Computational Screening & Design of Alkylamine-Functionalized Polymer Sorbents

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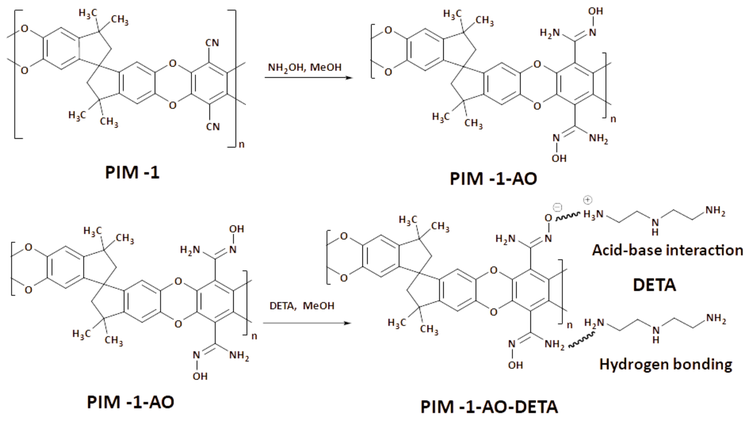
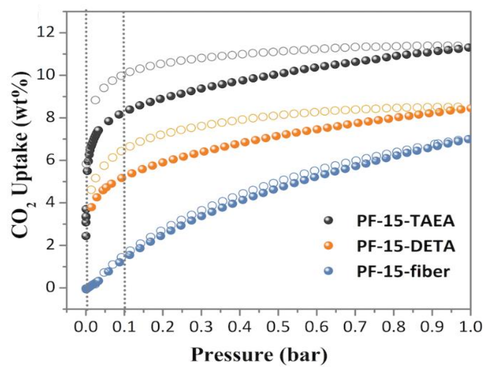
Motivation from Recent Experiment Work[1,2]



PIM-1 polymer fibers (PF-15) have been functionalized with amidoxime (AO) and aminated with TAEA (Tris(2-aminoethyl)amine) or DETA (Diethylenetriamine)



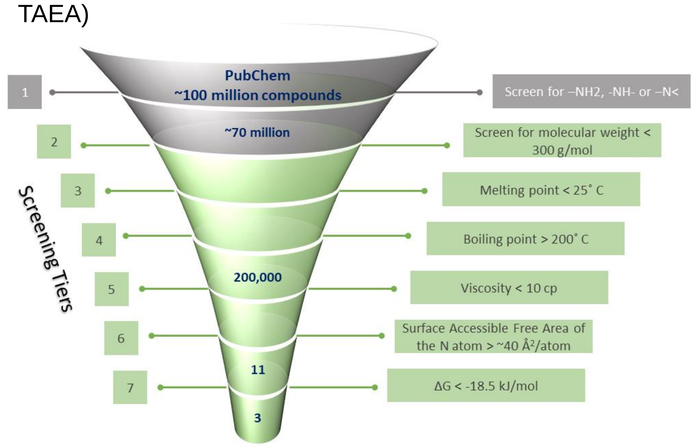
CO_2 uptake of aminated functionalized polymer (PIM-1-AO-DETA) is larger than corresponding neat polymers especially at low pressures

Finding Better Polymer-Amine Sorbents using Computational Tools

- A better combination of polymer-amine could exist that will have even higher CO_2 uptake
  - Millions of amines are available in literature and the PubChem database
  - Similarly, other porous polymers could perform better than PIM-1
- This project seeks to screen and design a better polymer-amine sorbent, understand CO_2 uptake process by the sorbent at a molecular level, and investigate the effects of water in CO_2 capture, such as CO_2 overall mass transfer and CO_2 uptake.

Screening of Amines

- ~100 million compounds in PubChem database
- Amines computationally screened based on physical properties and cheminformatics features:
  - ✓Molecular weight below 300 g/mol
  - ✓Must contain either NH_2, or NH, or both
  - ✓Number of (NH_2+NH_1)/molecular weight > 0.0199
  - ✓All amines are unique (repeats removed)
- 11 amines further down-selected
  - ✓Solvent accessible surface area (SASA) for each NH_2 amine > 58 Å^2 (larger than the largest value for TAEA)
  - ✓Summation of the above SASA > 162 Å^2 (larger that that for TAEA)



- Quantum mechanics calculations were performed on 11 amines to calculate CO_2 reaction free energy (ΔG_{ig}) and enthalpy (ΔH_{ig})
- Three of those amines have more favorable ΔG_{ig} and ΔH_{ig} than TAEA & EN
- The performance of these three theoretically screened amines will be tested in experiments.

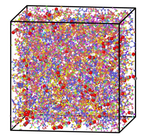
Amines	ΔG_{ig} (reaction, ig.298.2 K, 1 bar) (kJ/mol)	ΔH_{ig} (reaction, ig.298.2 K, 1 bar) (kJ/mol)	ΔS_{ig} (reaction, ig.298.2 K, 1 bar) (J/mol.K)
Ethylenediamine (EN)	531	485	-154
TAEA	460	401	-198
Screened amine 1	430, 432	368, 372	-208, -201
Screened amine 2	414, 395, 414, 389	328, 312, 339, 306	-288, -278, -252, -278
Screened amine 3	405, 418, 425, 397, 409, 412	344, 353, 370, 330, 353, 346	-205, -218, -184, -225, -188, -221

Screening of Polymers

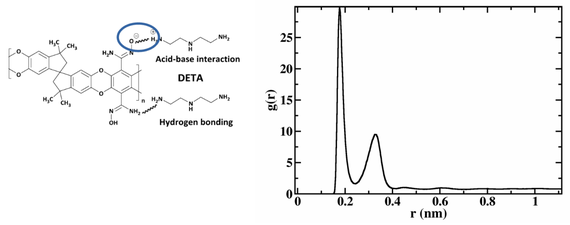
- Systematic literature survey was conducted for porous polymers
- A promising porous polymer PIM-EA-TB having surface area greater than PIM-1 has been identified based on synthesizability criteria

Computationally Testing the Polymer-Amine Sorbent

- Tools/methodologies are being developed to test the polymer-amine combination



Snapshot of molecular dynamics simulation of box containing PIM-1-AO-DETA and CO_2



Radial distribution function shows a strong interaction between the O of polymer and H of amine

Amine	PIM-1-AO-Amine interaction energy (kJ/mol)	Distance (Å)
EN	-36.64	1.80
DETA	-36.57	1.84
TAEA	-37.01	1.88

Hydrogen bond strengths calculated between functionalized PIM-1 and three different amines shows that

1. All three amines form strong hydrogen bonds with PIM-1-AO
2. All three amines will have almost same leaching

Conclusions

- Three amines and four polymers were identified for further study
- Computational tools are being developed to test the polymer-amine sorbents
- Future work will mainly focus on
  - Relationship between the amine structure and CO_2 loading and/or the reaction kinetics of CO_2 uptake
  - Understanding the role of water in the CO_2 capture process
  - Compare computational estimates for CO_2 loading performance ranking and investigation of amine-polymer stability

References

1. Miles, A., Wilfong, W. C., Hopkinson, D., & Sekizkardes, A. K. (2020). Alkylamine Incorporation in Amidoxime Functionalized Polymers of Intrinsic Microporosity for Gas Capture and Separation. *Energy Technology*, *8*(10), 2000419.
2. 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.