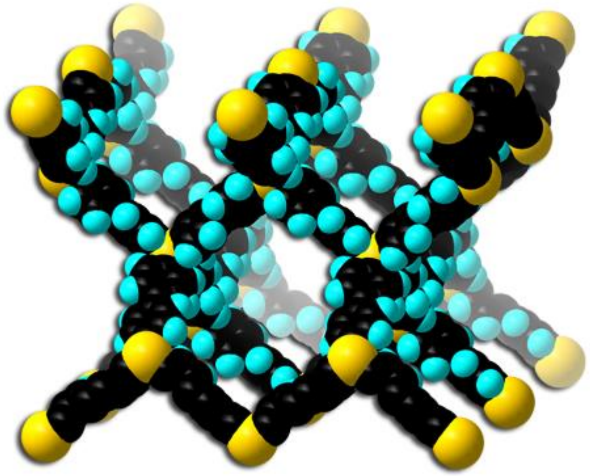
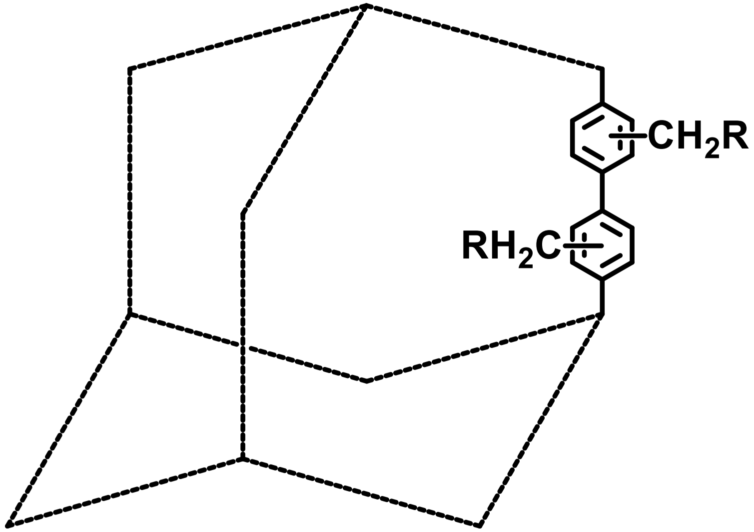
Evaluation of amine-incorporated porous polymer networks (aPPNs) as sorbents for post combustion CO_2 capture

DOE AWARD NUMBER: DE-FE0026472

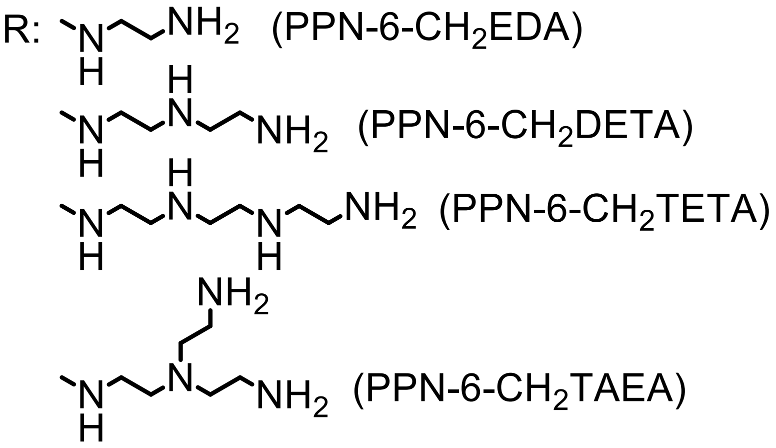
New Amine-decorated Porous Materials

- Porous Polymer Networks (PPNs)



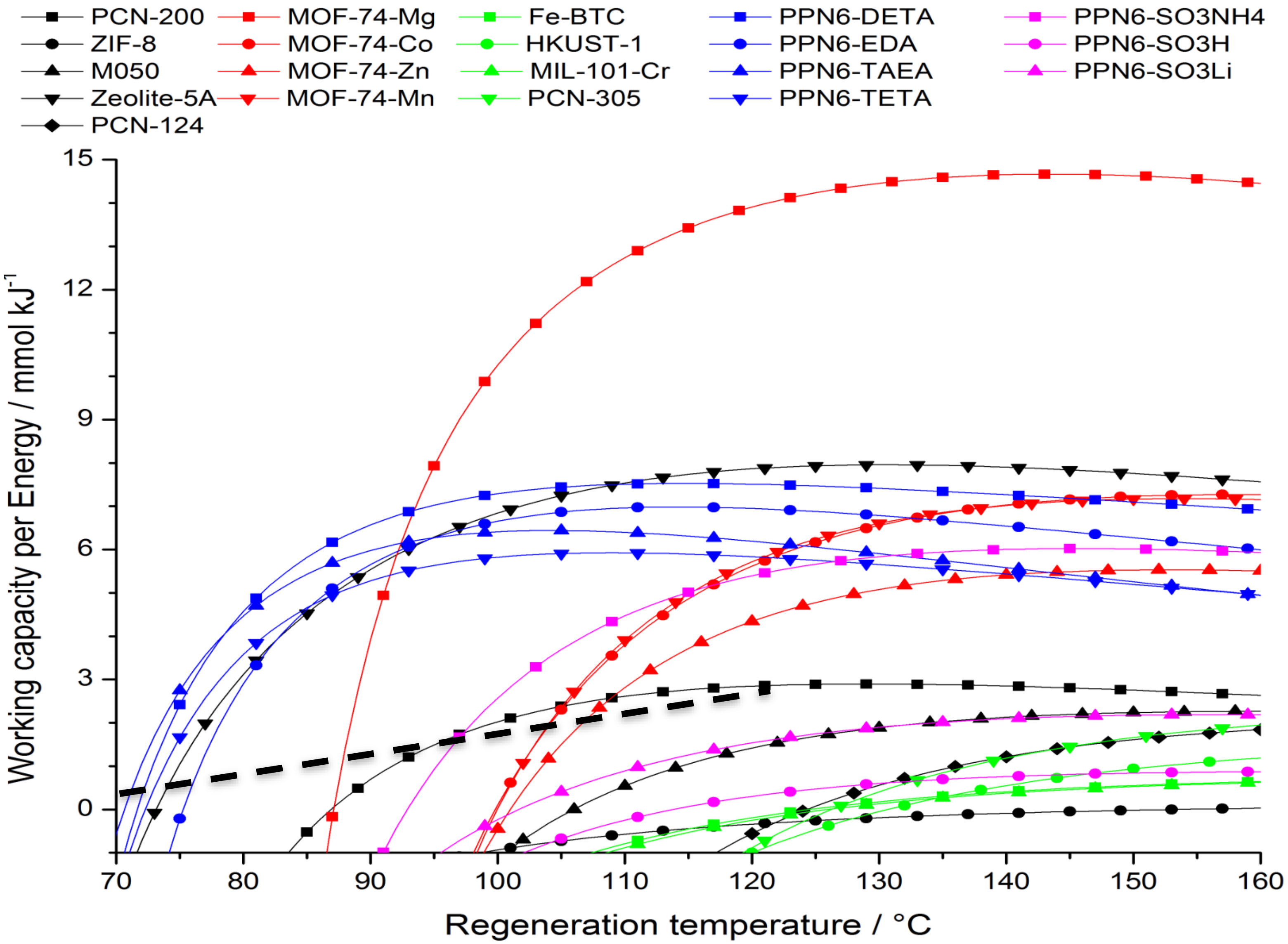


PPN-6-R



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.

Energy Efficiency



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 with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches

Project Overview

Timeline

- Start date: 10-1-2015
- End date: 9-30-2018

Budget

- Total Project funding $1,807,616
  - DOE Share: $1,446,086
  - Performer Share: $361,530

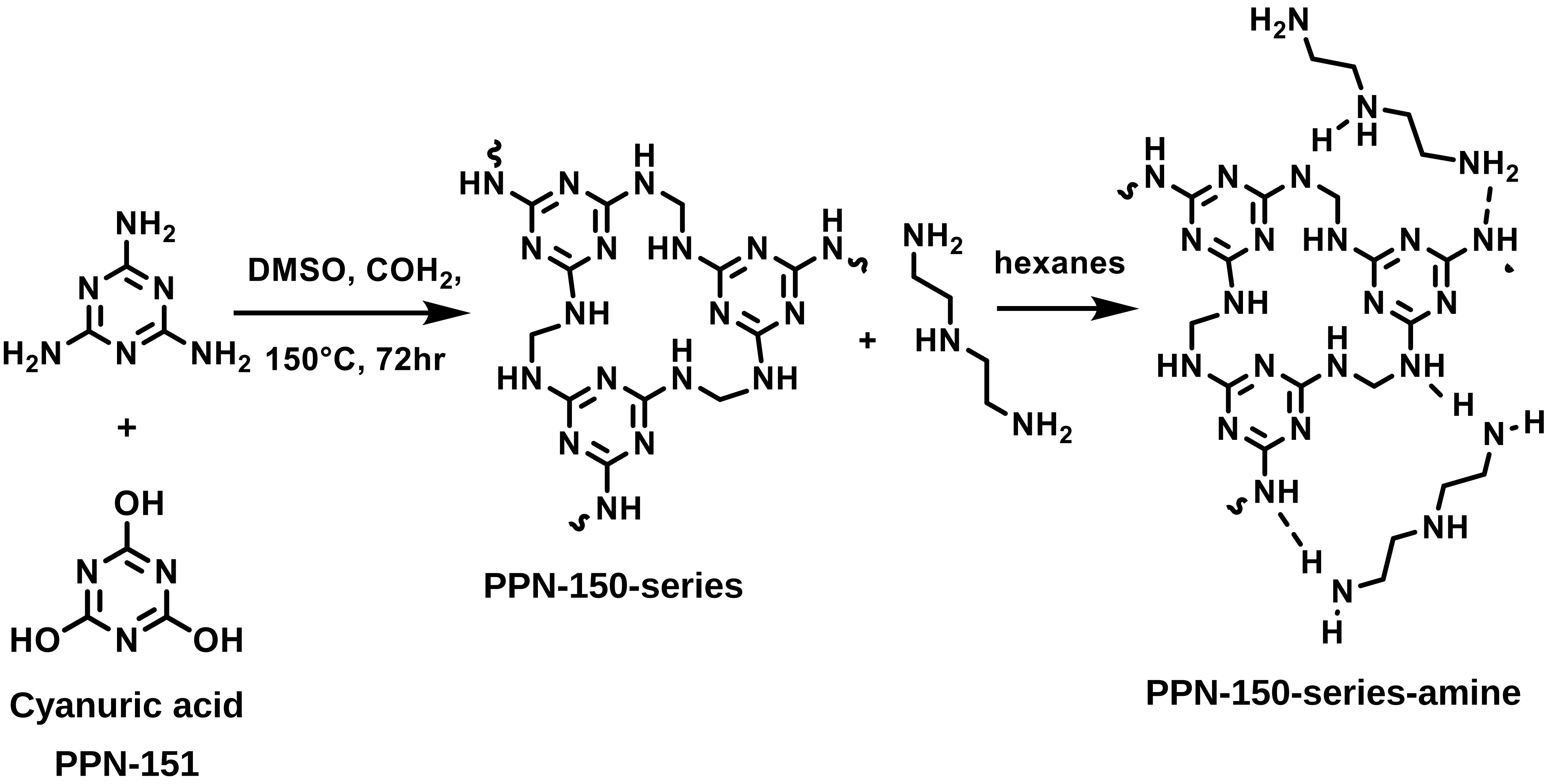
Research Team

- **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, Yujia Sun, Dr. Ning Huang
- **Past Members**: Dr. Lanfang Zou, Dr. Mathieu Bosch, Dr. Xuan Wang

Resource Loaded Schedule

					Budget Period 1				Budget Period 2				Budget Period 3			
Task	Mileston	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
1.0- Program Management and Planning	a, b	9/30/2015	9/30/2018	$ 187,853												
1.1-Project Management Plan		9/30/2015	9/30/2018													
1.2-Briefings and Reports		9/30/2015	9/30/2018													
2.0-Sorbent Synthesis and Optimization	c, f, J, k	9/30/2015	9/30/2016	$ 352,156												
3.0-Initial Sorbent Testing	d	9/30/2016	9/30/2016	$ 286,656												
3.1-Physisorption Tests	e	9/30/2015	6/30/2016													
3.2-Physical Property Characterization	g	1/30/2015	6/30/2016													
3.3-Initial TGA Tests	h	1/30/2016	6/31/16													
3.4-Initial Degredation Studies	i	3/30/2016	9/30/2016													
4.0-Sorbent Optimization	m	9/30/2016	9/30/2017	$ 202,042												
5.0-Initial Sorbent Scale-up	n, o	1/30/2017	6/31/2017	$ 191,585												
6.0-Initial Fixed Bed Testing	l, p	9/30/2016	9/30/2017	$ 65,000												
7.0-Attrition and Mechanical Hardness Tests	q	1/30/2017	6/30/2017	$ 34,300												
8.0-Sorbent Production	r	9/30/2017	6/30/2018	$ 221,330												
9.0-Optimal Fixed Bed Testing	s	1/30/2018	9/30/2018	$ 186,694												
10.0-Technology Assessment	t	3/30/2017	9/30/2018	$ 80,000												
			Total	$ 1,807,616												

PPN-150 Series



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

PPN-150-Series Synthesis Optimization

- **Select parameters optimized**
  - Reaction temperature
  - **Reaction time**
  - **Reactor headspace**
  - Reactor pressure
  - Stirring rates
  - **Solvent systems**
  - Templating agents
  - Wash cycles
  - Grinding conditions
  - **Amine loading times and conditions**

Reactor Headspace Optimization

Reactor headspace optimization for PPN-150				
Headspace	**Reaction vessel**	**BET Surface Area (m^2/g)**	**Pore Size Å**	**Pore Volume (cm^3/g)**
81.7%	**Pressure Tube**	**856.6**	**77.8**	**0.68**
50.0%	**Pressure Tube**	**838.4**	**79.2**	**0.89**
11.6%	**Pressure Tube**	**722.5**	**78.2**	**0.80**

- Headspace <80% yields optimal surface area

Solvent System Optimization

Solvent optimization data for PPN-150			
Solvent Mixture	BET Surface Area (m^2/g)	Pore Size Å	Pore Volume (cm^3/g)
Ethylene glycol	356.3	98.4	0.76
DMSO	854.1	87.1	1.11
Ethylene glycol/Ethanol	251.5	103.7	0.54
DMSO/H_2O	113.9	84.7	0.14
Ethylene glycol/H_2O	298.0	107.0	0.65
Ethylene glycol/Methanol	278.6	104.2	0.60
DMSO/Methanol	518.3	92.1	0.51

- Neat DMSO yields highest surface area

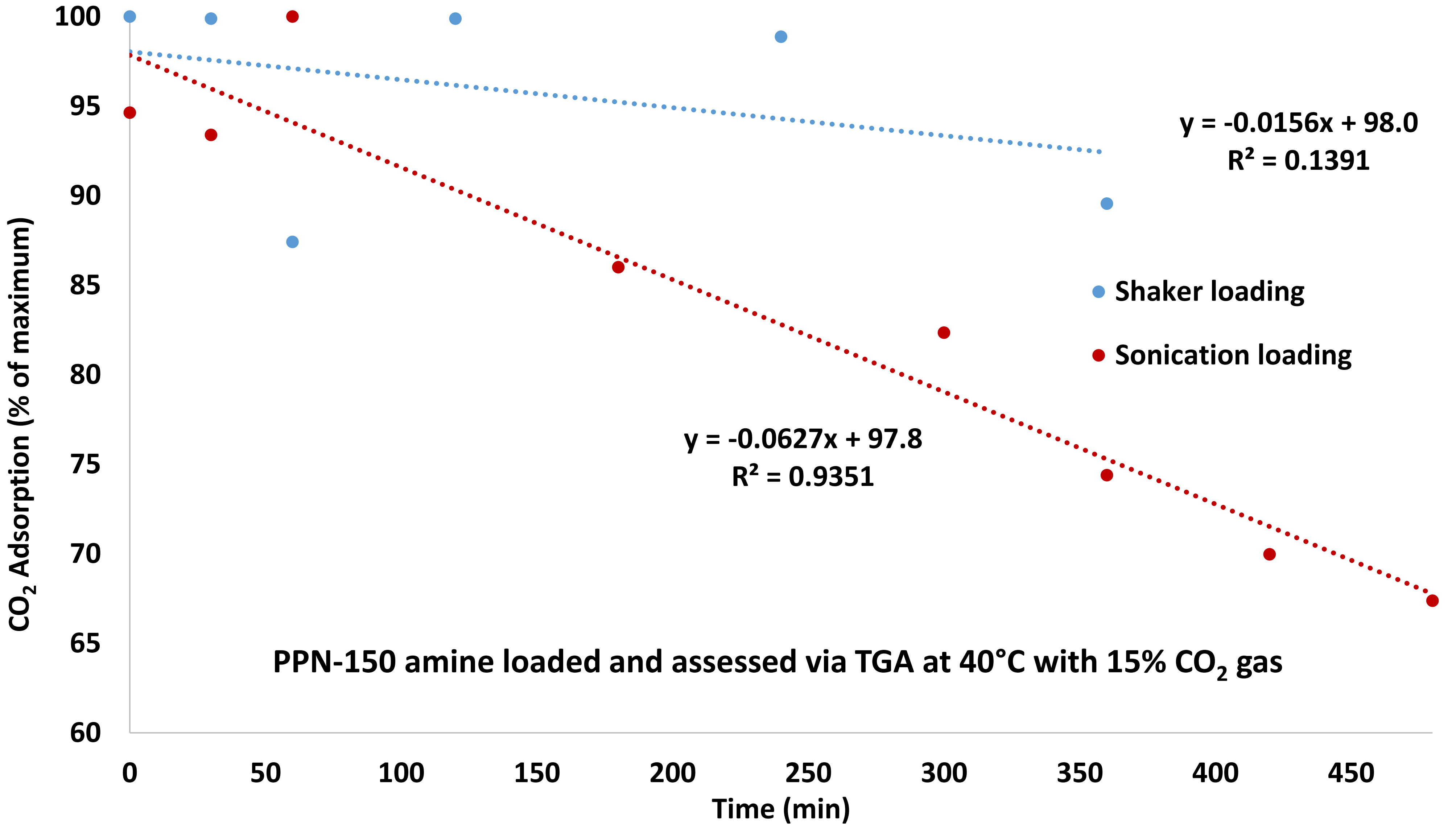
Reaction Time Optimization

Time optimization for PPN-150			
Synthesis time (days)	BET Surface Area (m^2/g)	BET Pore Volume (cm^3/g)	TGA CO_2 Uptake (wt%)
3	730	0.30	9.6%
5	640	0.28	9.2%
7	1014	1.04	5.3%

- 3-5 days yields sorbent with highest "useful" porosity

Amine Loading Optimization

Shaker shows more consistent loading

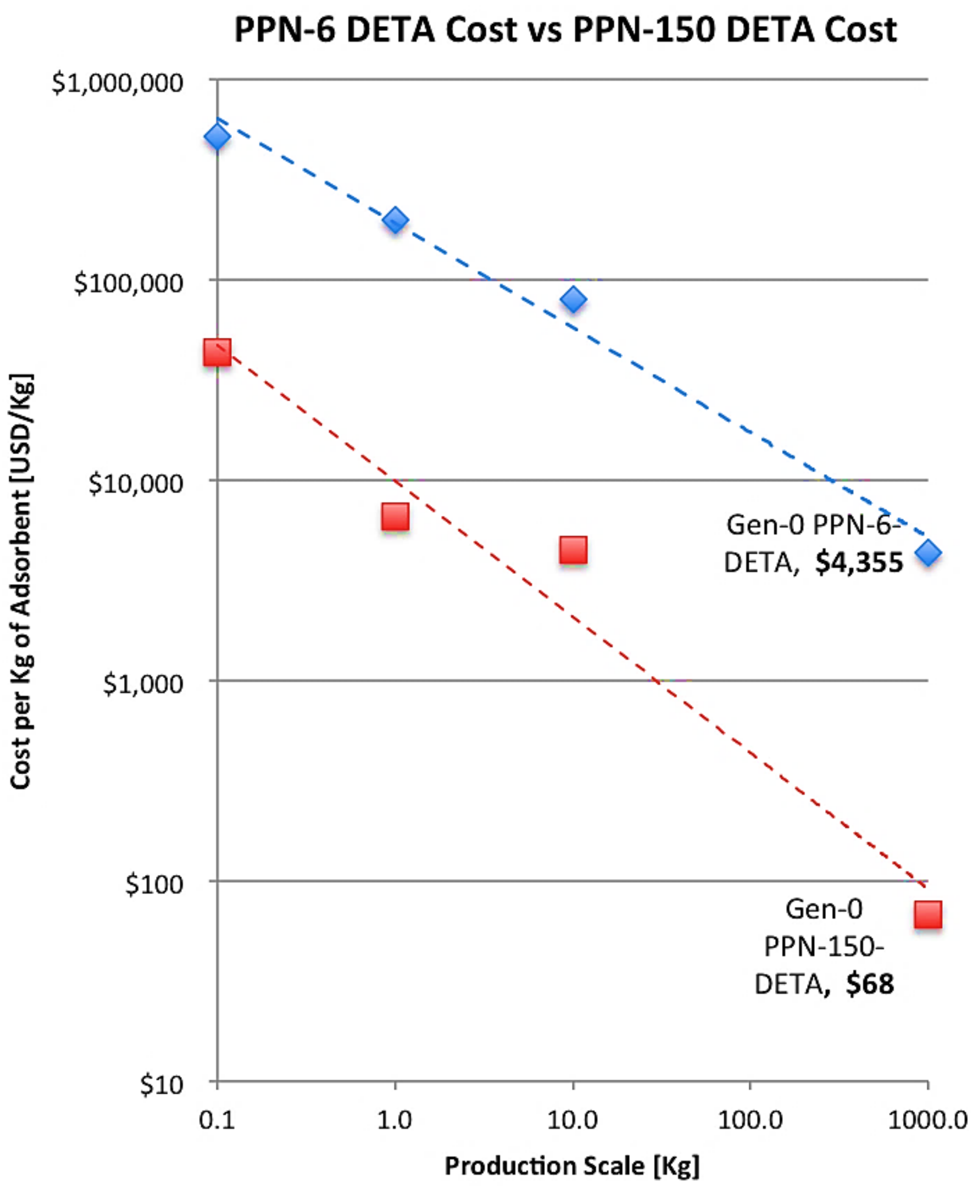


PPN-150-Series Synthesis Optimization

- **Parameters optimized**
  - Reaction temperature → **150-170°C**
  - **Reaction time → 3-5 days**
  - **Reactor headspace → 80-90%**
  - Reactor pressure → **Low pressure**
  - Stirring rates → **Static**
  - **Solvent systems → DMSO**
  - Templating agents → **Cyanuric acid**
  - Wash cycles → **Acetone, tetrahydrofuran, dichloromethane, methanol**
  - Grinding conditions → **Ball-milled**
  - **Amine loading times and conditions → DETA, 1 h shaker, hexane solvent, THF wash**

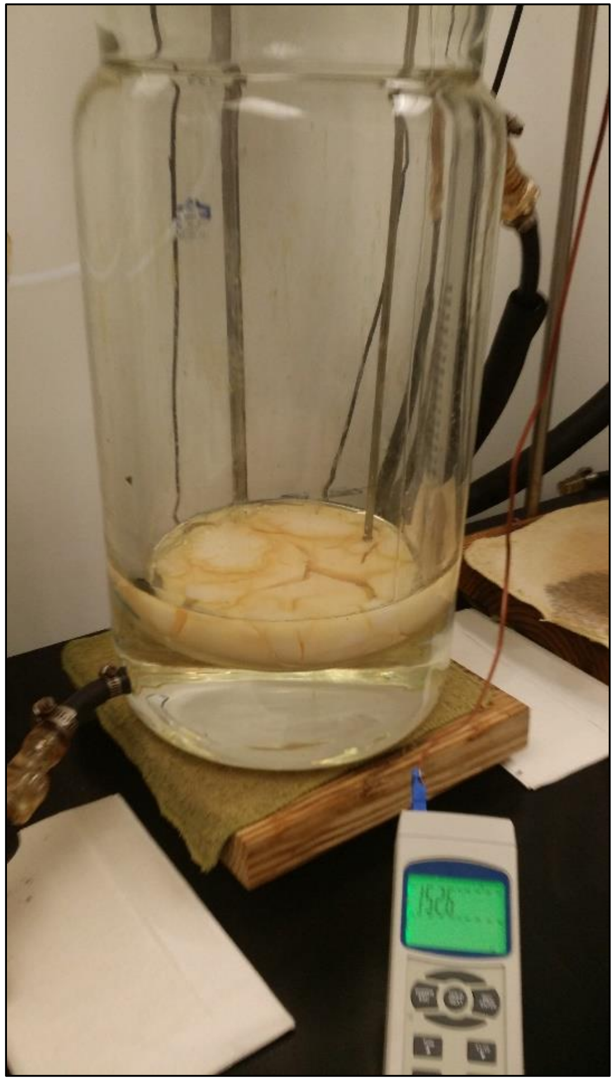
Initial Cost Analysis

- *Framergy*™ assists in sorbent scale-up and industrial partnership
- Initial cost analysis shows increasing cost reduction as synthesis scales-up
- Further cost reduction predicted with improved solvent recycling

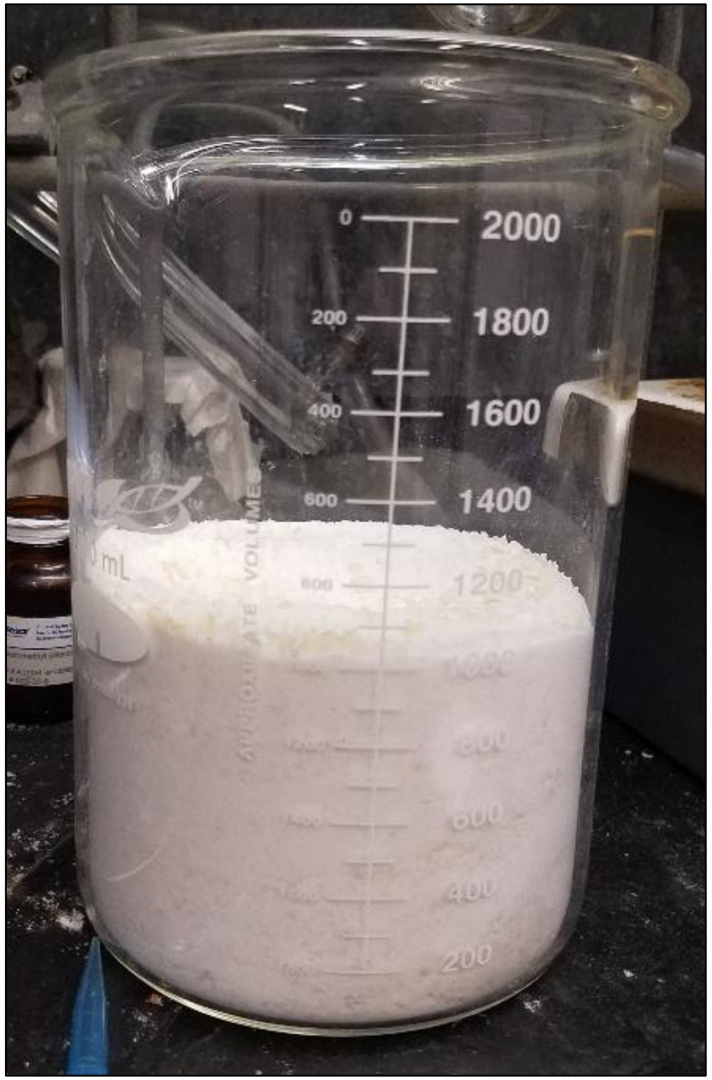


Initial 50 g Scale-up

- The team utilized *framergy*’s 10 L jacketed solvothermal reactors to scale-up the sorbent synthesis
- Real-time monitoring with webcams



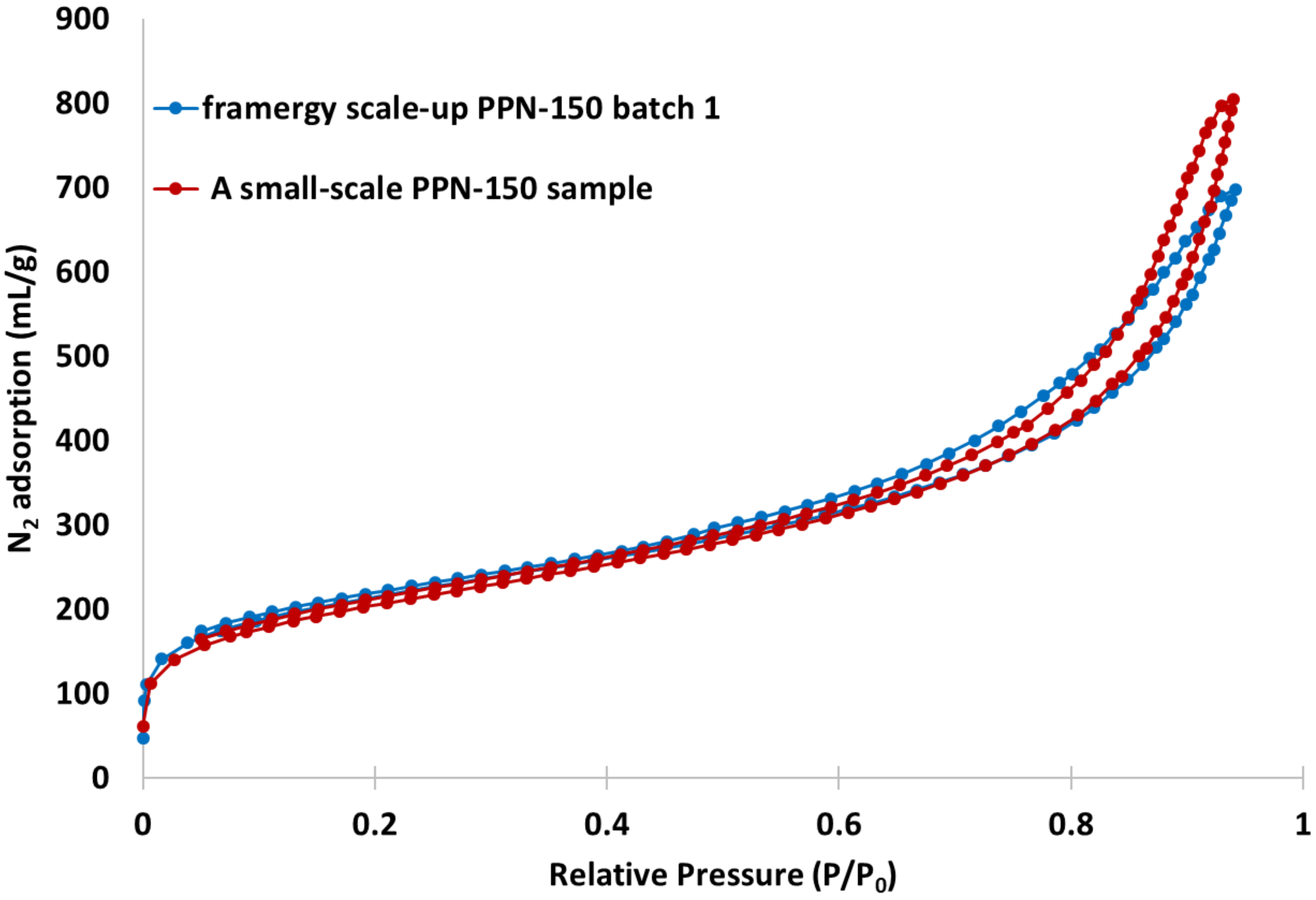
Reactor



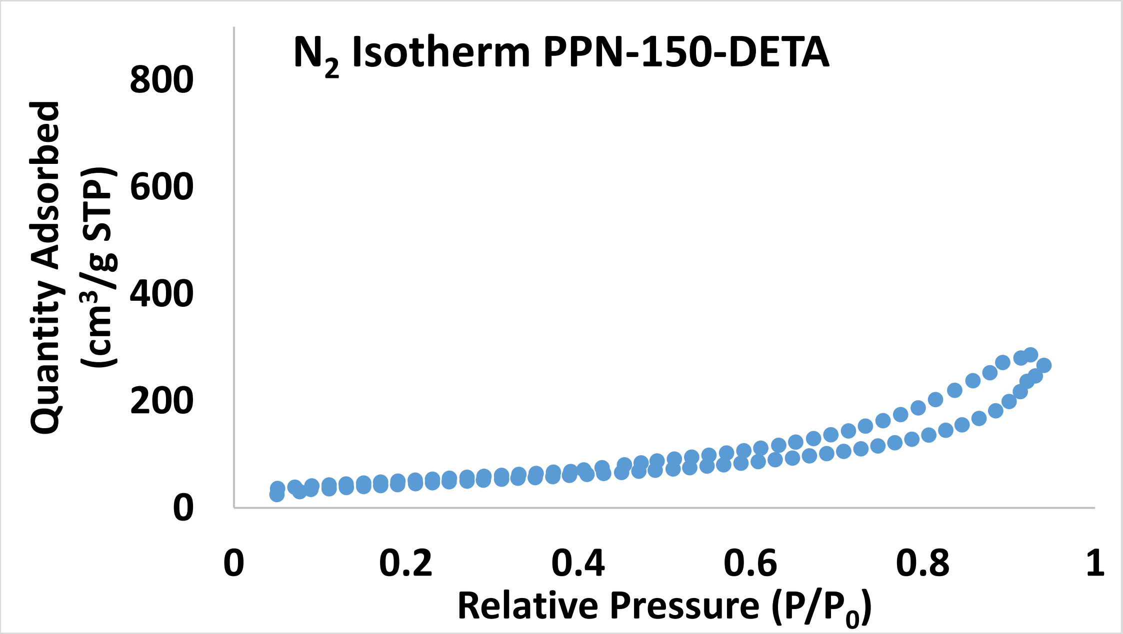
~1 L of PPN-150

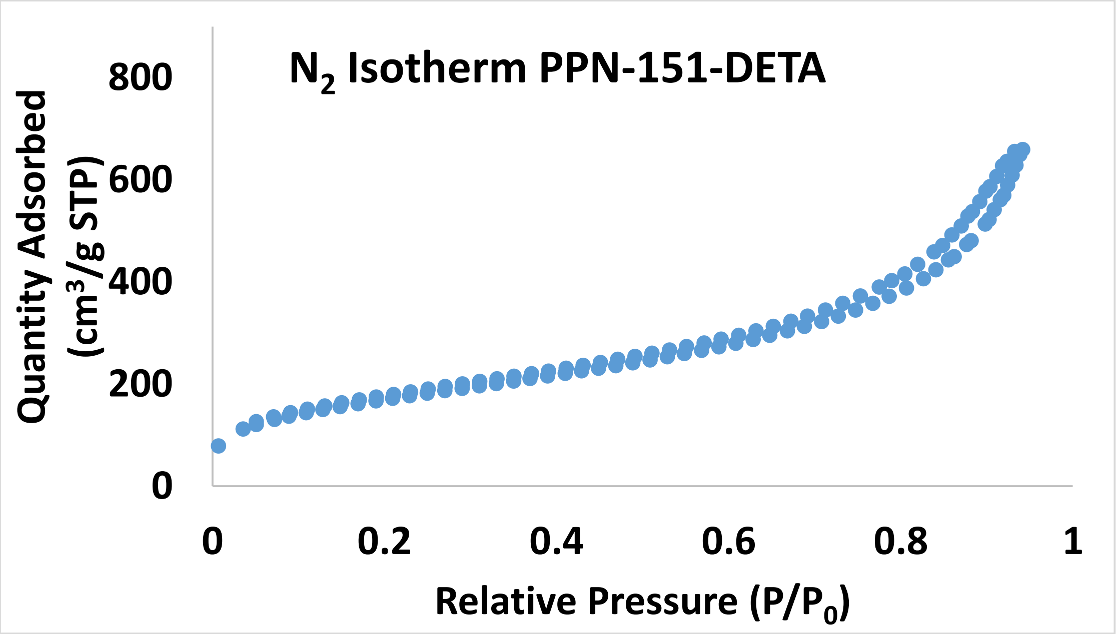
Initial 50 g Scale-up: BET Evaluation

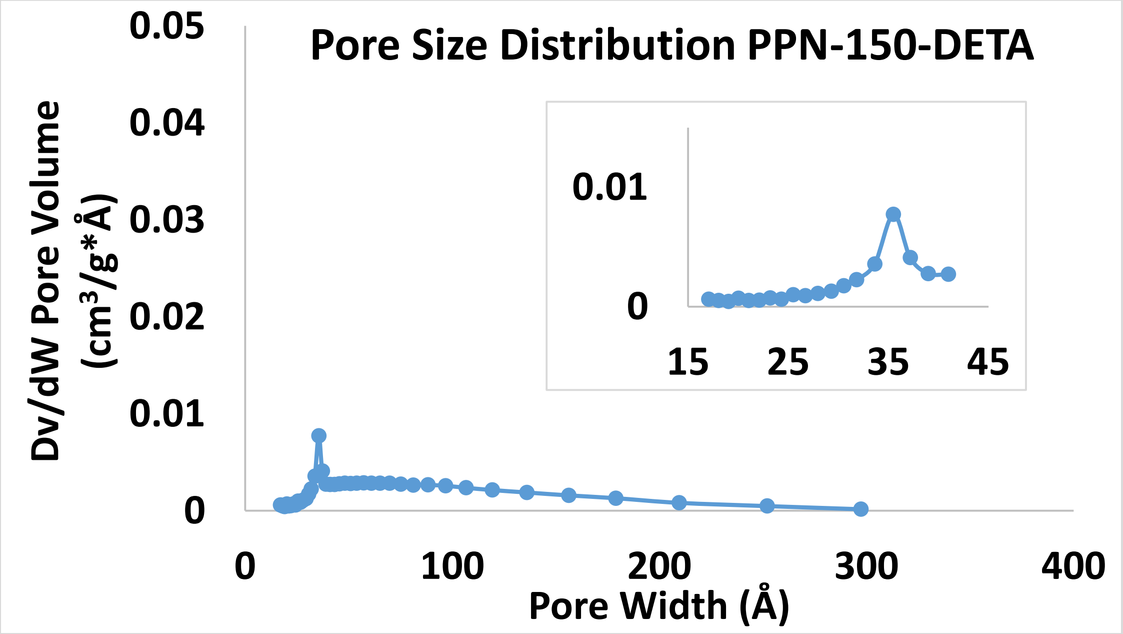
- Comparable BET isotherms between small and large batches

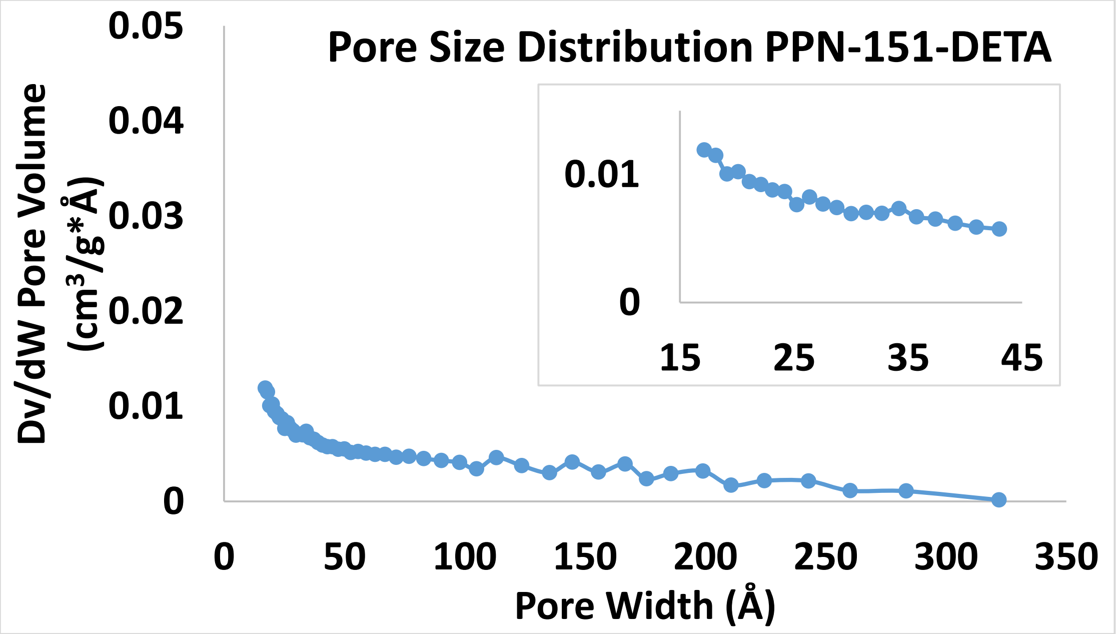


50 g DETA-Loaded PPN-150-series: Pore-Size Analysis

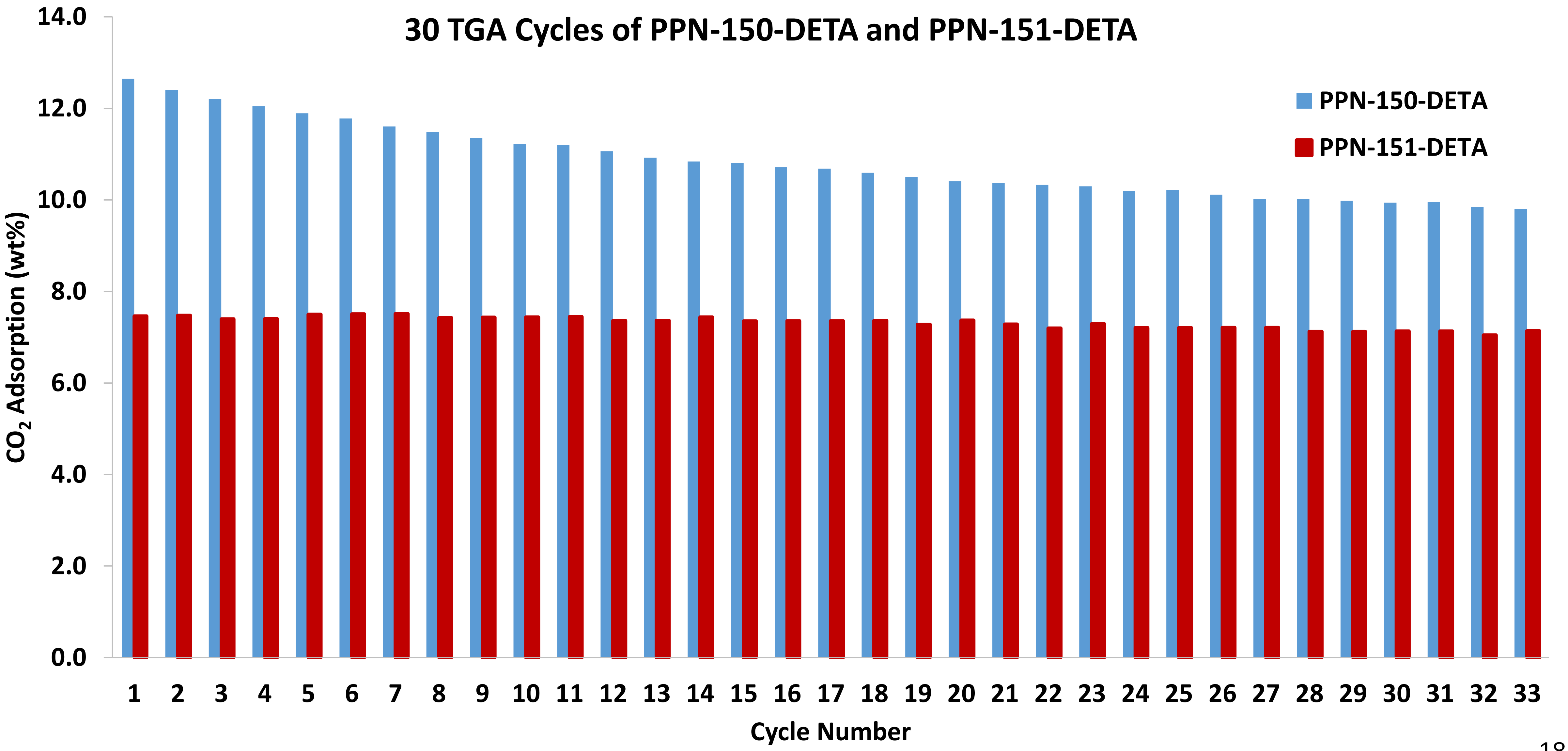




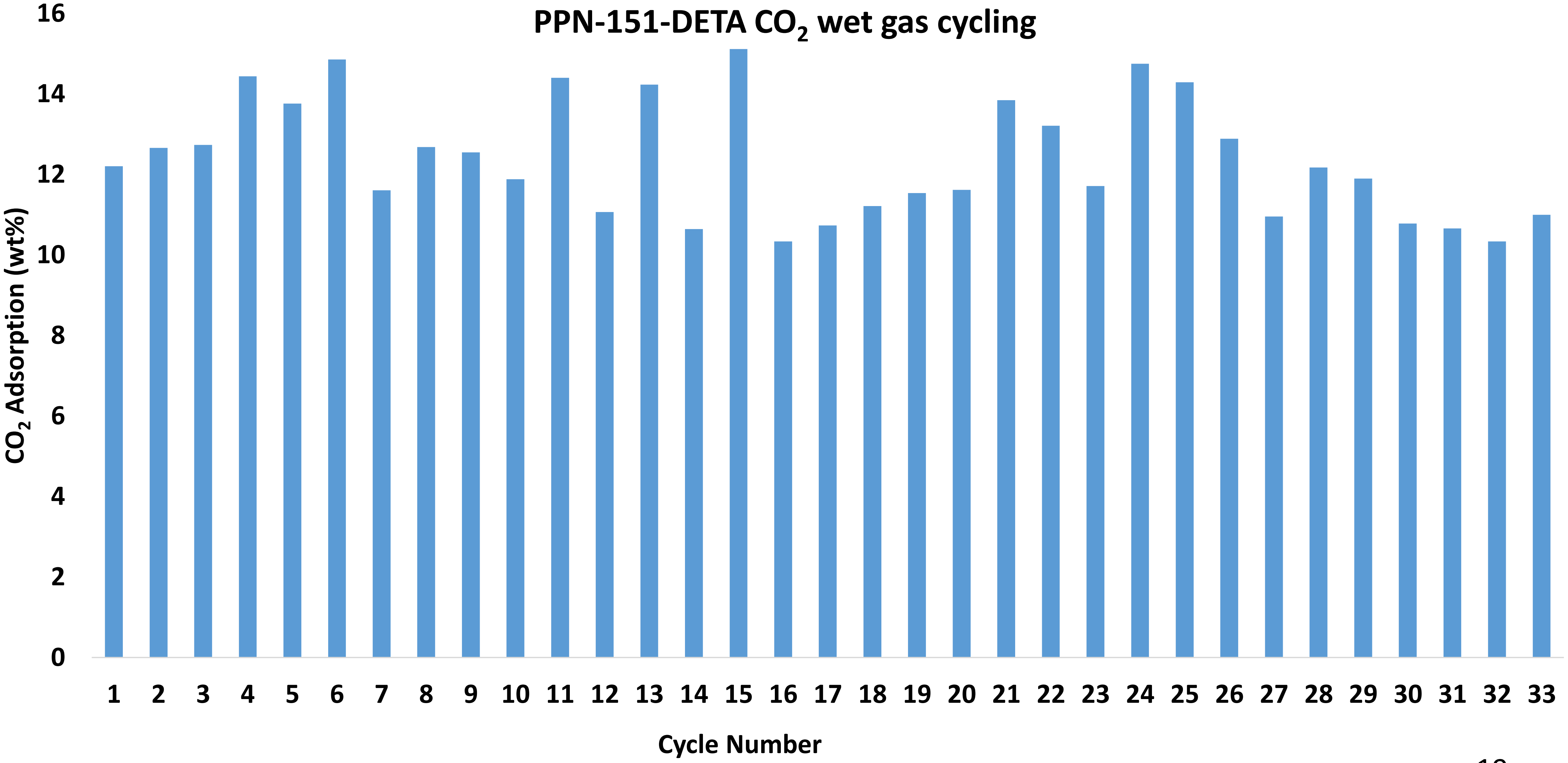




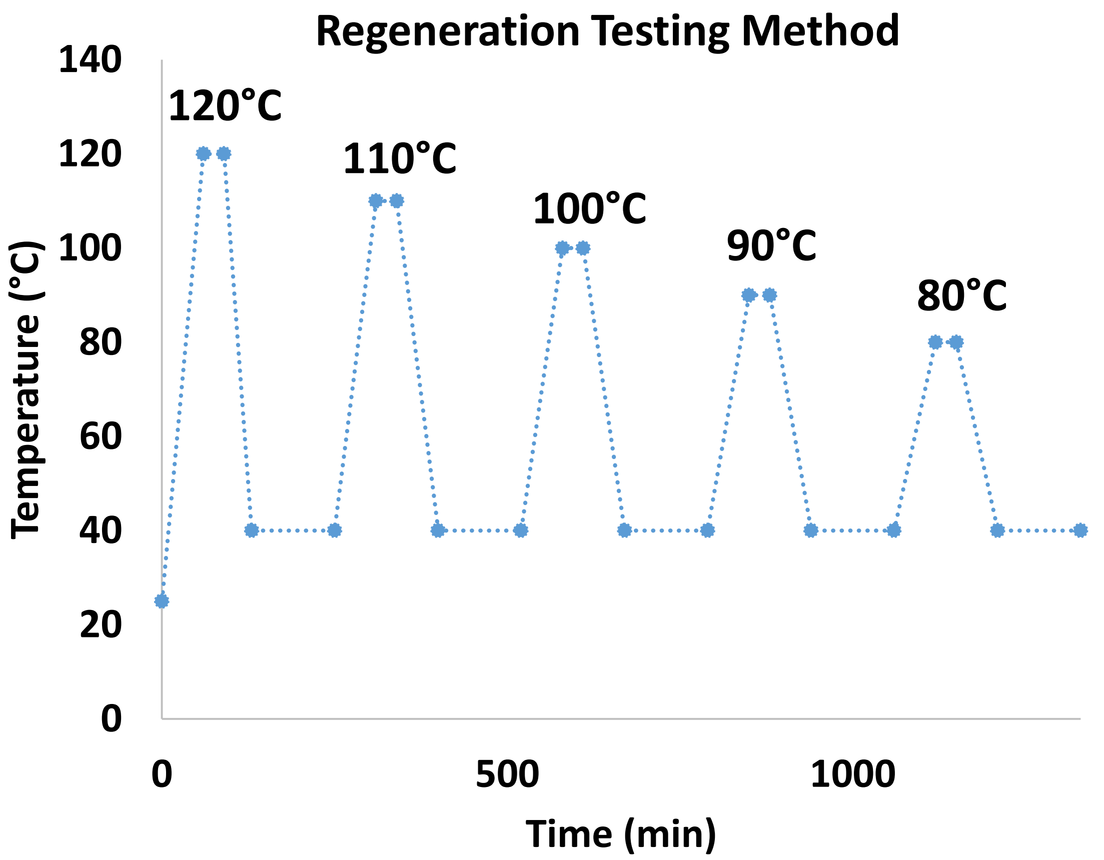
50 g Scale-up: TGA Cycling

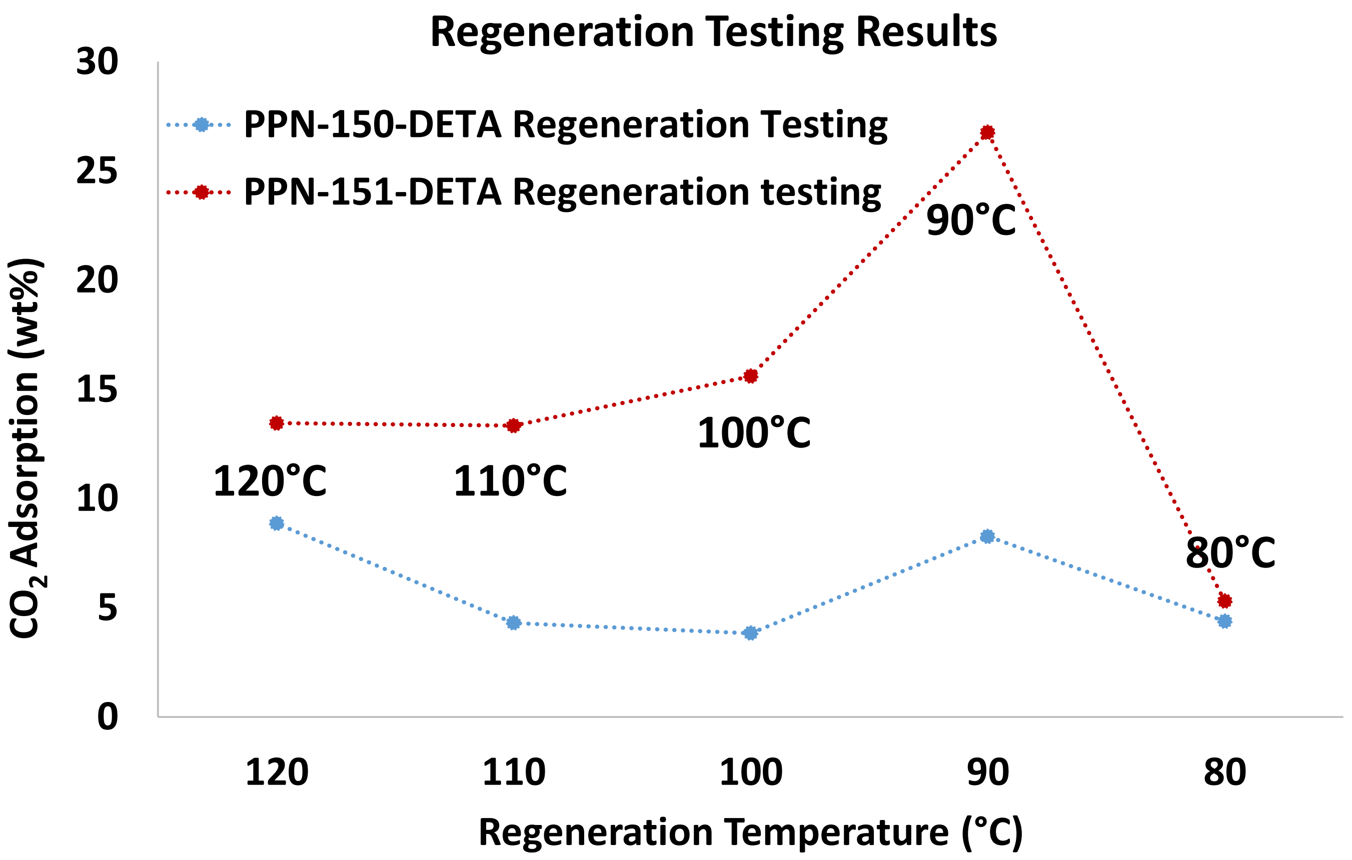


Fixed-bed Testing Long-term Wet Cycling



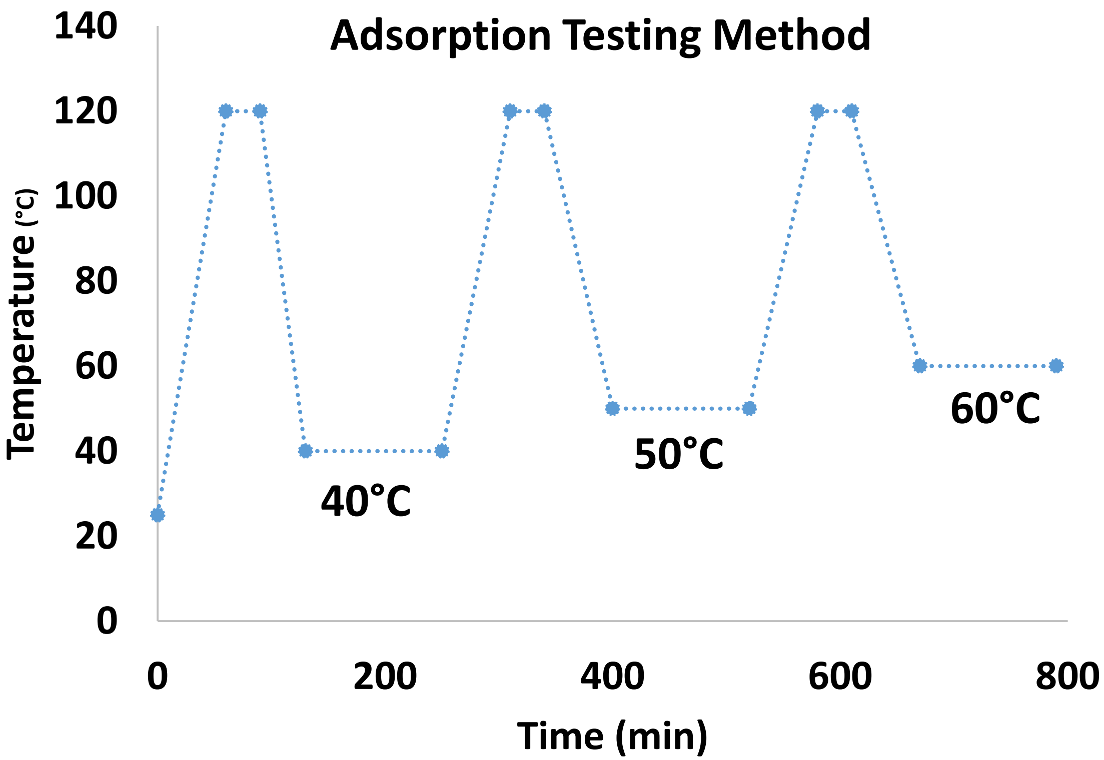
Fixed-bed Regeneration Testing

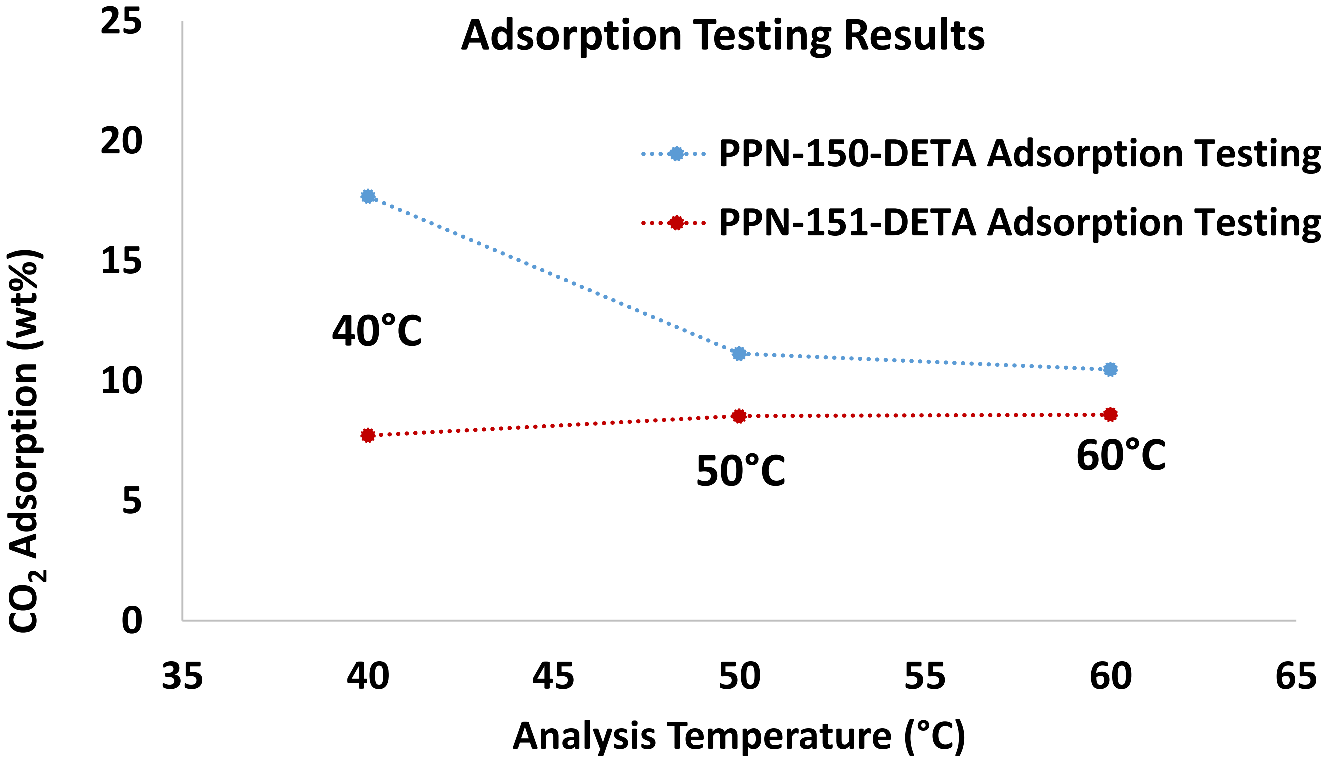




Uptake values for regeneration testing are based upon 40°C adsorption testing performed after regeneration at the given temperature

Fixed-bed Regeneration Testing



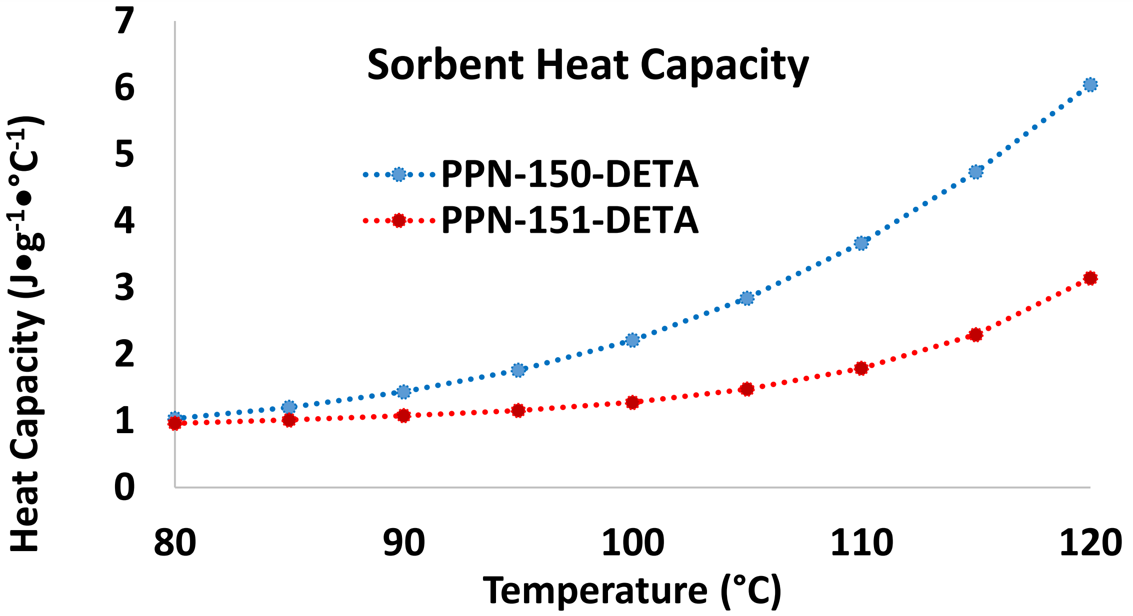


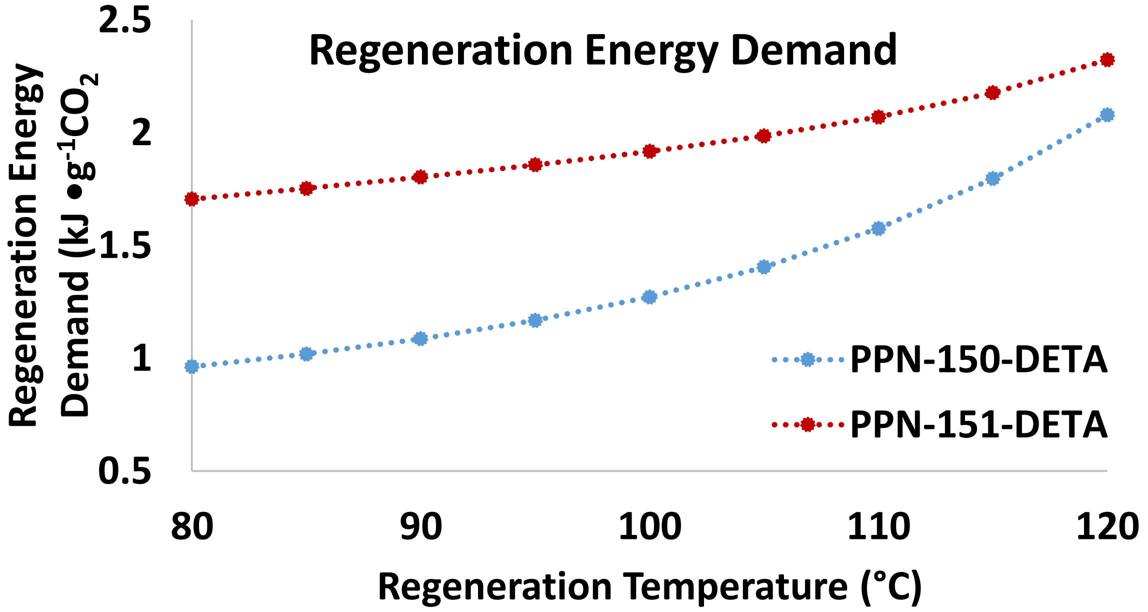
Adsorption test runs are conducted after a 120°C regeneration step to ensure full desorption of CO_2

Regenerative Energy Demand

- Heat of adsorption at 150 mbar CO_2 and 40°C:
  - PPN-150-DETA: 0.66 MJ/kg CO_2
  - PPN-151-DETA: 1.40 MJ/kg CO_2
- Heat capacity increases exponentially with higher temperatures
- Regenerative energy demand at 85°C
  - PPN-150-DETA: 1.0 MJ/kg CO_2
  - PPN-151-DETA: 1.8 MJ/kg CO_2

(Typical CO_2 scrubber: 3.8 MJ/kg CO_2)

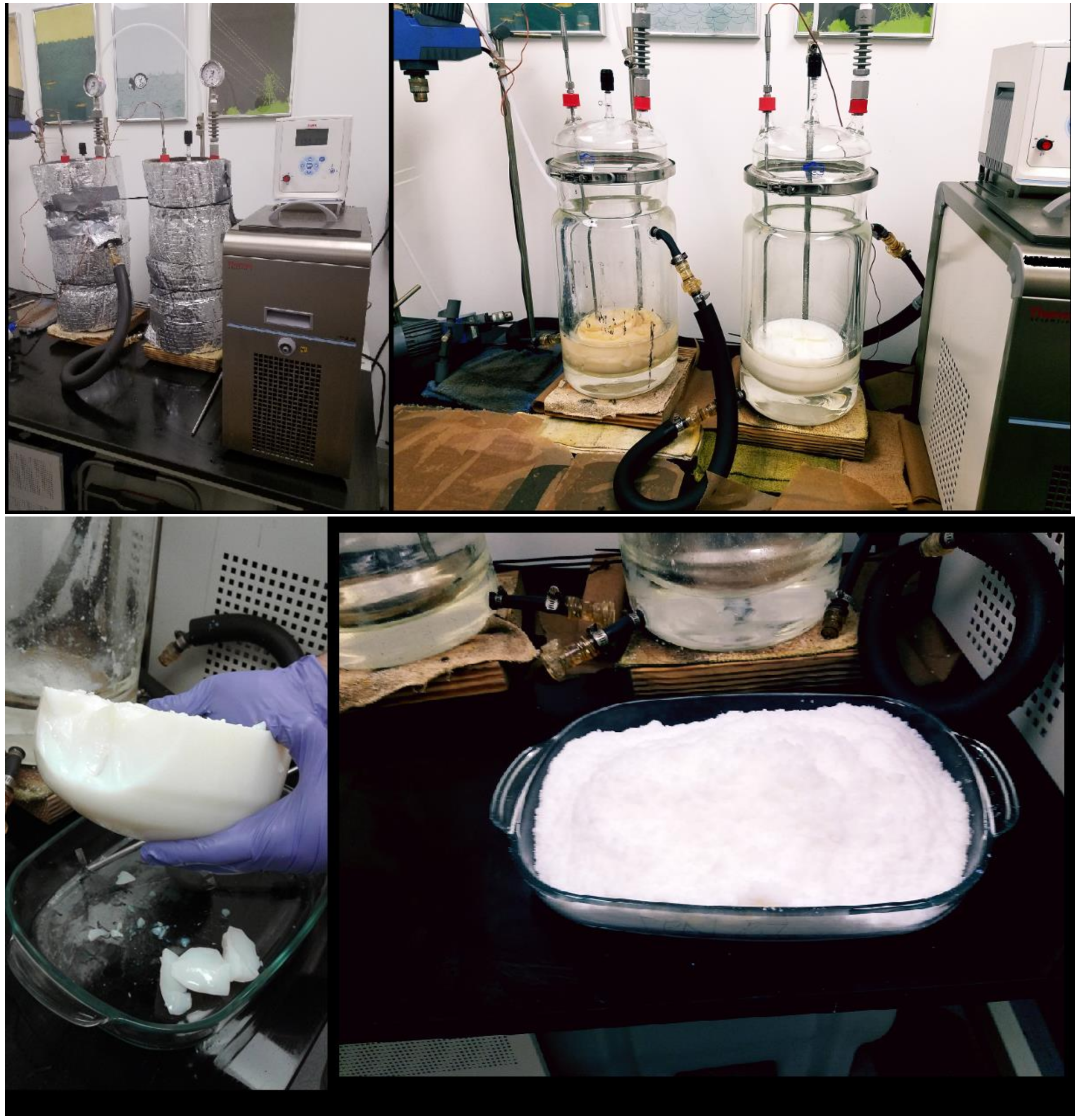




The Next Step: 200 g Scale-up

- The team utilized *framergy*'s 10 L jacketed solvothermal reactors to scale-up the sorbent synthesis to <200 g
- ~250 g batches of the sorbent were 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

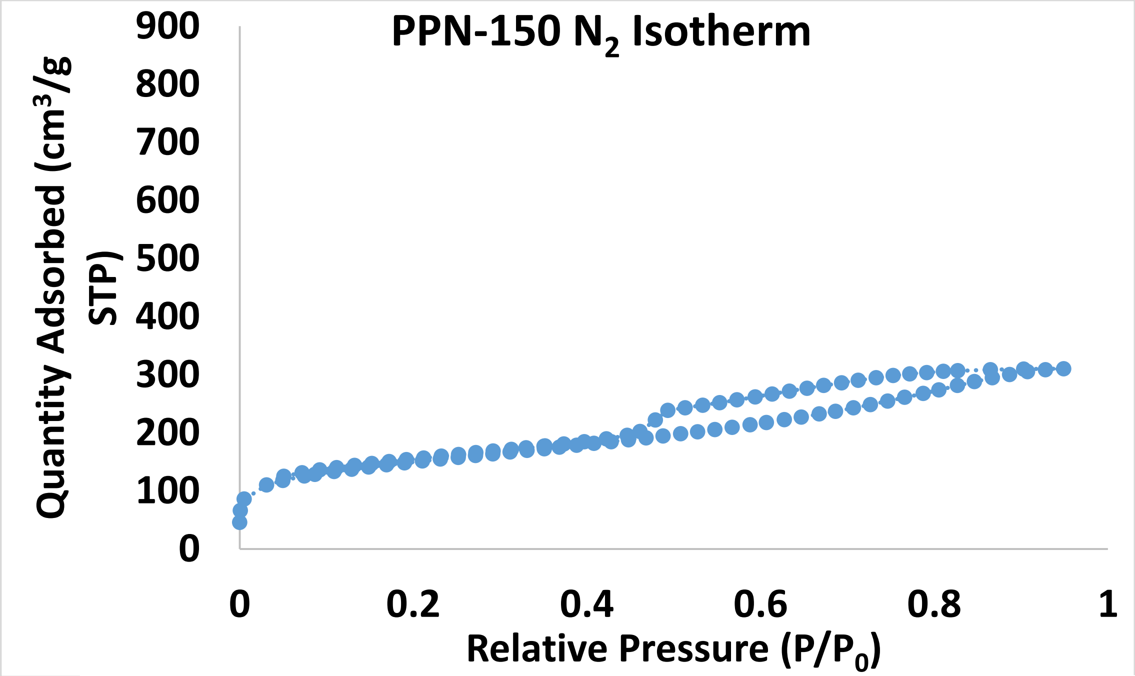


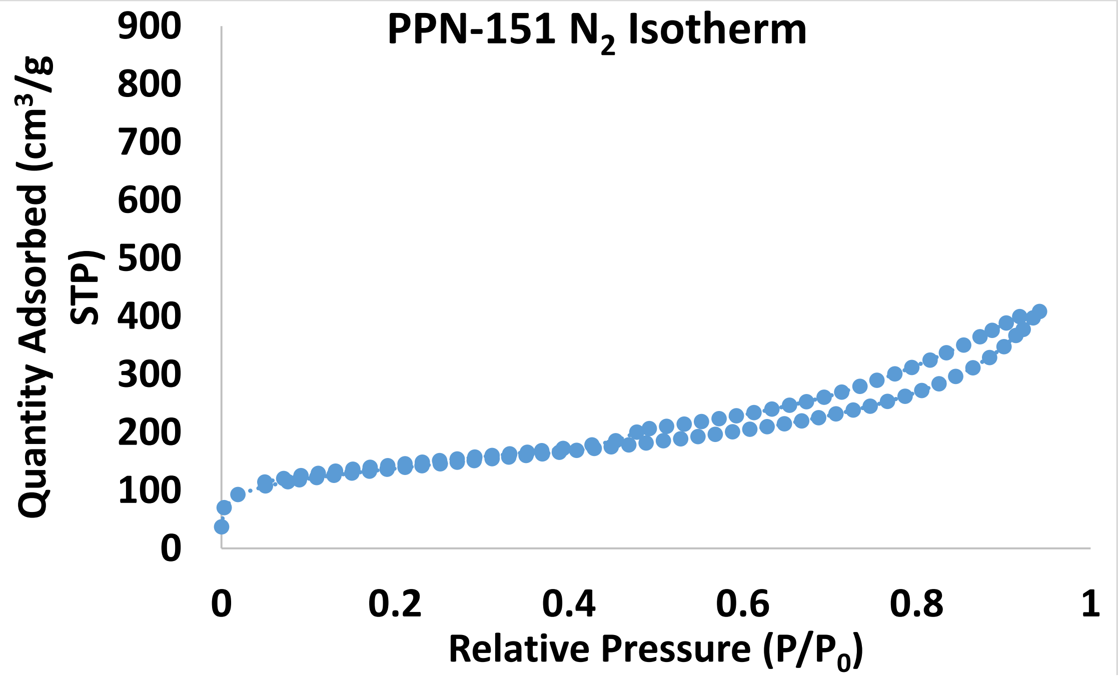
200 g Scale-up: Processing

- *framergy*'s Nutsche filter system utilized to wash sorbent (acetone, THF, DCM, methanol)

- Sorbent dried under vacuum before amine-incorporation

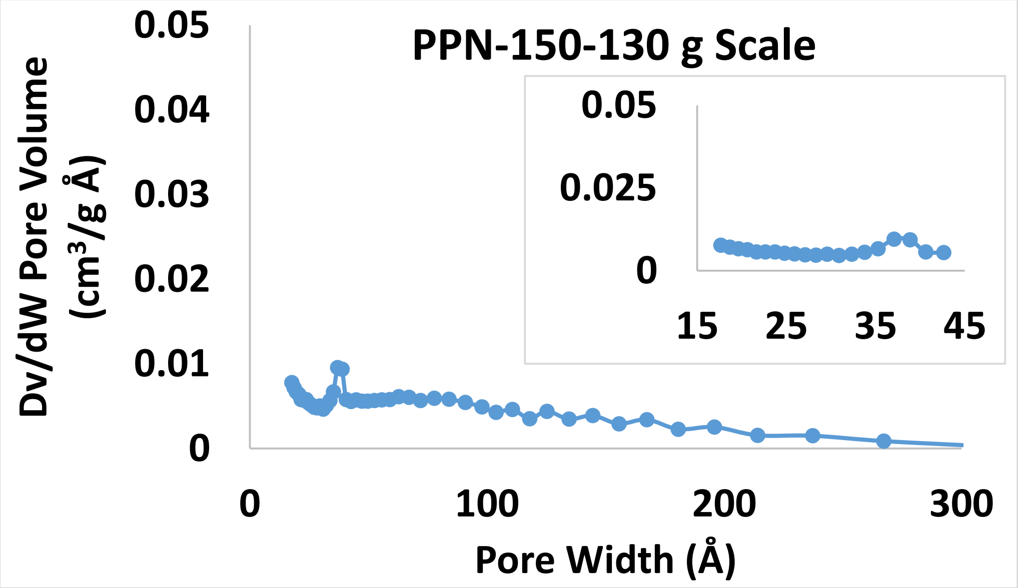
200 g Scale: BET Evaluation

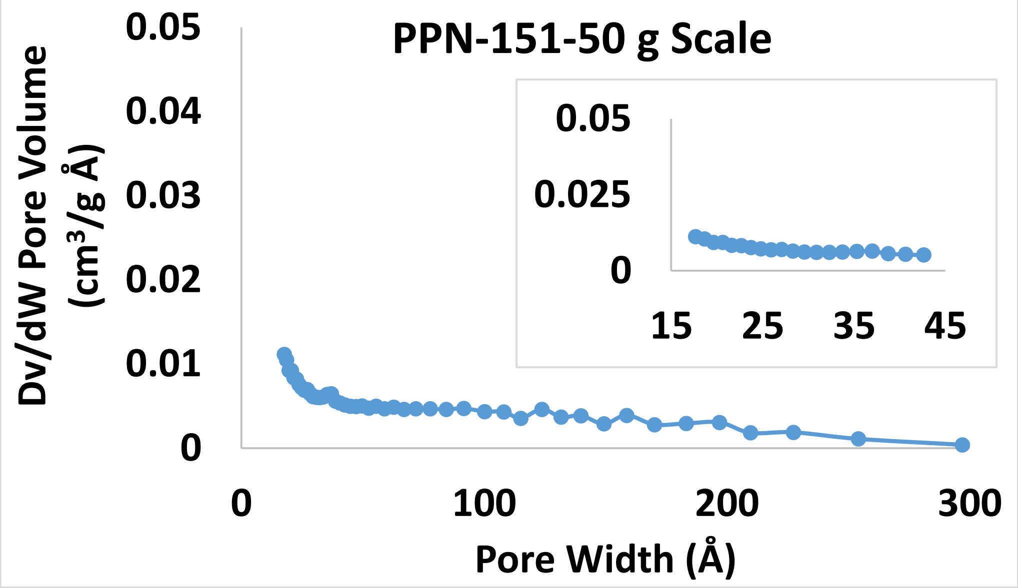


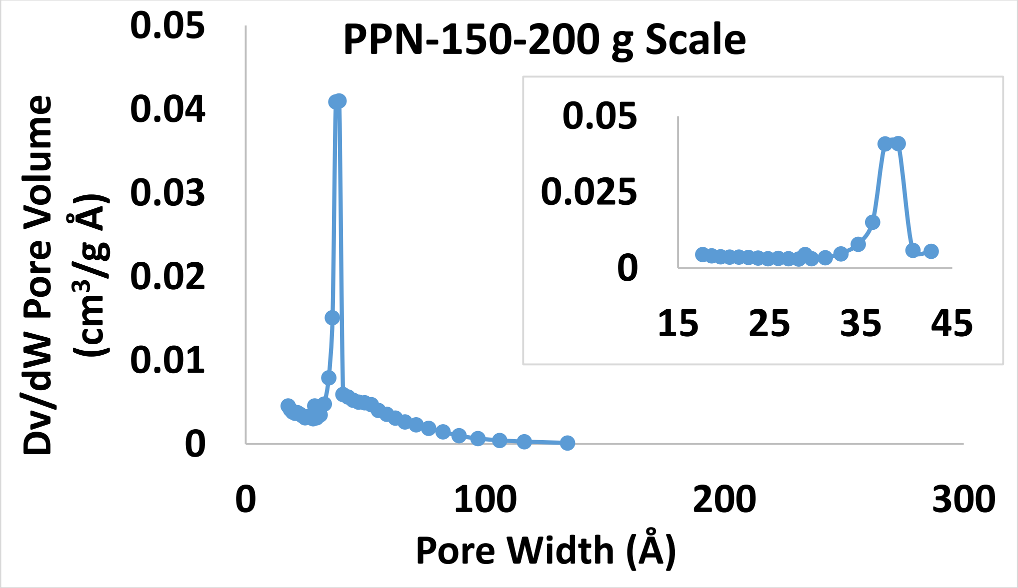


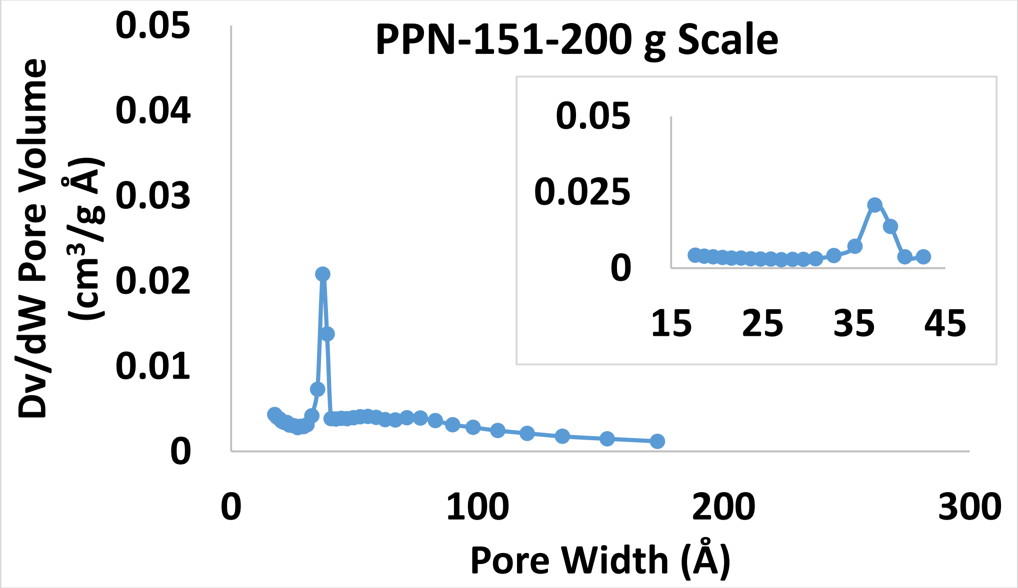
Sorbent	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)	CO_2 Uptake for DETA loaded sorbent at 40°C & 150mbar (kg/kg) (BET)
PPN-150-130g	778.1	0.897	79.1	0.033
PPN-151-50g	898.4	0.748	68.1	0.036
PPN-150-200g	538.1	0.365	10.5	0.020
PPN-151-200g	499.7	0.427	10.2	0.071

Comparison of Pore Size Distribution









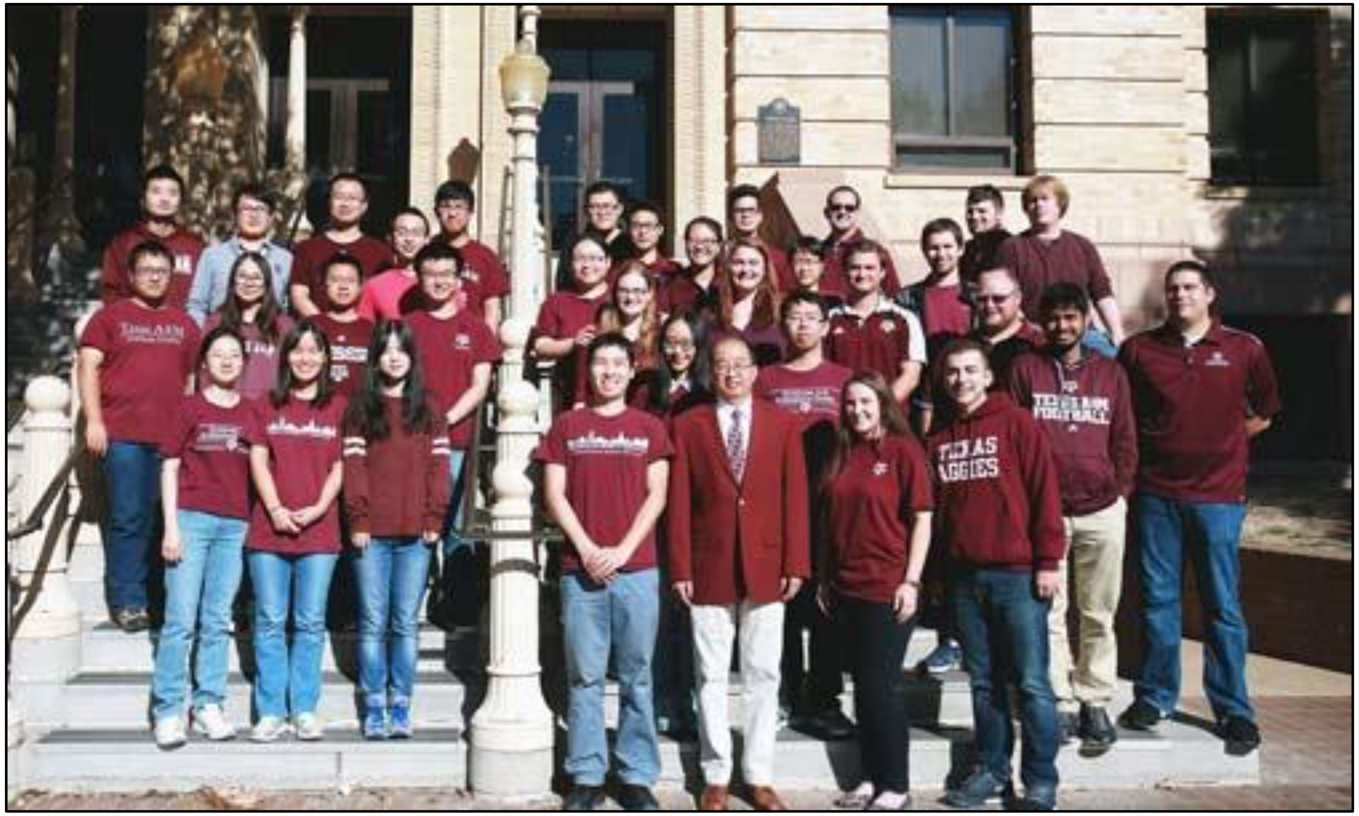
Summary

- PPN-150 series sorbents can achieve > 0.1 g/g CO_2 loading
  - A scalable alternative to “Gen 0” PPN sorbents
  - Synthesis optimization allows improved sorbent parameter control
  - Sorbent tuning during synthesis can produce unique performance properties
- Cycle testing can be conducted on lab scale batches allowing for fast data collection
  - Future cycle testing will be conducted using larger sorbent columns for better evaluation of bench scale sorbents
- Regeneration energy demand for PPN-150 series sorbents is promising to reach the DOE goal
- Bench scale synthesis and testing conducted partnership with *framergy*
  - 50 g and 200 g batches successful
  - 1 kg scale planned for BP3 work

Acknowledgement and Disclaimer

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

Acknowledgements



- DOE NETL
  - Project Manager - Andrew Jones
- *framergy*
  - Ray Ozdemir

Publications

- W. M. Verdegaal, K. Wang, J. P. Sculley, M. Wriedt and H.-C. Zhou. *ChemSusChem*, 2016, **9**, 636-643.
- Zou, L.; Yang, X.; Yuan, S.; Zhou, H.-C. *CrystEngComm*, 2017.
- Huang, N.; Day, G.; Yang, X.; Drake, H.; Zhou, H.-C. *Science China Chemistry*, 2017.
- Yang, X.; Zou, L.; Zhou, H.-C. *Polymer*, 2017.
- Zou, L.; Sun, Y.; Che, S.; Yang, X.; Wang, X.; Bosch, M.; Wang, Q.; Li, H.; Smith, M.; Yuan, S.; Perry, Z.; Zhou, H.-C. *Advanced Materials*, 2017

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