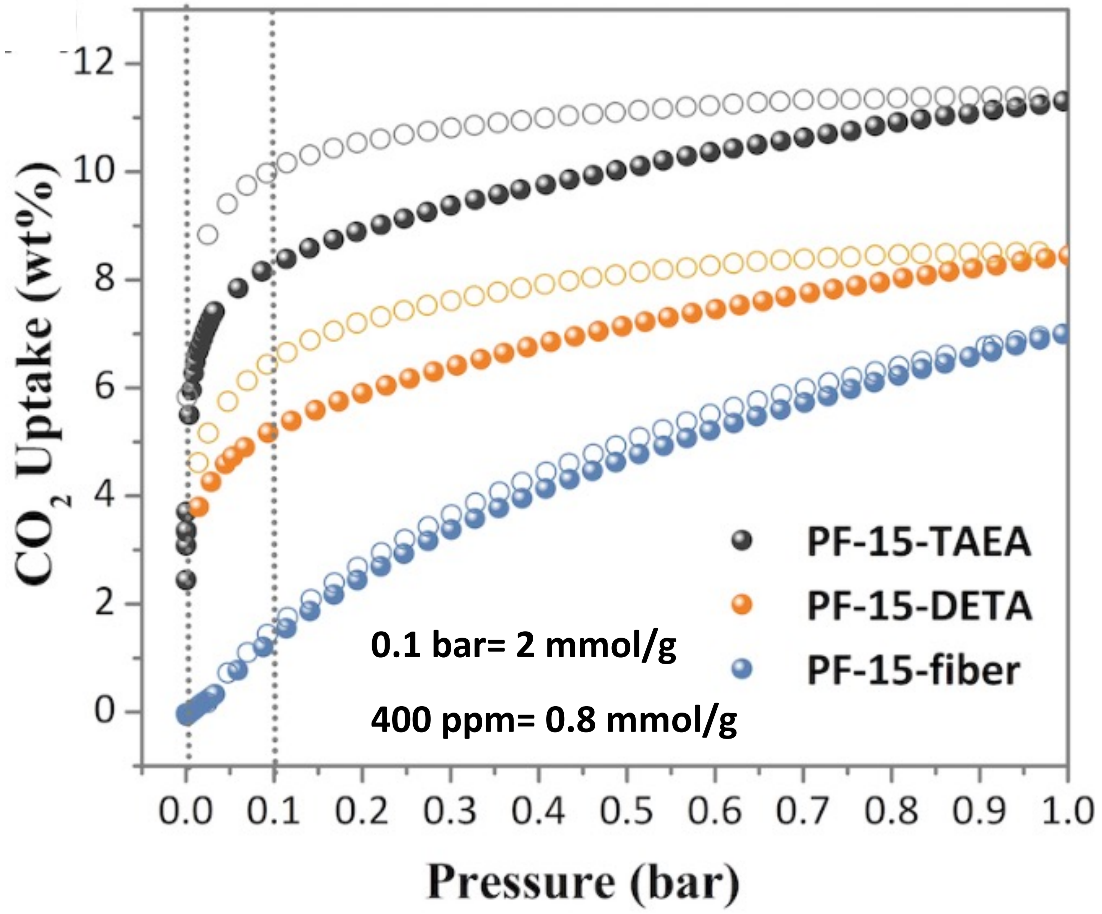


- Fibers procced only from the sorbent formulation, no additives need2ed
- Cost efficient synthesis and large scale processibility
- High surface area substrate polymer
- Molecular amine use enabled by amidoxime functionality
- Amine loading is <25% in the sorbent

Sekizkardes, A.; Kusuma, V.; Culp, J.; Muldoon, P.; Hoffman, J.; Hopkinson, D. Single Polymer Sorbent Fibers for High Performance and Rapid Direct Air Capture. *ChemRxiv* **2022**. DOI 10.26434/chemrxiv-2022-jgpqv

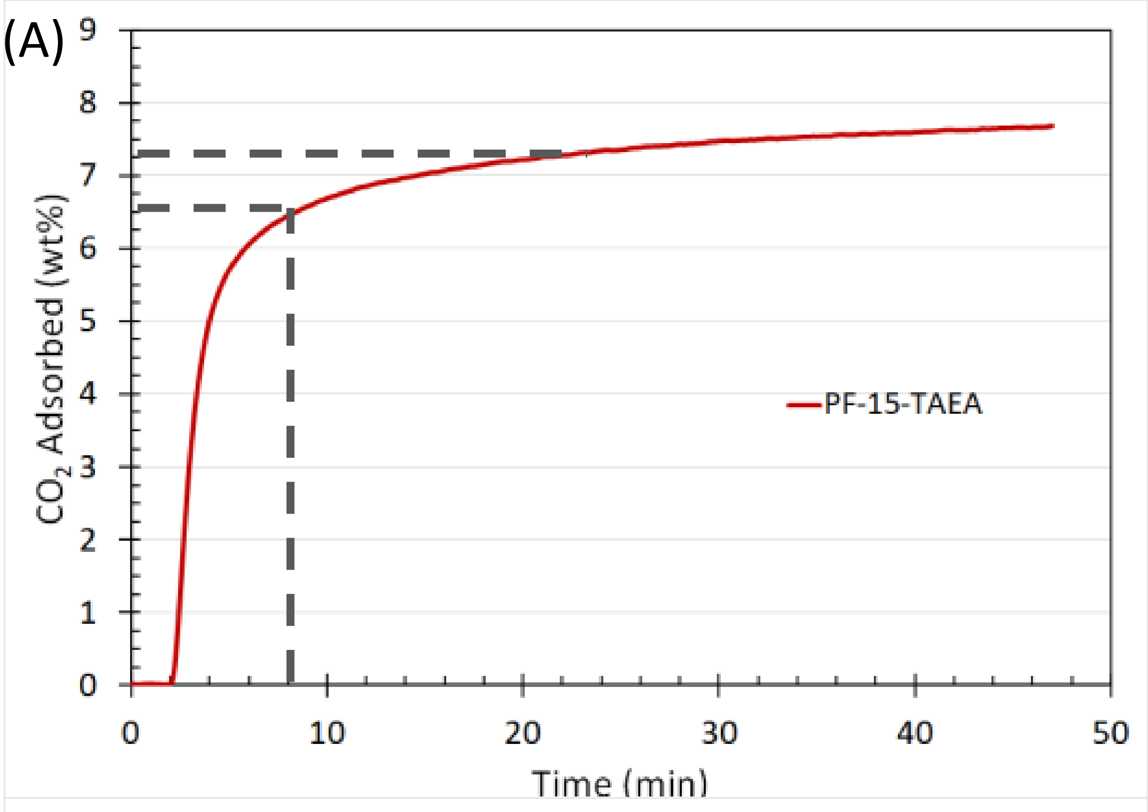
CO_2 adsorption test

Equilibrium CO_2 adsorption test (solid fibers)



Mixed-gas CO_2 adsorption rate and cyclability

NATIONAL ENERGY TECHNOLOGY LABORATORY



Figures: CO_2 uptake in PF-15-TAEA. (A) measured in flowing gas at a total pressure of 100mbar, 25°C. The switch from pure N_2 to 10%CO_2/90%N_2 occurs at 2 min. (B) adsorption / desorption cycles in flowing gas at a total pressure of 1bar. Conditions: (1) pure N_2, 25°C; (2) 10%CO_2/90%N_2; (3) temperature ramp in pure N_2 at 3°C/min to 70-75°C (black) or 75-80°C (red).

K. Min, W. Choi, C. Kim and M. Choi, *Nat Commun*, 2018, **9**, 726.
Q. T. Vu, H. Yamada and K. Yogo, *Ind. Eng. Chem. Res.*, 2021, **60**, 4942–4950.

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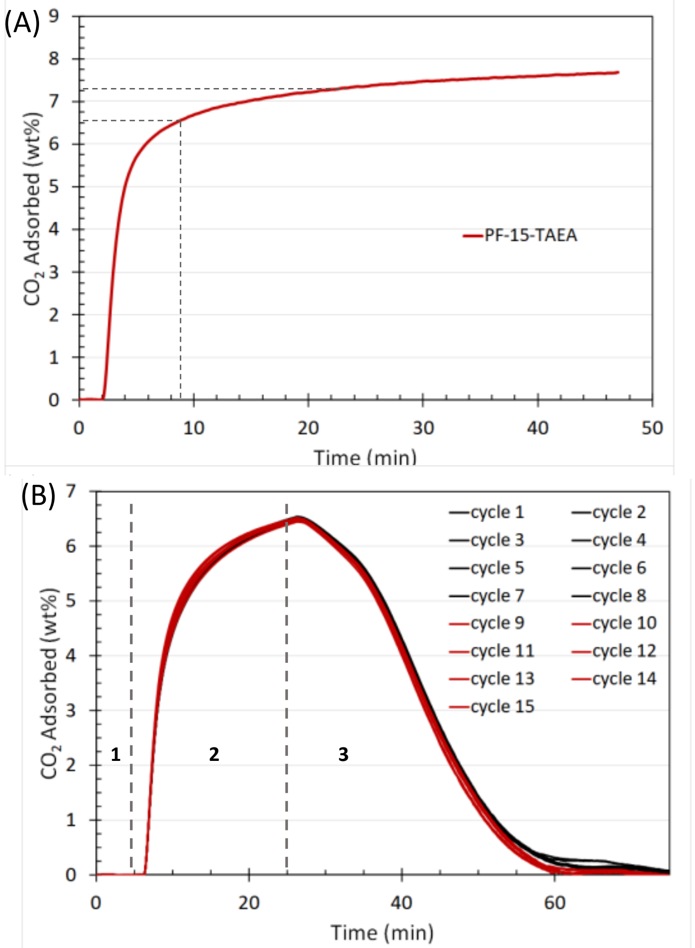

PF-15-TAEA fiber sorbent

7 min of CO_2 adsorption cycle

- **1.7 mmol.g^{-1}**

CO_2 adsorption rate

- **0.45 mmol.g^{-1}.min^{-1}**

Regeneration temp

- **70-75 ^{o}C**

Processibility

- yes/no need for binder

Pressure drop

- less likely compared to powder

Figures: CO_2 uptake in PF-15-TAEA. (A) measured in flowing gas at a total pressure of 100mbar, 25°C. The switch from pure N_2 to 10%CO_2/90%N_2 occurs at 2 min. (B) adsorption / desorption cycles in flowing gas at a total pressure of 1bar. Conditions: (1) pure N_2, 25°C; (2) 10%CO_2/90%N_2; (3) temperature ramp in pure N_2 at 3°C/min to 70-75°C (black) or 75-80°C (red).

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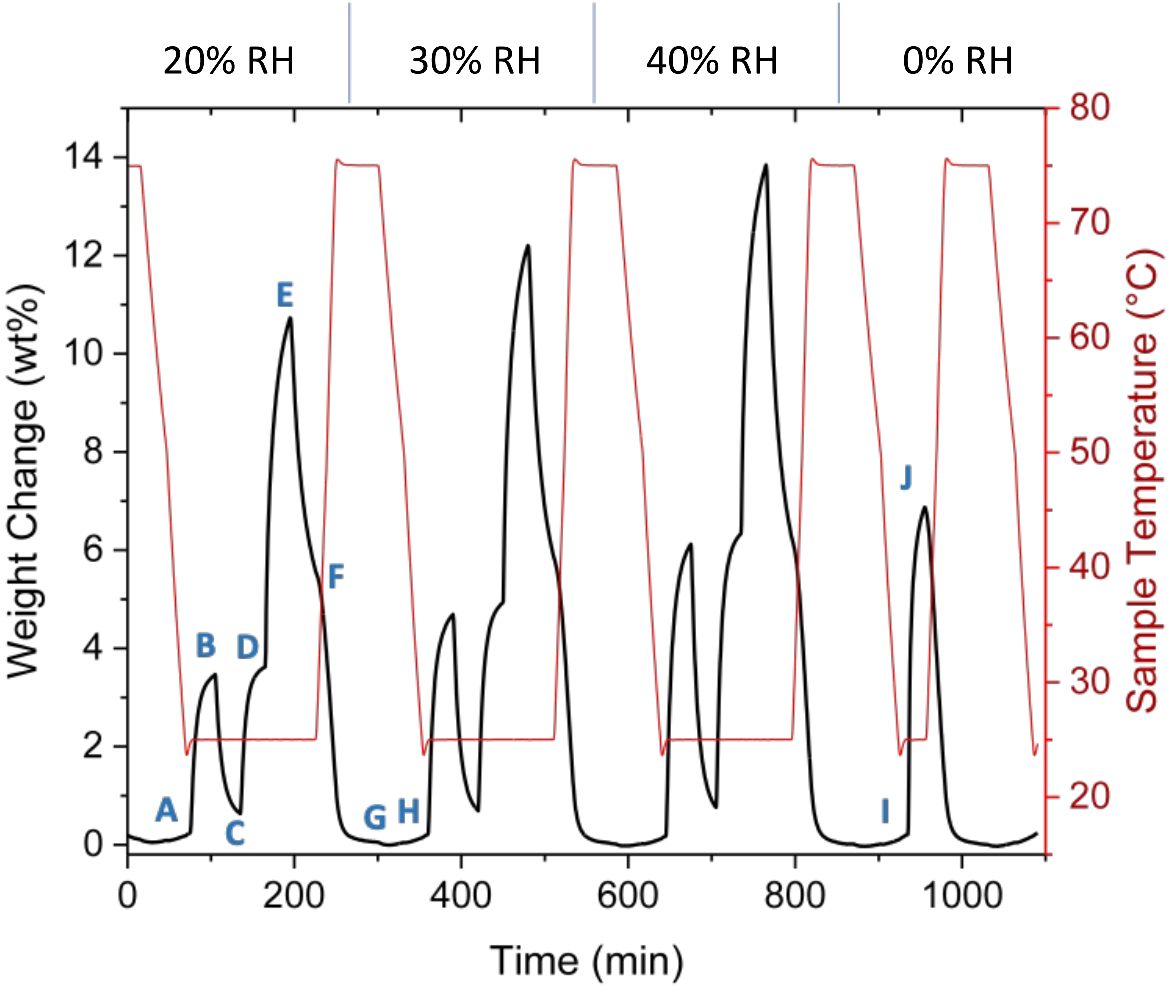
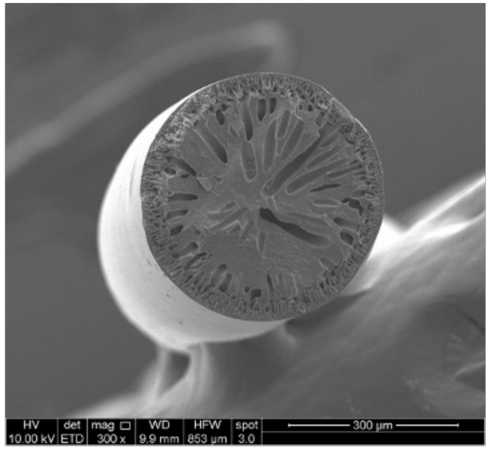
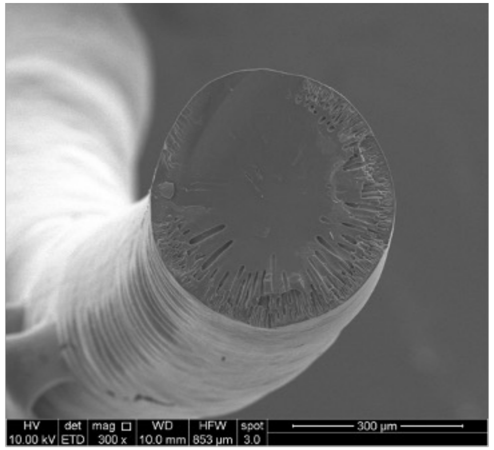
Effect of humidity on CO_2 uptake

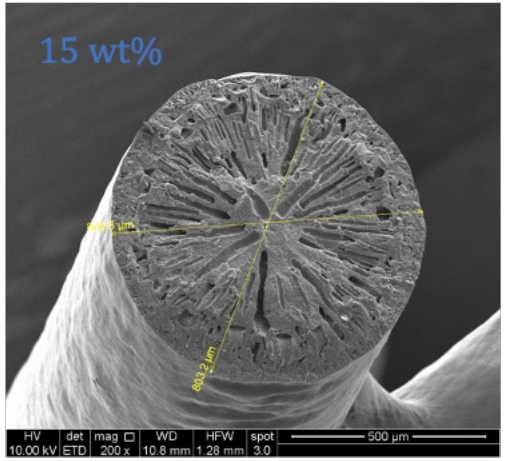


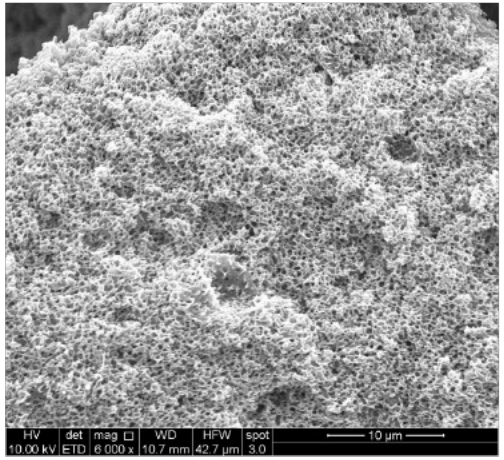
<u>The testing sequence:</u> The sections are labeled according to the percentage of humidified N_2 used in each cycle. A cycle consists of starting in dry N_2 at 25°C, then (**A**) switching to humidified N_2 for 30 minutes, (**B**) switching back to dry N_2 for 30 minutes, then (**C**) switching back to humidified N_2 for 30 minutes, then (**D**) adding in 10% dry CO_2 to the humidified N_2 stream for 30 minutes, then (**E**) switching back to dry N_2 for 30 minutes, then (**F**) ramping temperature to 75°C to complete regeneration, then (**G**) cooling back to 25°C, then (**H**) repeating the cycle using a new percentage of wet N_2 (see section labels above the chart for % humid N_2). For the final cycle from t = 900min, (**I**) switching from 100% dry N_2 to dry 10% CO_2 / 90% dry N_2 then (**J**) switching back to 100% dry N_2 and heat to regenerate the sorbent.

Fiber sorbent processing





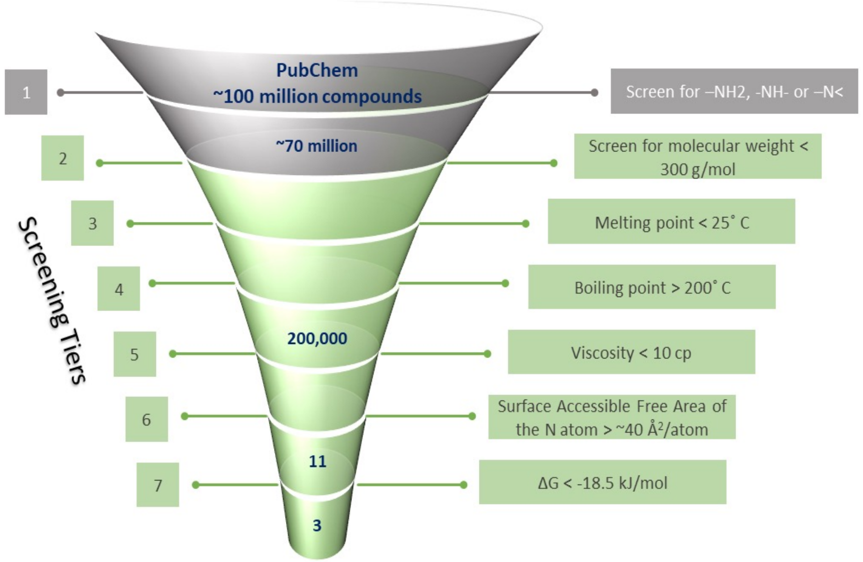




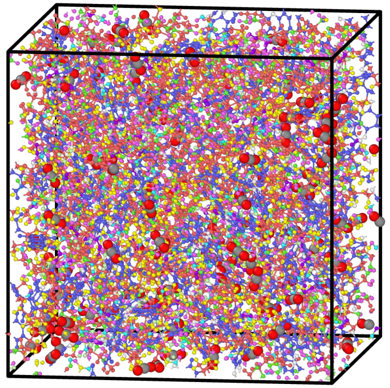
Parameters

- Solubility, viscosity
- Solvent mixture
- Polymer dope concentration
- Porosity adjustment
- Coagulation bath temperature and solution

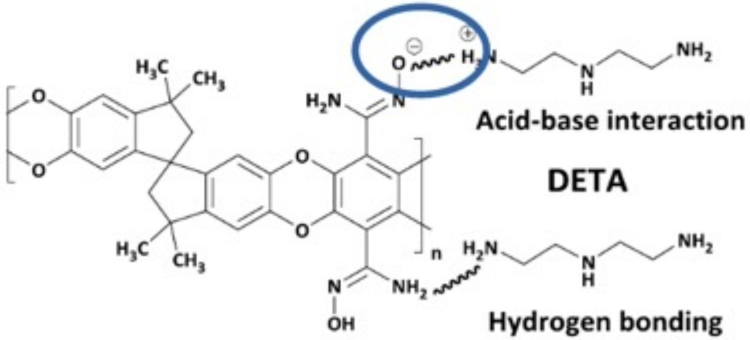
Computational Design of Alkylamine-Functionalized Polymer Sorbents

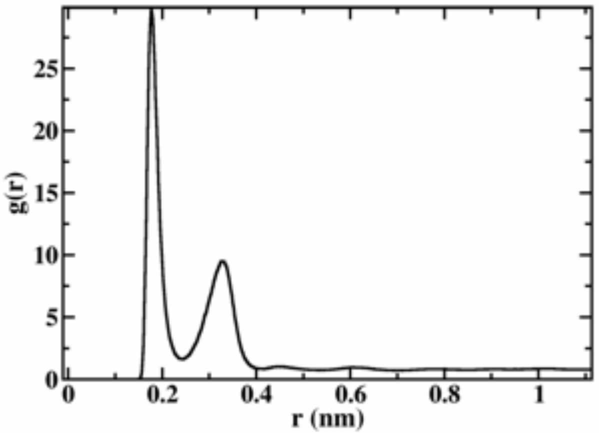


Screening of amines
(A final three amines exhibit more favorable CO2 reaction free energy and enthalpy than the existing TAEA amine)



An MD simulation box
containing polymer, amine and CO2





Molecular dynamics (MD) simulations are used for screening and to understand the adsorption mechanism

Please see poster by Dr. Surya Tiwari for more details

Current Research Interest

- Development the polymer material to reach the milestone
- Explore different sorbent formulation with the help of computational team. See the presentation of Surya Tiwari
- Monolith fiber scale up
- Electrospun fiber production
- Testing the sorbents under simulated DAC conditions
- Exploring the filler candidates to be used in the polymer

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Janice Steckel

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Victor Kusuma
Jeffrey Culp
Shouliang Yi

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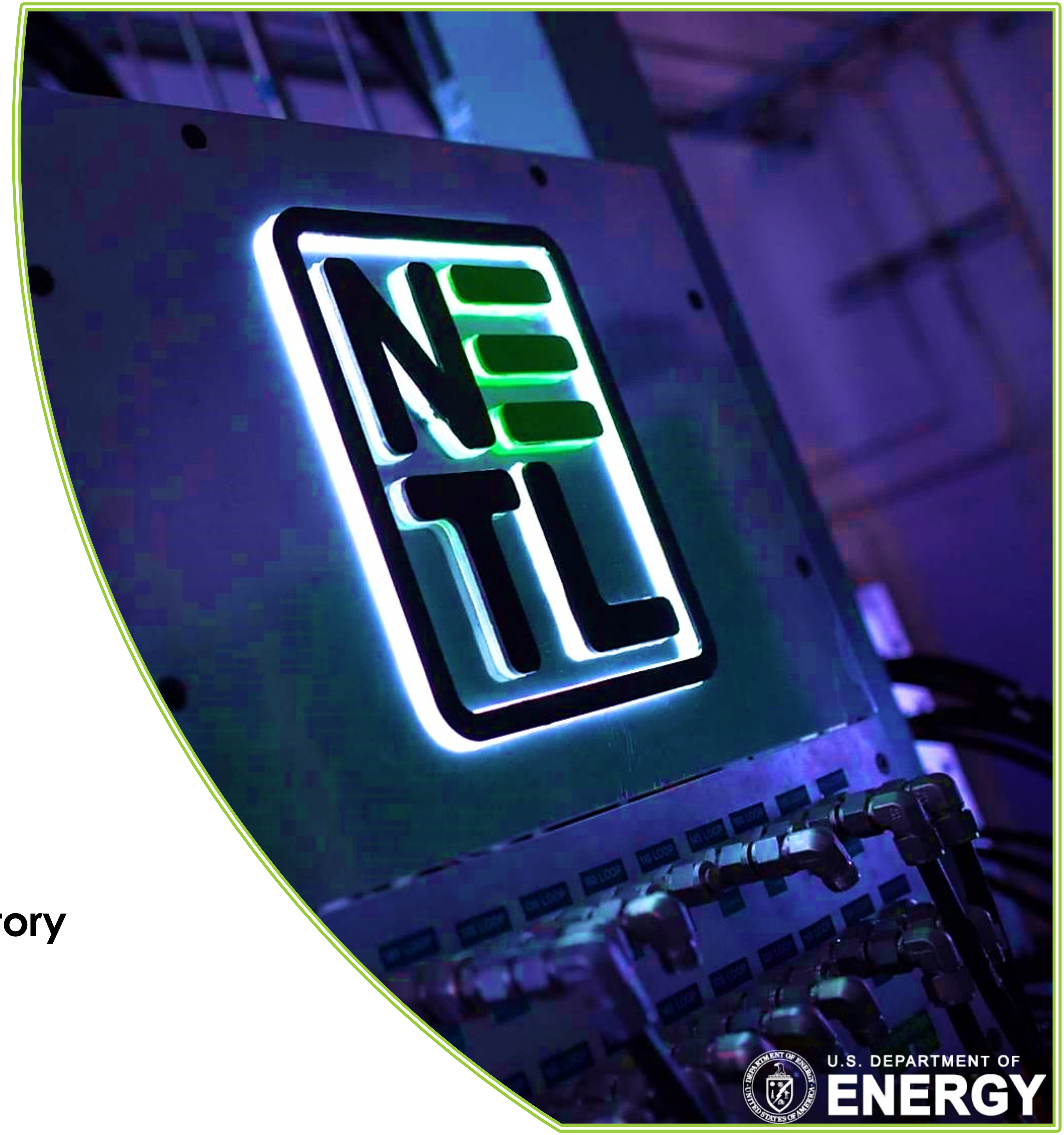

Thank you