TEXAS A&M UNIVERSITY

Evaluation of amine-incorporated porous polymer networks (aPPNs) as sorbents for post combustion CO_2 capture

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Project Overview

Research Team

- **Principle Investigator**: Dr. Hong-Cai "Joe" Zhou
- **Industrial partners**: Koray "Ray" Ozdemir (*framergy*)
- **Team leaders**: Jeremy Willman, Gregory Day
- **Team members**: Elizabeth Joseph, Hannah Drake, Xinyu Yang, Jialuo Li, Zachary Perry
- **Past Members**: Dr. Lanfang Zou, Dr. Mathieu Bosch, Dr. Xuan Wang, Dr. Yujia Sun, Dr. Ning Huang

Outline

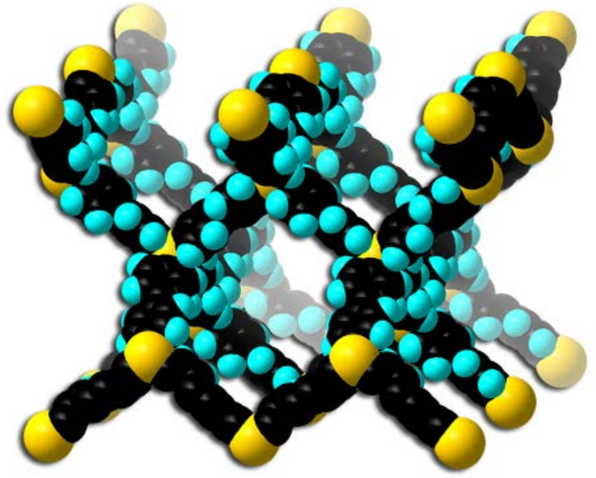
- Introduction
  - Objectives
  - Porous Polymer Networks
  - PPN-151-DETA
- Sorbent Scale-up
  - Improving 250 g synthesis
  - Evaluation of Washing procedure
  - 1 kg reactor design and scale-up
- Remaining Tasks

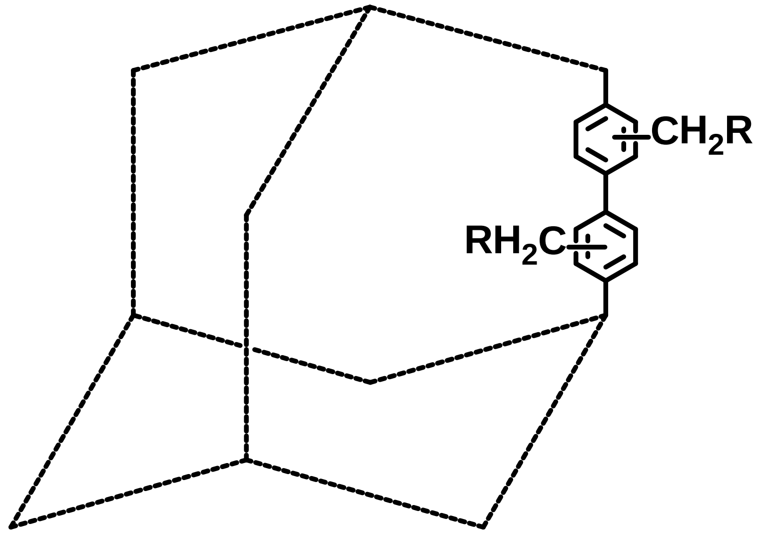
Project Objectives

- A scalable highly-robust and highly-efficient sorbent that can be delivered and validated through lab-scale testing
- A sorbent that will be economically feasible to scale-up and use in commercial carbon capture processes
- An ideal sorbent for post-combustion CO_2 capture that will approach the goal of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches

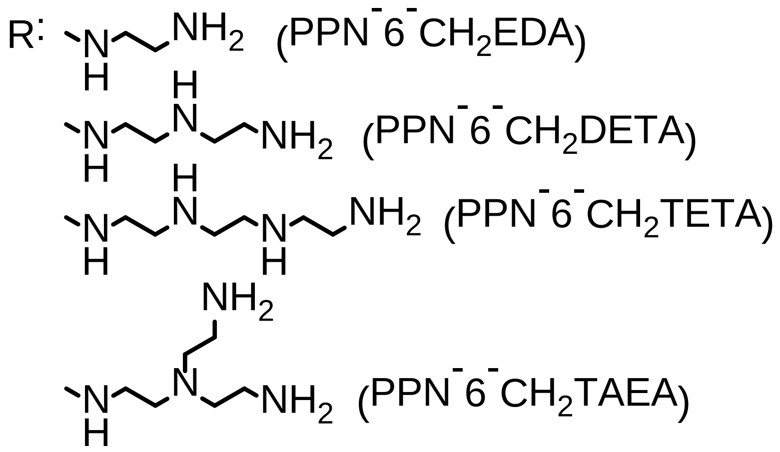
Amine-decorated Porous Materials

- Porous Polymer Networks (PPNs)



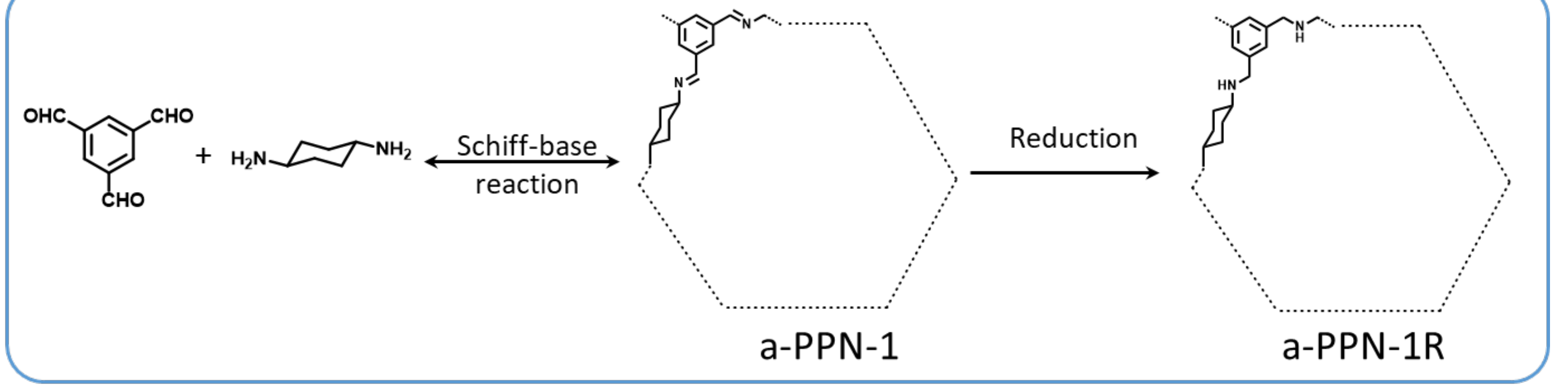


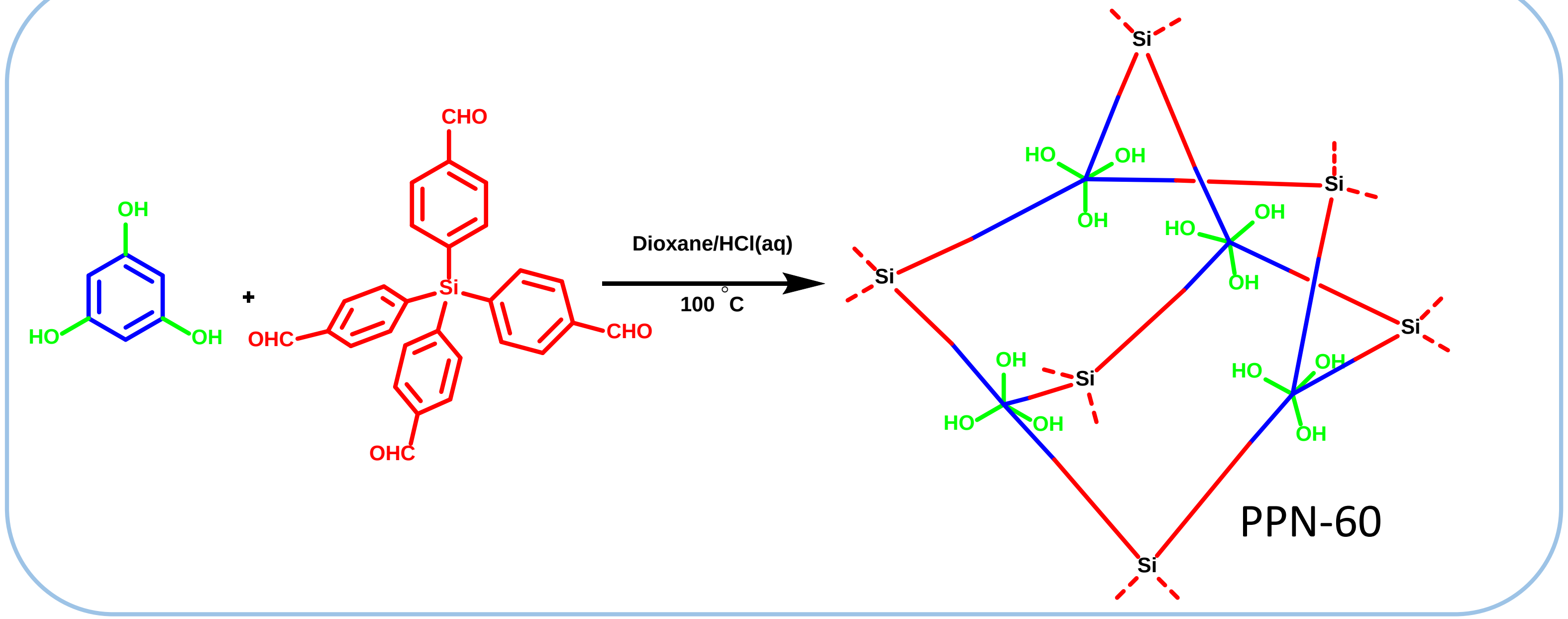
PPN-6-R

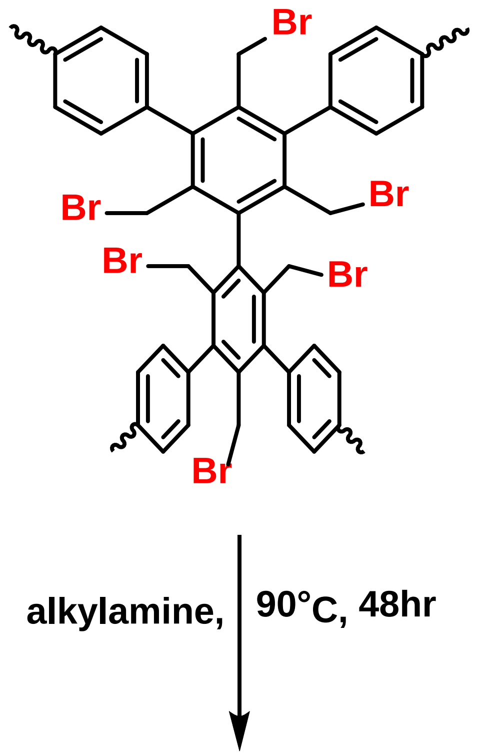


A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.*, **2014**, *136*, 8863-8866.
McDonald, T. M.; Long, J. R., *Nature* **2015,** *519* (7543), 303-308.
Lu, W.; Sculley, J. P.; Yuan, D.; Krishna, R.; Wei, Z.; Zhou, H.-C., *Angew. Chem. Int. Ed.* **2012,** *51*, 7480.

Initial PPN Candidate Materials





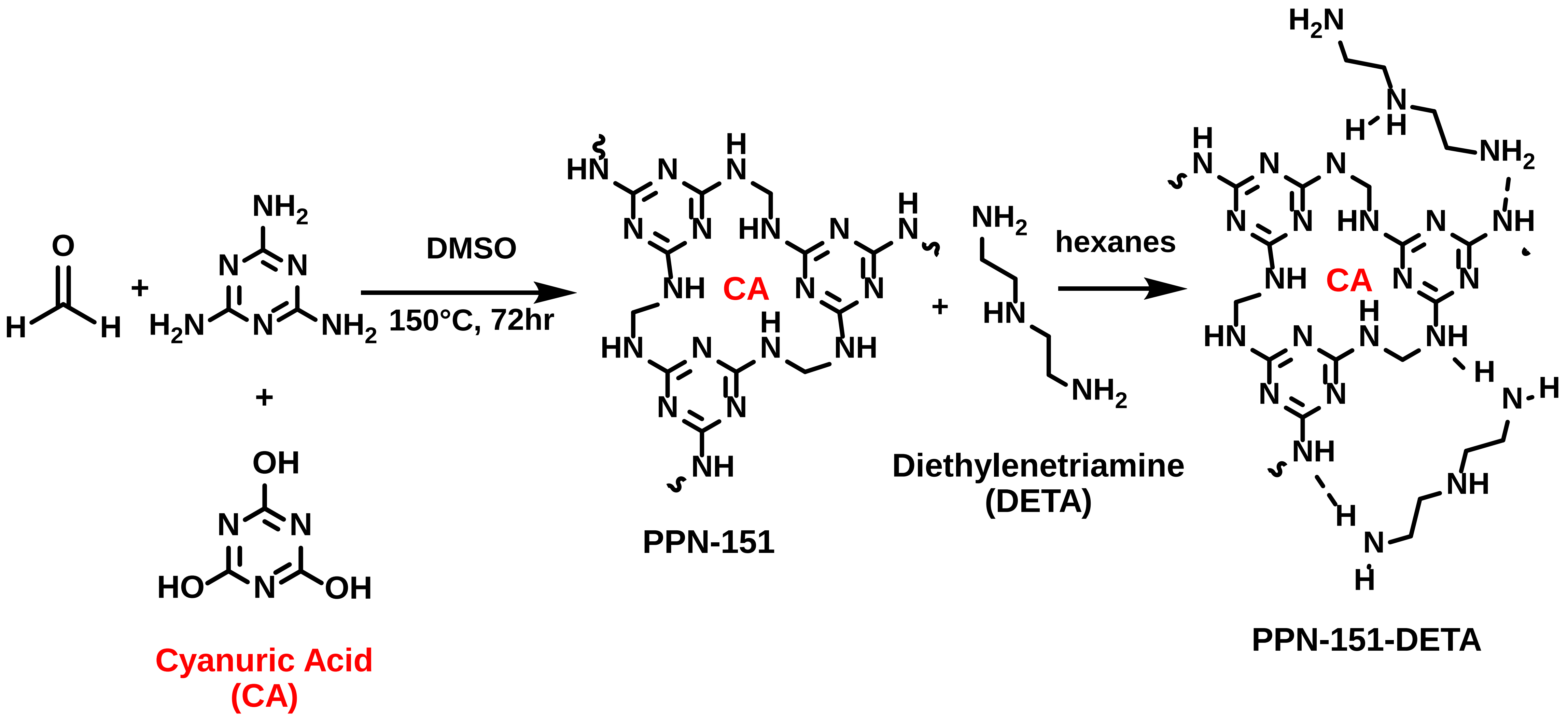


PPN-200-EDA
PPN-200-DETA
PPN-200-TETA
PPN-200-TAEA

Zou, L. et al. *CrystEngComm*. **2017**

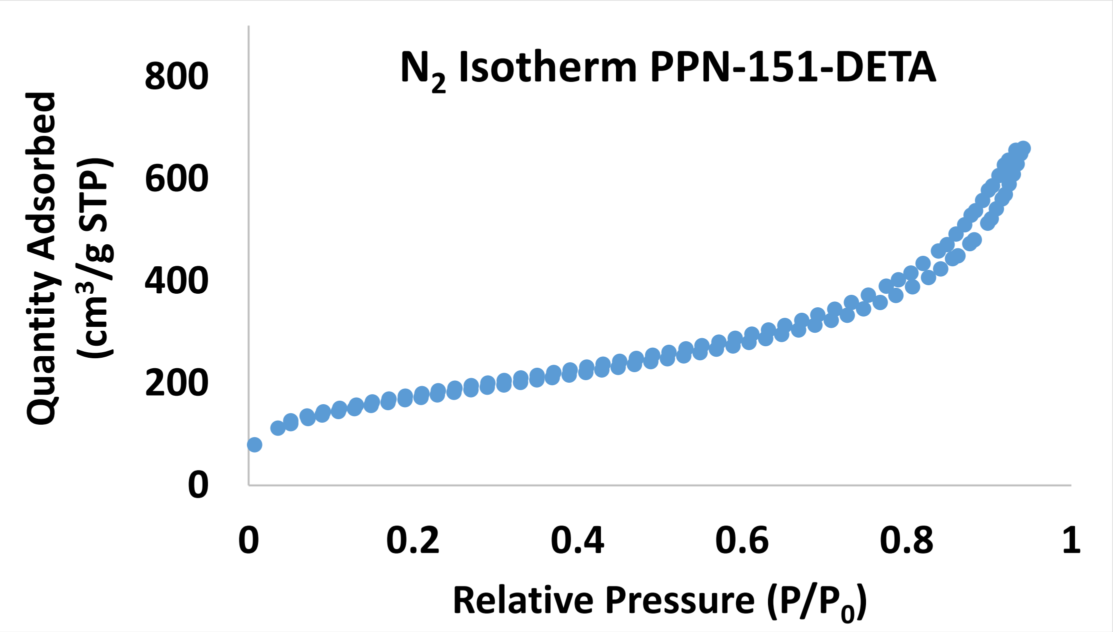
Yang, X. et al., *Polymer*. **2017**

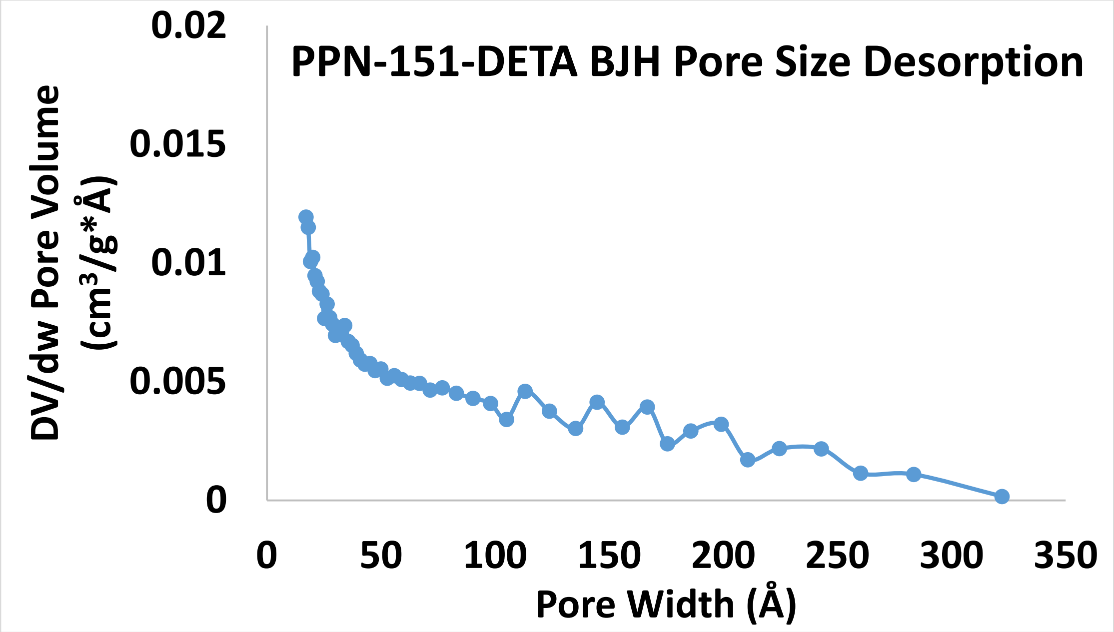
PPN-151-DETA



Tan, M. X., et al. *ChemSusChem*. **2013**, *6*, 1186

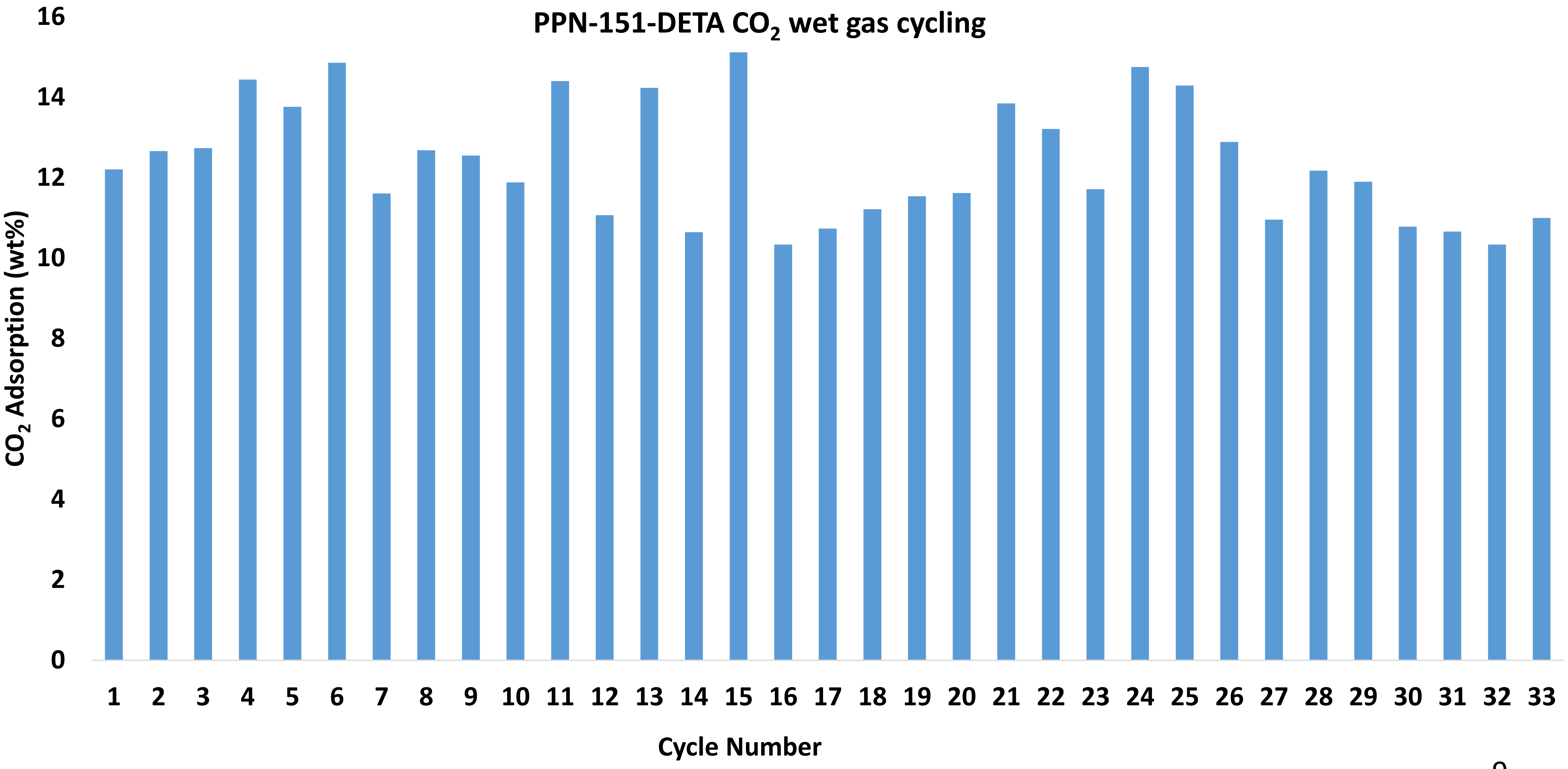
PPN-151 Porosity Measurements





BET SA (m^2/g)	Pore Volume (cm^3/g)	Average Pore Size (Å)
804	0.784	67.3

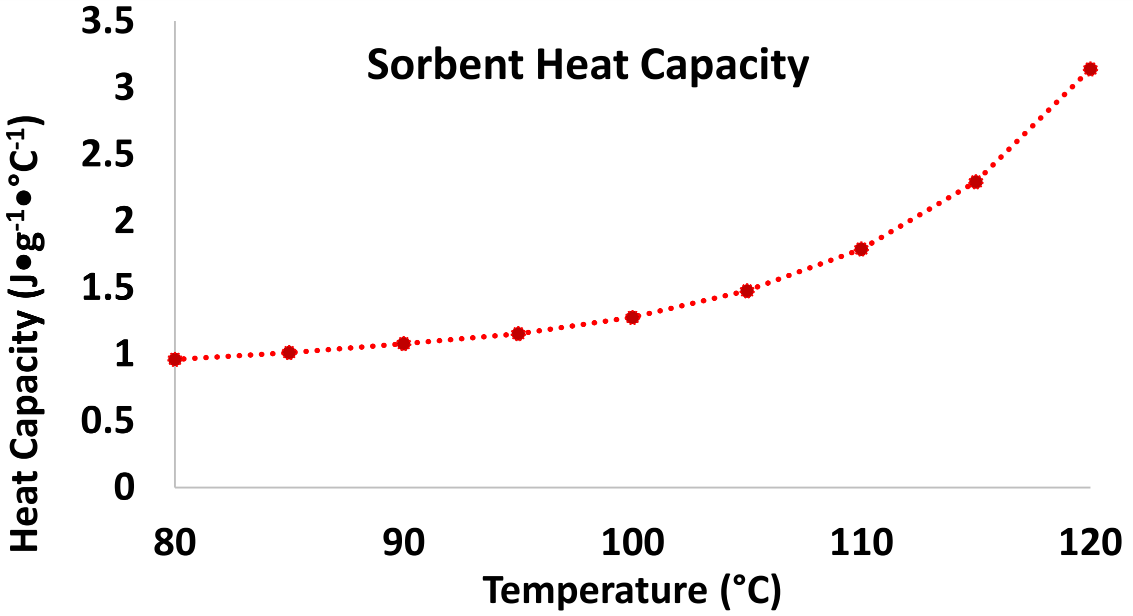
PPN-151-DETA Fixed-bed Testing Long-term Wet Cycling

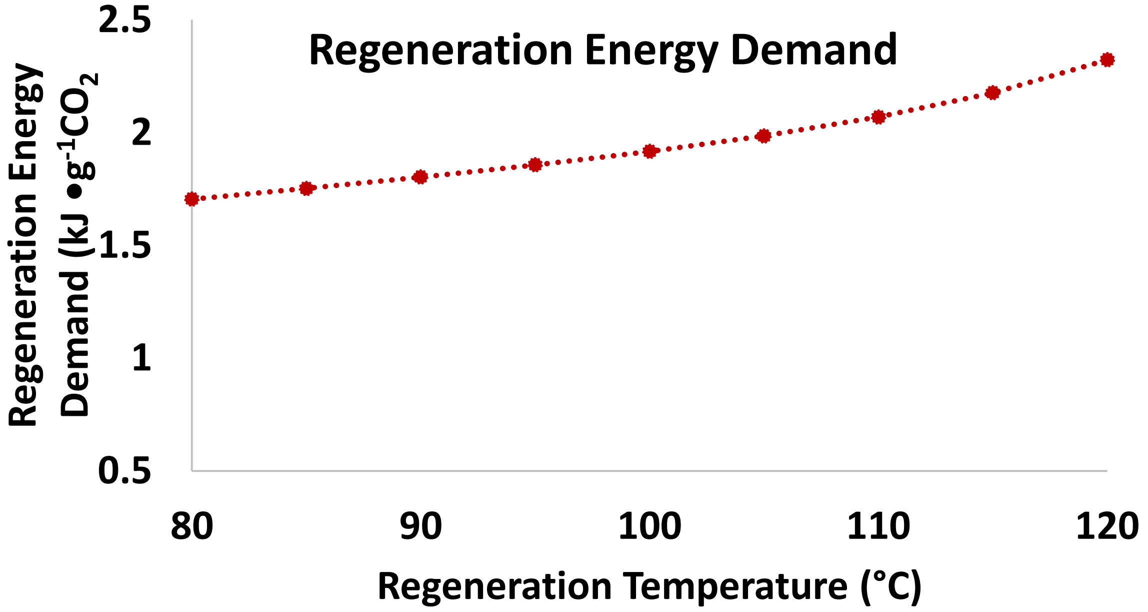


Regenerative Energy Demand

- Heat of adsorption at 150 mbar CO_2 and 40°C:
  - PPN-151-DETA: 1.40 MJ/kg CO_2
- Heat capacity increases exponentially with higher temperatures
- Regenerative energy demand at 85°C
  - PPN-151-DETA: 1.8 MJ/kg CO_2

(Typical MEA process: 3.8 MJ/kg CO_2)

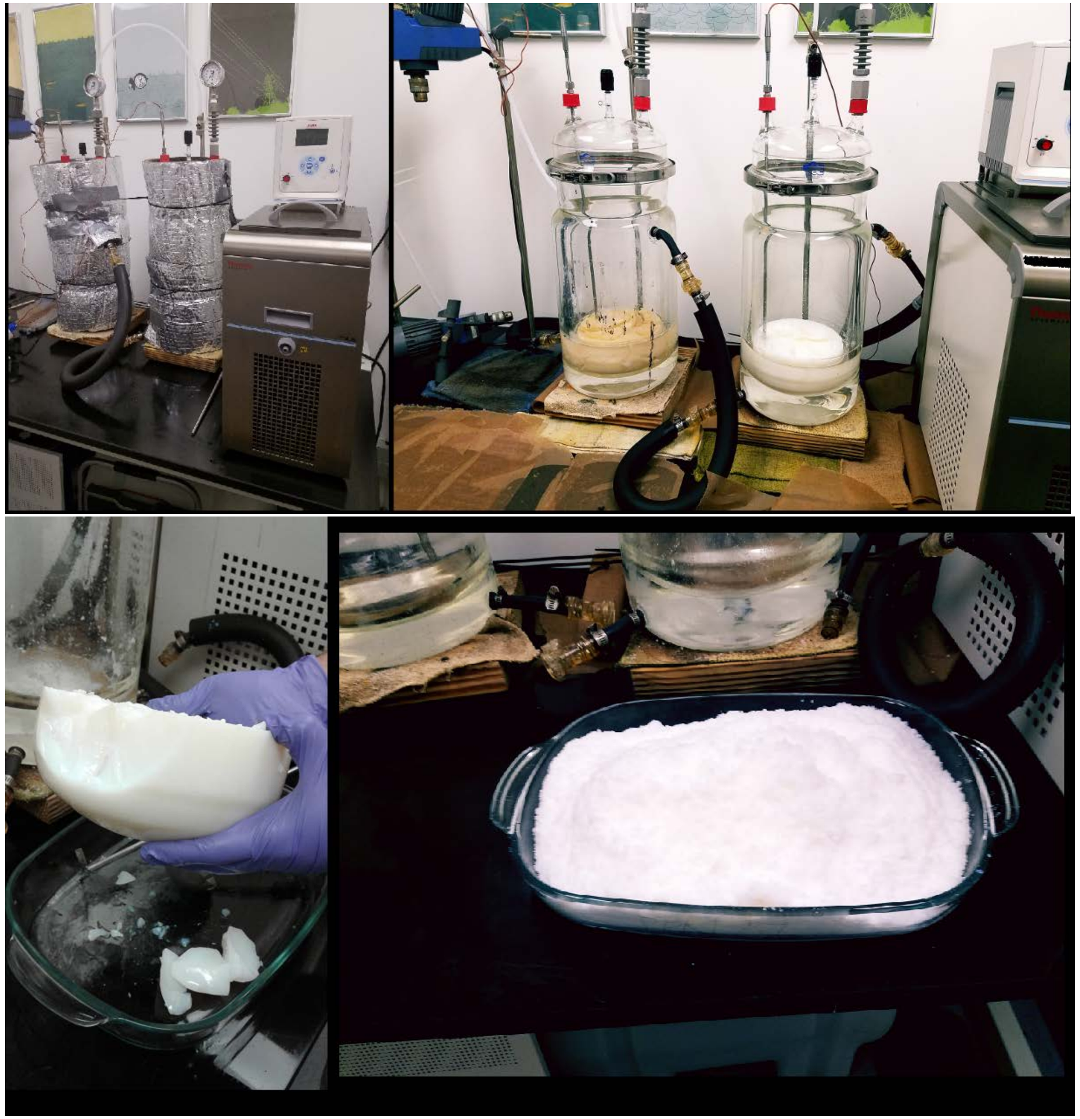




250 g Scale-up

- The team utilized *framergy*'s 10 L jacketed solvothermal reactors to scale-up the sorbent synthesis to >250 g
- ~250 g of the sorbent was produced

Parameter	Value
Temperature	150°C
Time	5 day
Headspace	~80%
Melamine	201.62 g
Paraformaldehyde	108.00 g
Cyanuric acid	15.48 g
Dimethyl Sulfoxide (DMSO)	2080 mL
BET surface area (m^2/g)	500

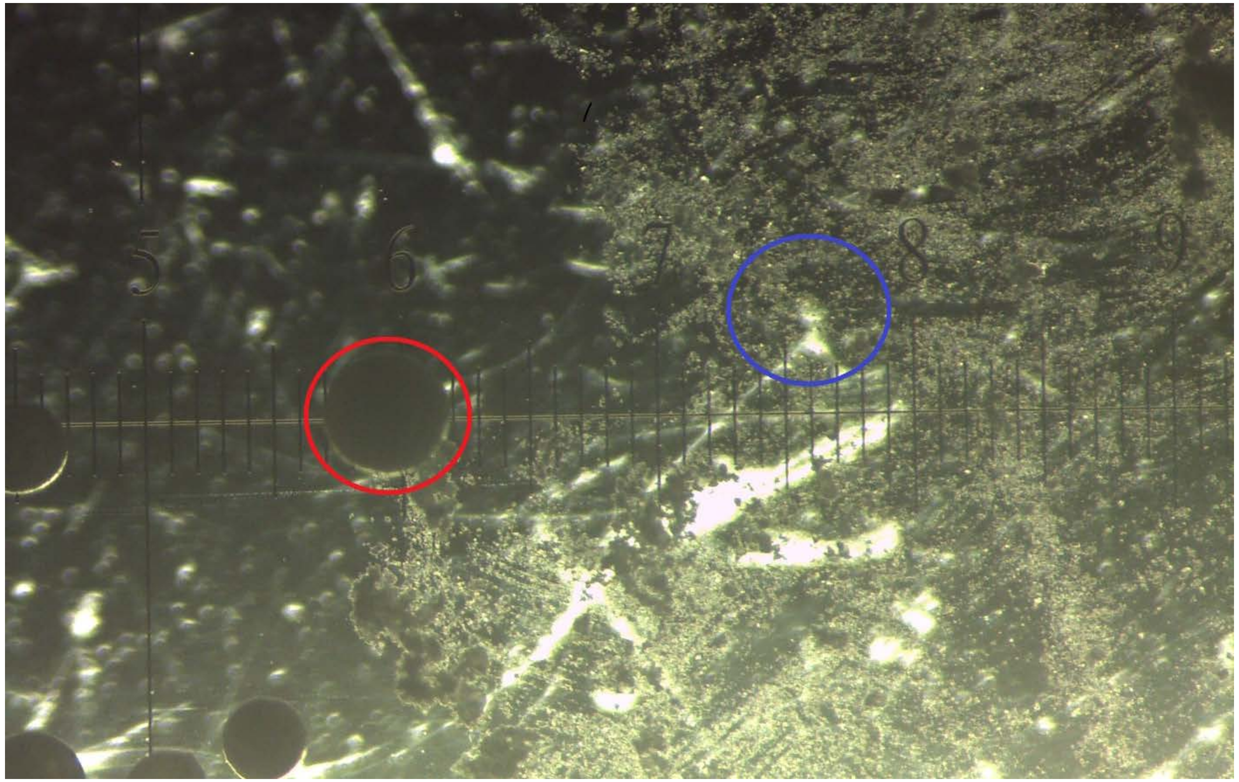


The Importance of Formaldehyde Morphology

The initial 250 g syntheses had low BET surface areas and showed a high degree of inhomogeneity

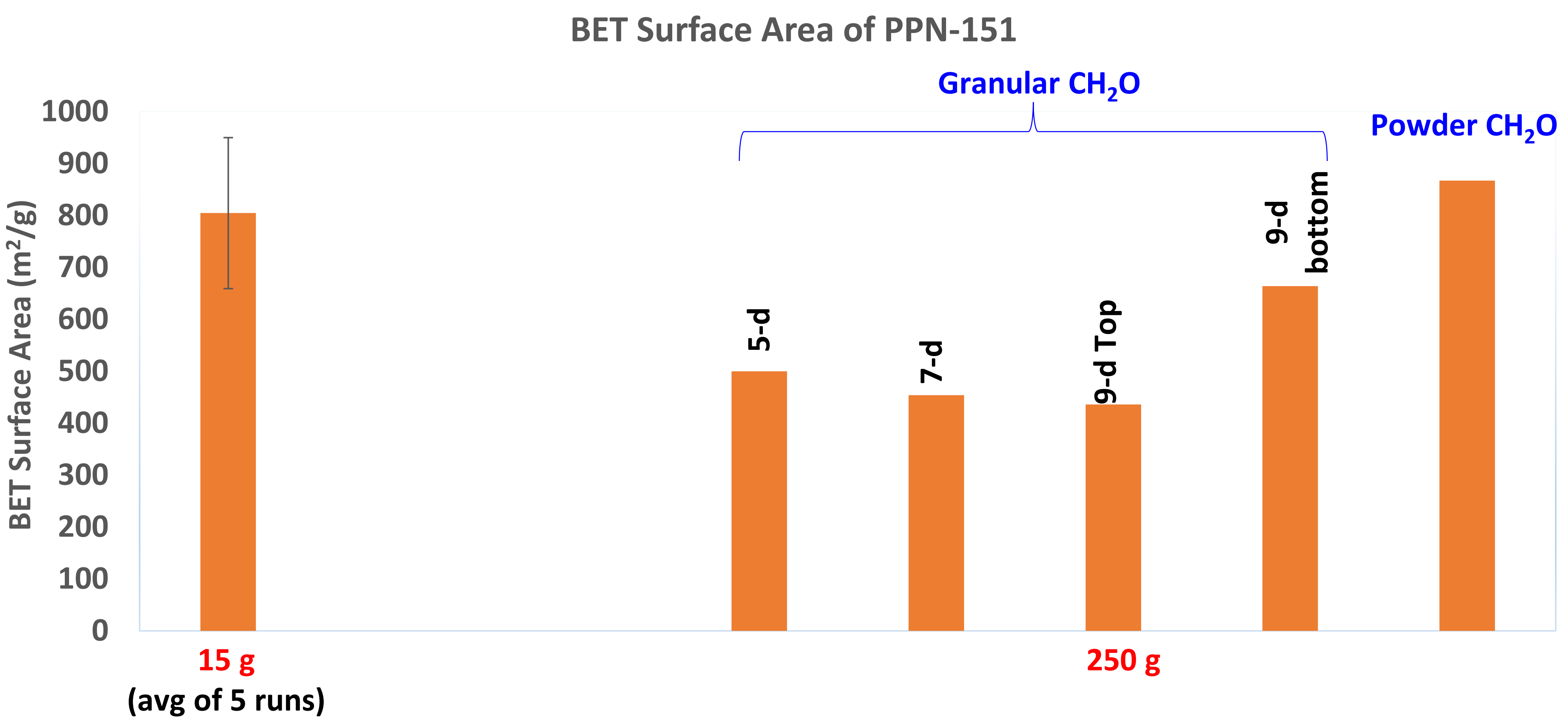
Initial 250 g batch utilizing granular paraformaldehyde

250 g batch utilizing powdered paraformaldehyde



Granular form slows down dissolution, causing inhomogeneity in the polymer and reducing the overall surface area

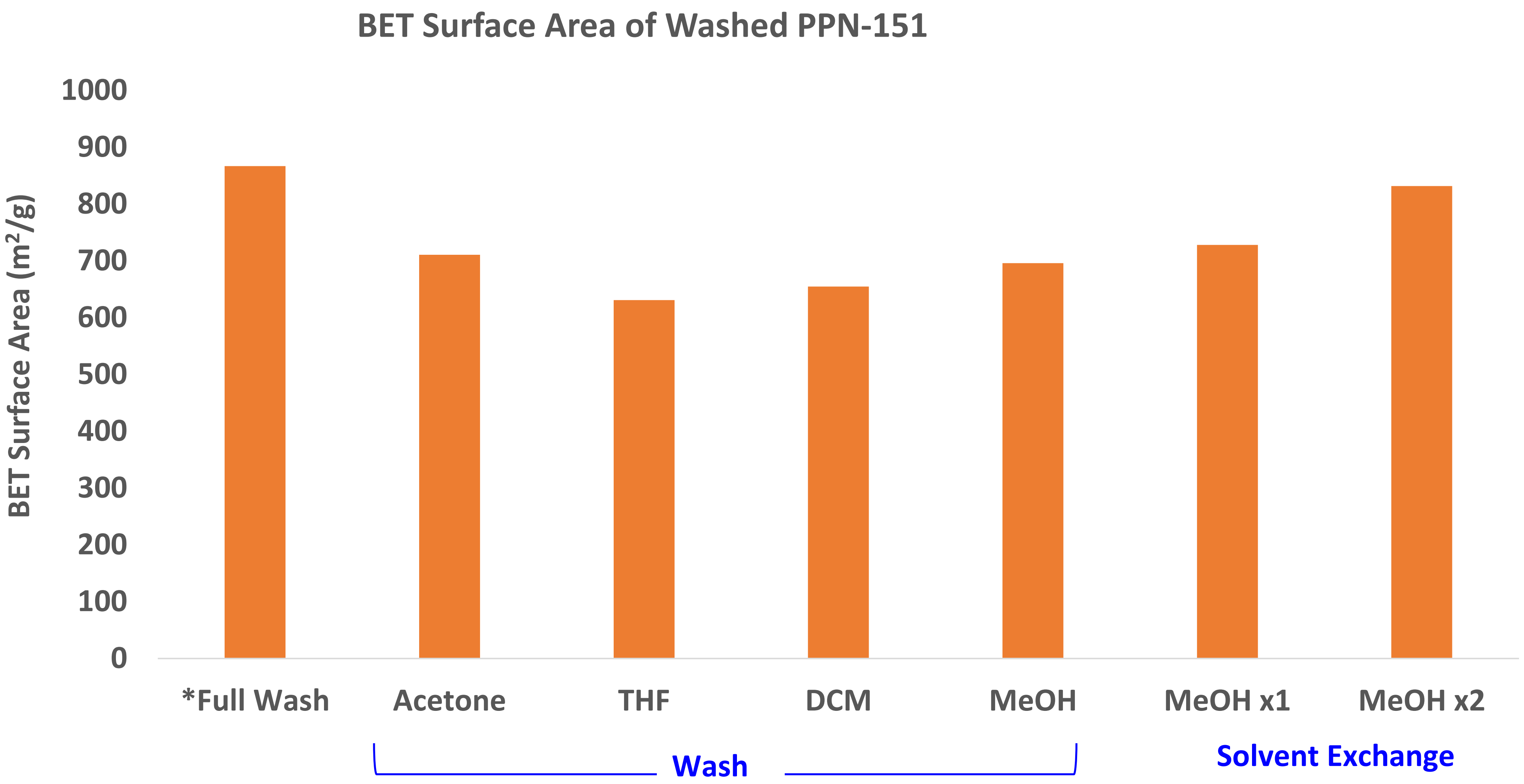
Comparison of BET Surface Area Through Scale-Up



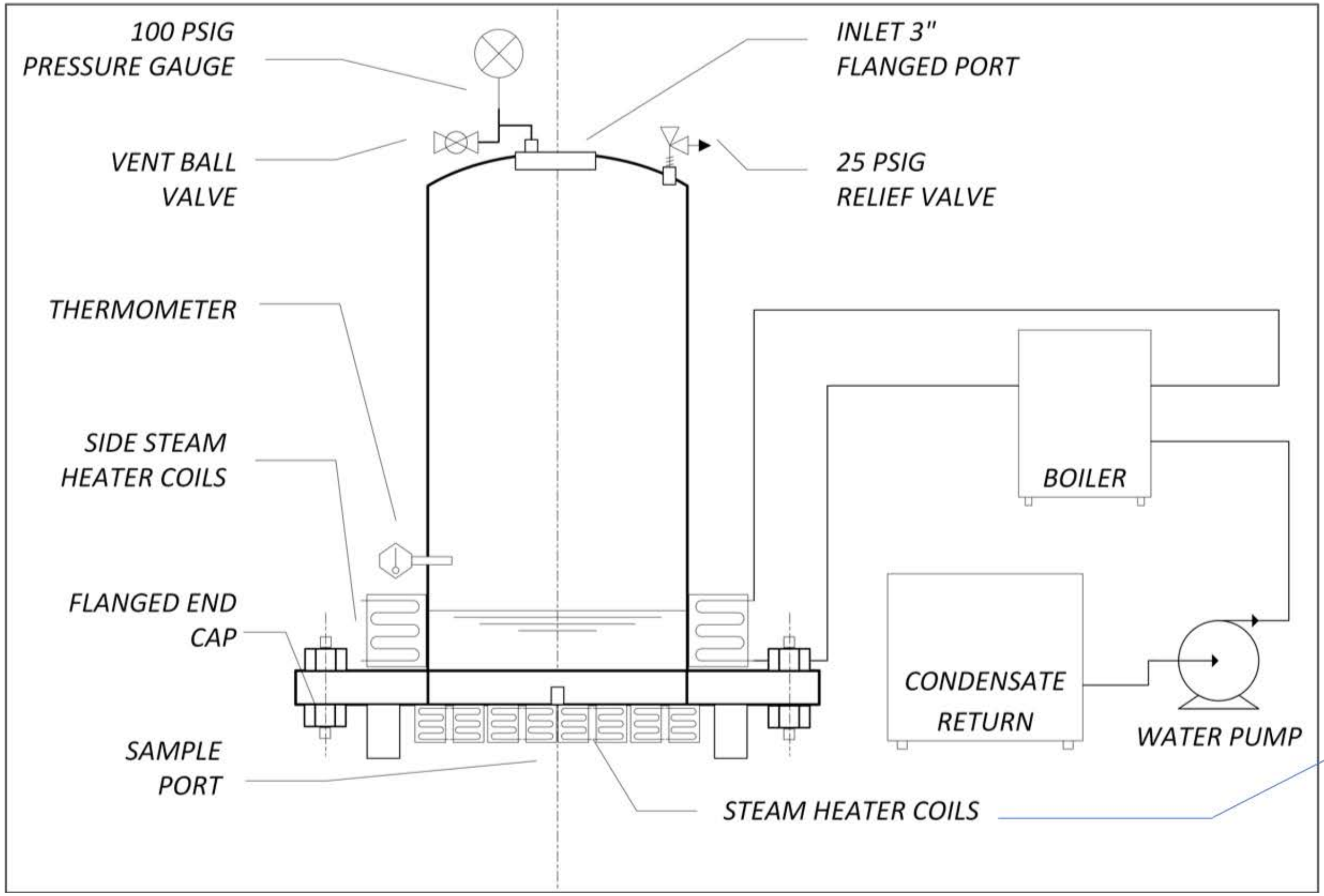
250 g Scale-up: Processing

- *framergy*'s Nutsche filter system utilized to wash sorbent (acetone, THF, DCM, methanol)
  - For 250 g batch wash with 4 L of each solvent
- Solvent Exchange (heat to 60°C in sealed Nutsche filtration device for 12 hr while agitating) twice with methanol
  - Additional 4 L

Reducing Solvent Washing: Improving Cost of Processing Steps



1 kg Scale-Up Reactor

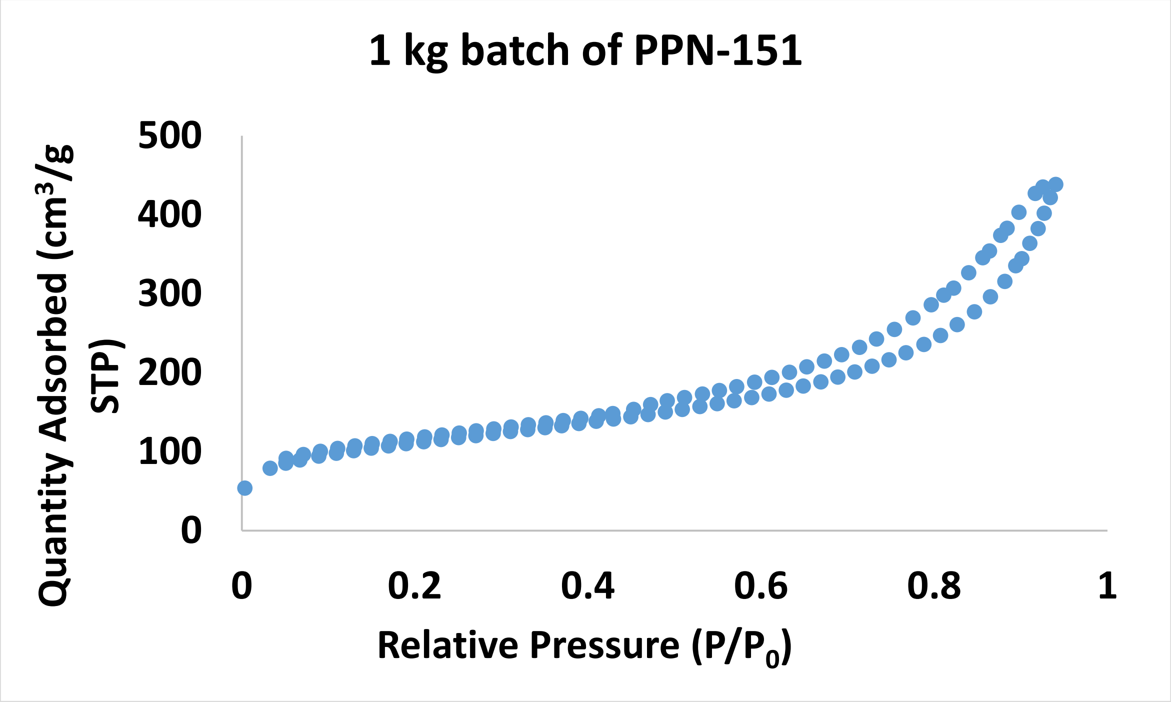


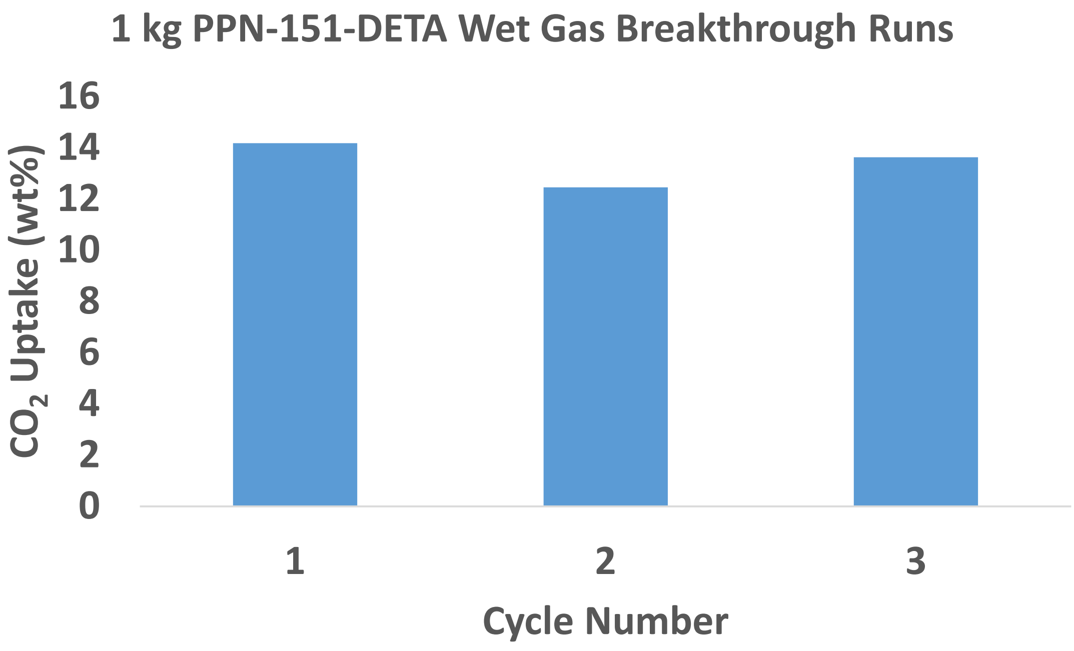
1 kg Scale-up at Vapor Point

Reaction Set-up

PPN Removal

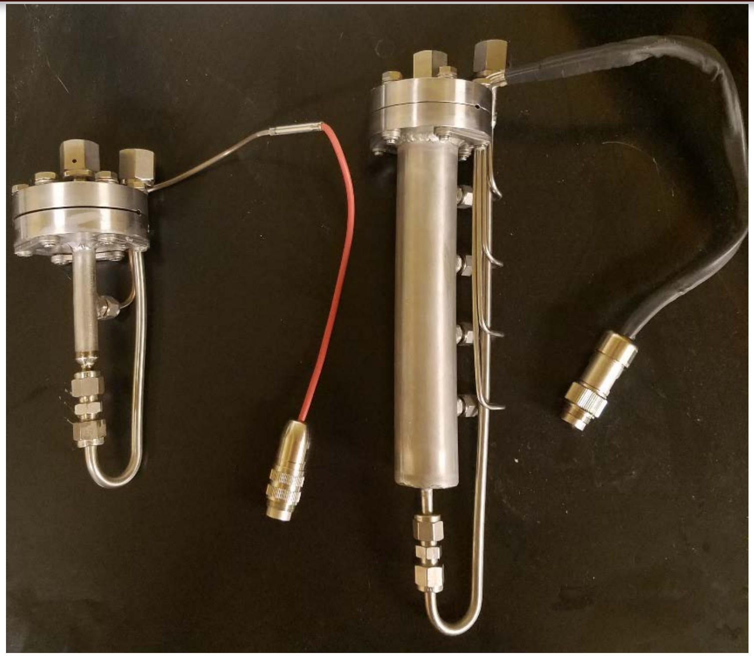
Parameters and Performance of 1 kg Batch

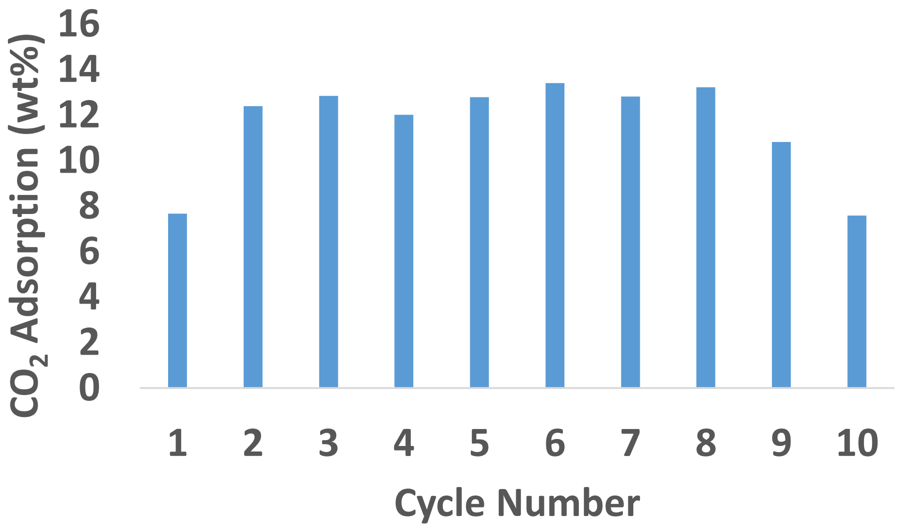




100 mL column cycling

- Previous Lab scale wet gas testing performed using a 5 mL column
- Long-term cycling tests will be done with 100 mL column
- Multiple thermocouples will inform us on temperature gradients
- Manual testing resulted in non-uniformity of runs.
  - Tests will need to be repeated upon instrument repair





Remaining Tasks

- Final cycling tasks require the fabrication of 1.5 L adsorber:
  - 400 mm double walled column, adsorber stand, heat insulation, larger mass flow controller and upgrade kit for software integration
- Instrument Manufacturer, Quantachrome Instruments, was recently bought out by Anton Paar USA Inc. delaying fabrication
- DynaSorb BT has also been shipped back for upgrades and repairs

Summary

- PPN-151-DETA can achieve > 0.1 g/g CO_2 loading at large scale
  - Parameters that have been ignored during lab scale testing can have a large impact on polymer porosity
- 1 kg synthesis performed in partnership with *framergy* and Vapor Point
  - 1 kg batch shows > 0.12 g/g CO_2
- Final cycling tests will be performed
  - 1.5 L adsorber column has been ordered from Anton Paar

Acknowledgement and Disclaimer

- Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number DE-FE0026472."

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- Vapor Point
  - Ken Mattheson

Publications

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