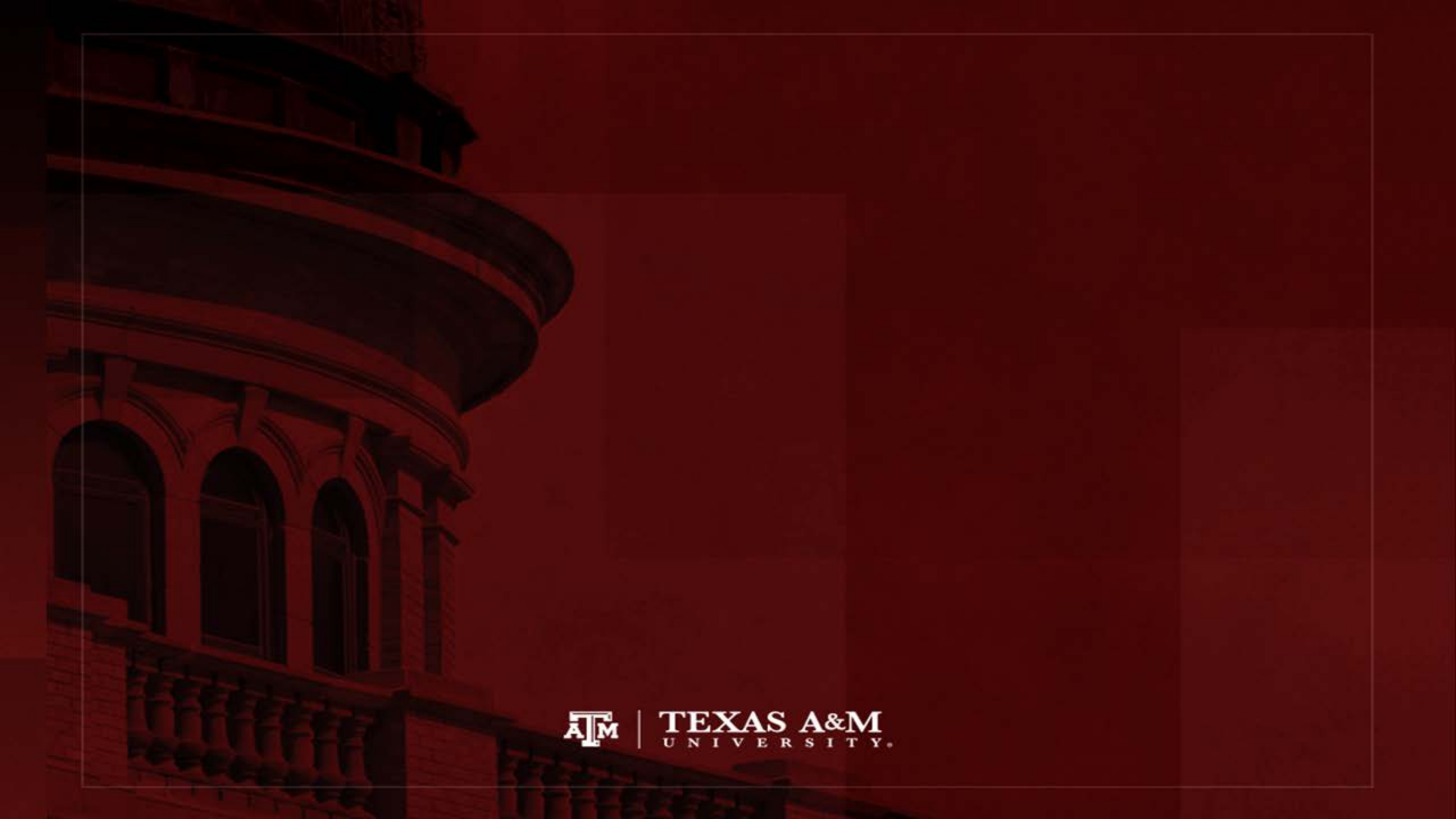

TEXAS A&M
UNIVERSITY

Evaluation of amine-incorporated porous polymer networks (aPPNs) as sorbents for post combustion CO2 capture

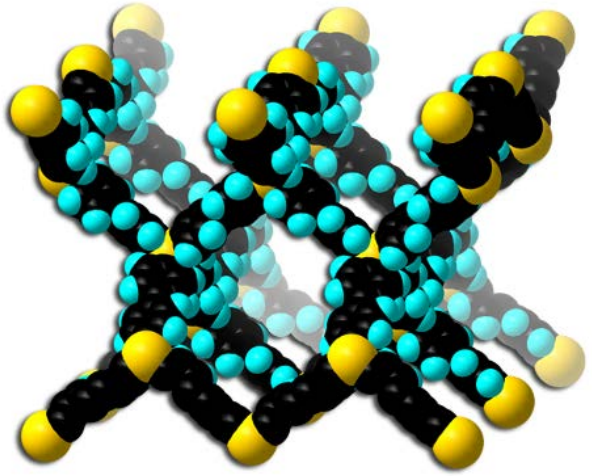
DOE AWARD NUMBER: DE-FE0026472

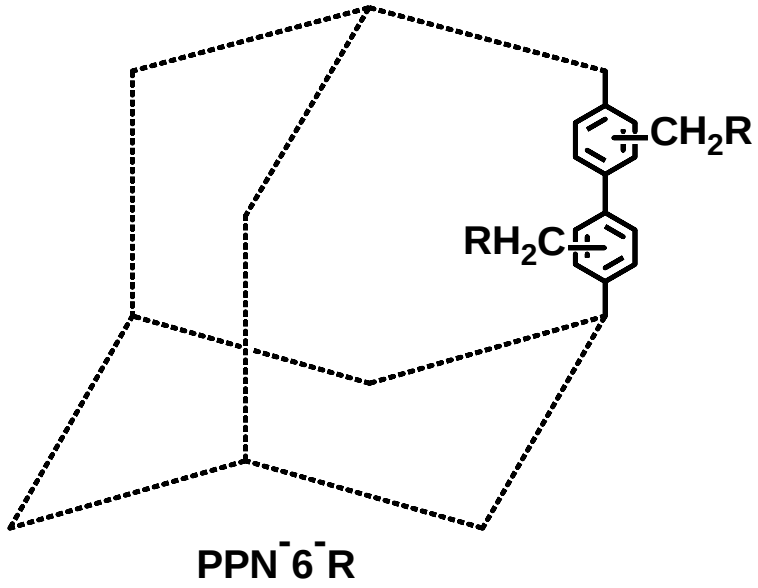
Outline

- Introduction
  - Carbon capture
  - Amine-materials
  - Objectives
  - Budget
- BP1 Milestones
- BP2 Milestones
  - Synthesis optimization
  - Scale-up
  - Breakthrough
  - Pelletization, Attrition, and mechanical hardness
- BP3
  - Overview
  - Budget

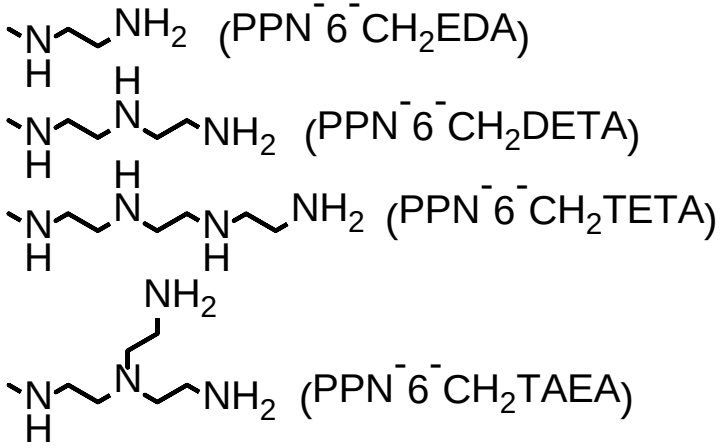
Amine-decorated Porous Materials

- Porous Polymer Networks (PPNs)





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.

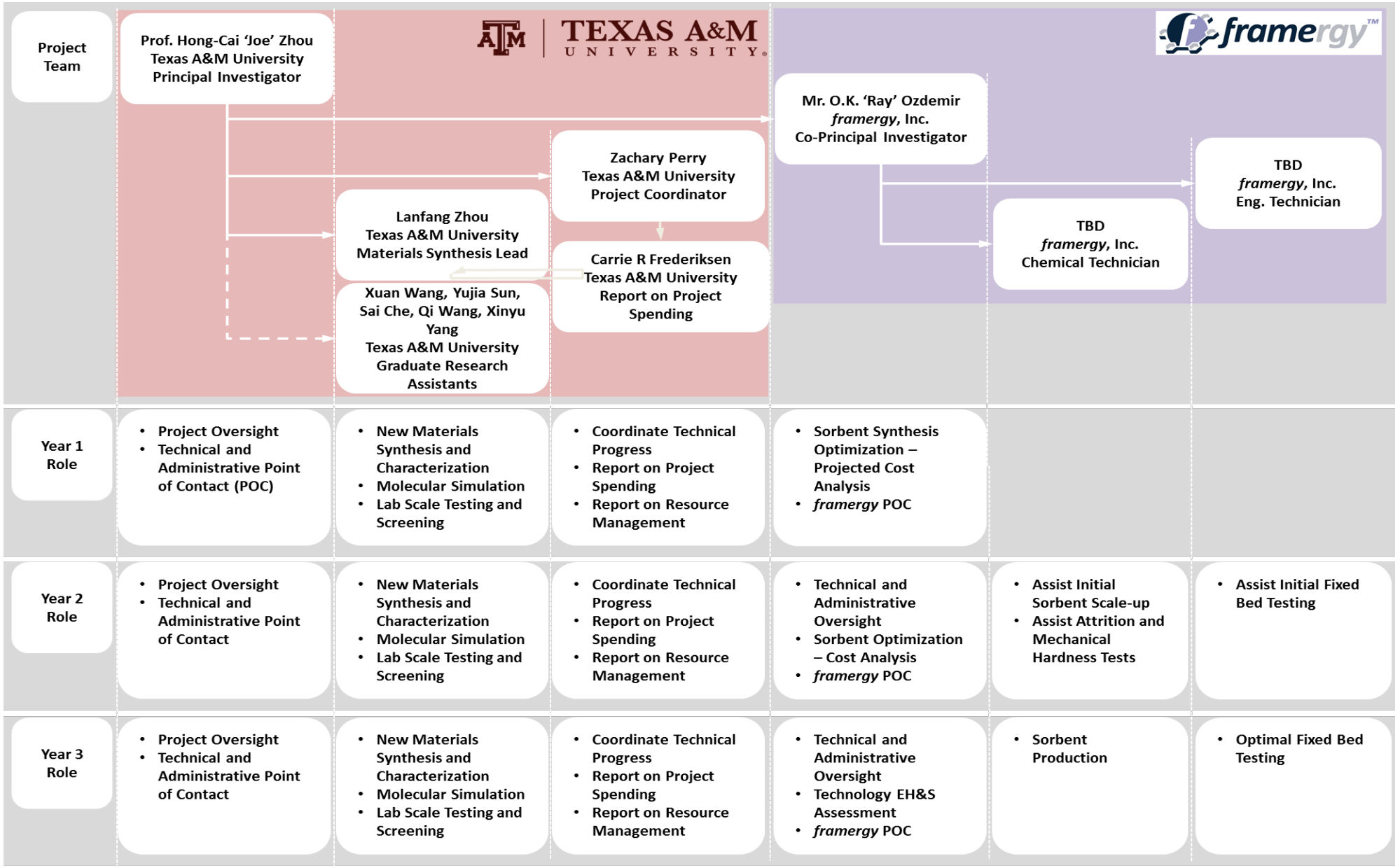
Project Objectives

- To improve and optimize sorbent and process technologies so that, by the end of the 36-month effort, a scalable highly-robust and highly-efficient sorbent can be delivered and validated through lab-scale testing in a fixed-bed carbon capture/sorbent regeneration system

- The cost of the advanced sorbents will be reduced to a point where it will be economically feasible to scale-up and use the sorbents in commercial carbon capture processes

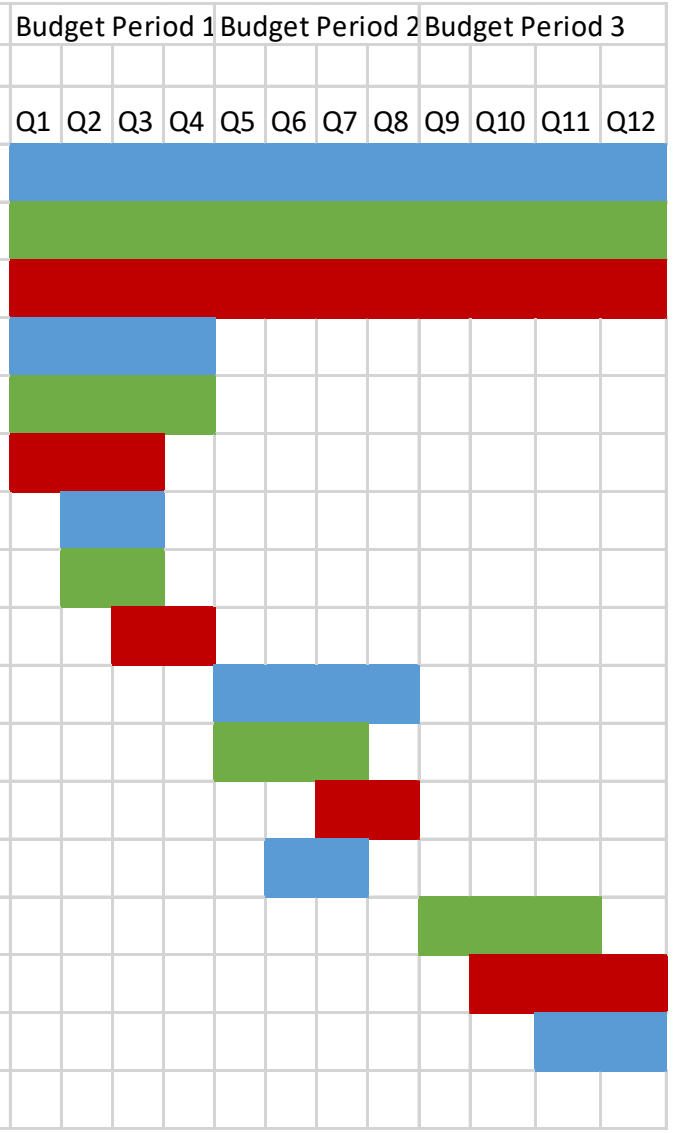
- The ideal sorbents for post-combustion CO_2 capture at project's end will demonstrate significant progress toward achievement of the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches.

Project Organization Chart



Resource Loaded Schedule

Task	Mileston	Start Date	End Date	Cost
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



Outline

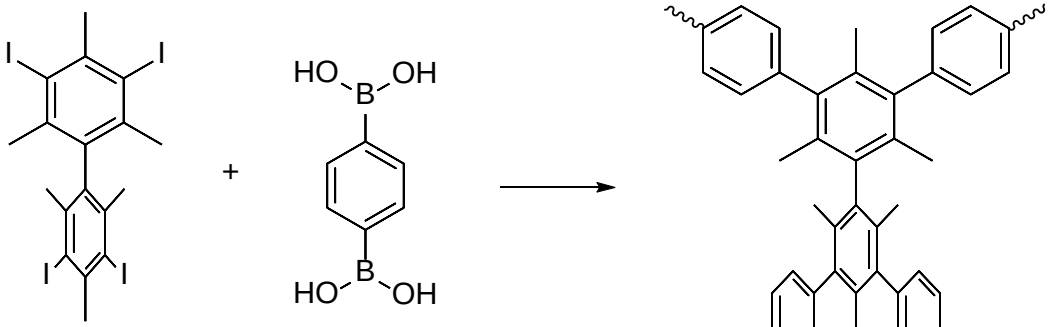
- Introduction
  - Carbon capture
  - Amine-materials
  - Objectives
  - Budget
- BP1 Milestones
- BP2 Milestones
  - Synthesis optimization
  - Scale-up
  - Breakthrough
  - Pelletization, Attrition, and mechanical hardness
- BP3
  - Overview
  - Budget

BP1 Milestone Log

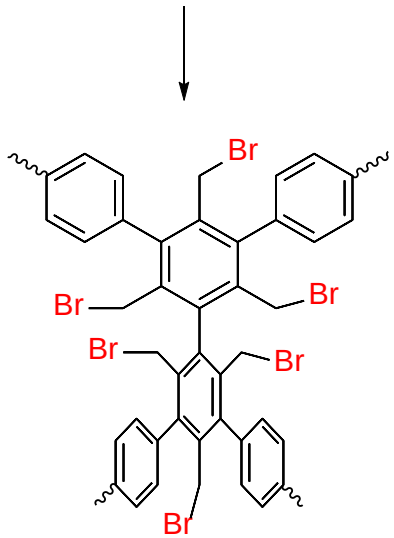
ID	Task	Milestone Description	Planned Completion	Actual Completion	Percentage Complete	Verification Method
a	1	Updated Project Management Plan	10/31/2015	10/31/2015	100%	Project Management Plan file
b	1	Kick-off Meeting	12/31/2015	12/31/2015	100%	Presentation file
c	2	Complete synthesis of least 5 novel aPPN sorbent formulations at small-scale (~100 milligrams)	1/31/2016	1/31/2016	100%	Results reported in the quarterly report
d	3.0	Complete synthesis of two Gen 0 materials (PPN-125-DETA and MOF-74-Mg) for standardization of measurements	1/31/2016	1/31/2016	100%	Results reported in the quarterly report
e	3.1	Complete initial CO_2 adsorption testing with at least five aPPN sorbent formulations and generate CO_2 loading isotherms	3/31/2016	3/31/2016	100%	Results reported in the quarterly report
f	2	Complete synthesis of 5 or more additional aPPN sorbents (~100 mg)	5/31/2016	5/31/2016	100%	Results reported in the quarterly report
g	3.2	Complete initial aPPN sorbent physical property characterization (heat capacity, heat of reaction, density, particle size, etc.)	6/30/2016	6/30/2017	100%	Results reported in the quarterly report
h	3.3	Complete initial TGA testing with the top-performing aPPN sorbents (>0.08 kg/kg CO_2 capacity) in the presence of moisture	6/30/2016	6/30/2017	100%	Results reported in the quarterly report
i	3.3	Complete initial thermal and chemical stability (H_2O, SO_2) studies via TGA cycling and small breakthrough	8/30/2016	5/31/2017	100%	Results reported in the quarterly report
j	2	Sorbent Synthesis Optimization – Projected Cost Analysis	8/30/2016	8/30/2016	100%	Results reported in the quarterly report
k	2	Produce ~50 grams of at least the two top-performing aPPN sorbent formulations	9/30/2016	4/18/17	100%	Results reported in the quarterly report

PPN-200 Series

- Post-synthetic modification via PPN-200-Br to yield amine tethered PPN materials



PPN-200



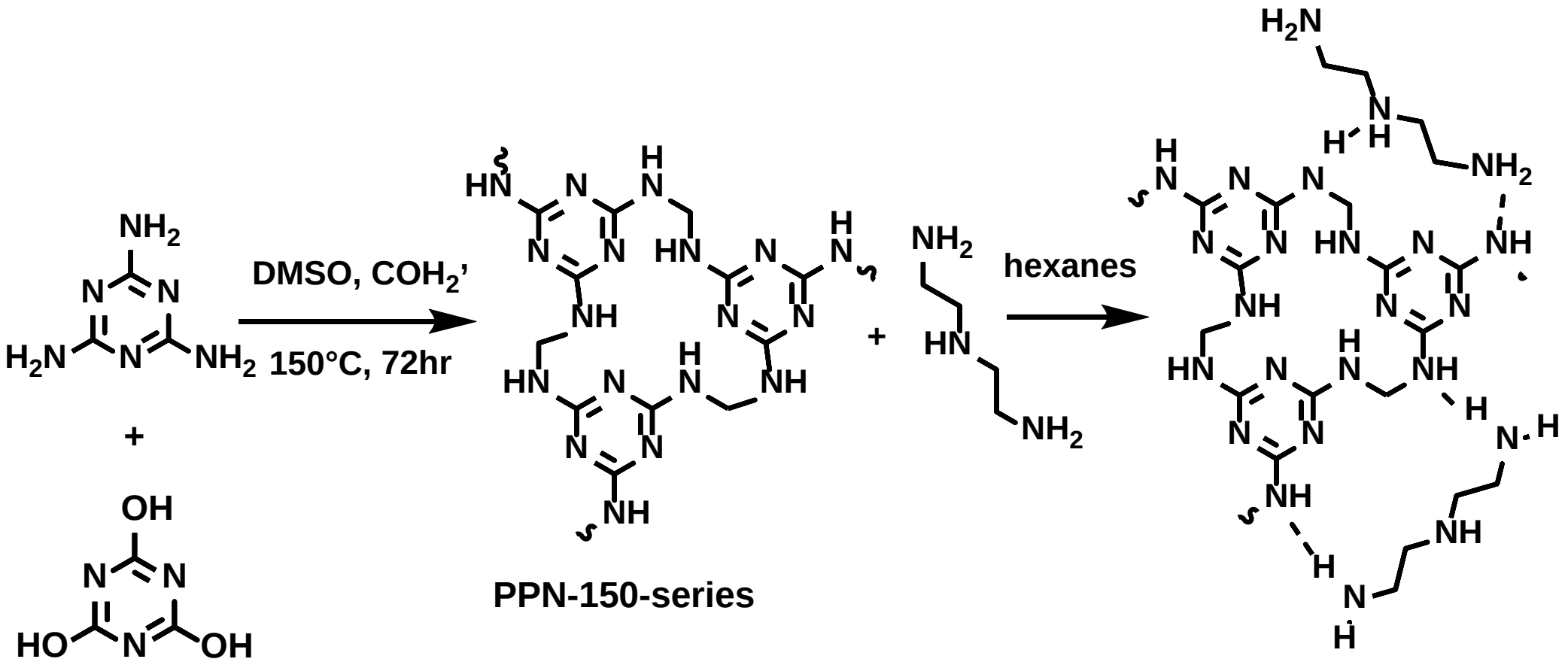
PPN-200Br

Amine-PPNs

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

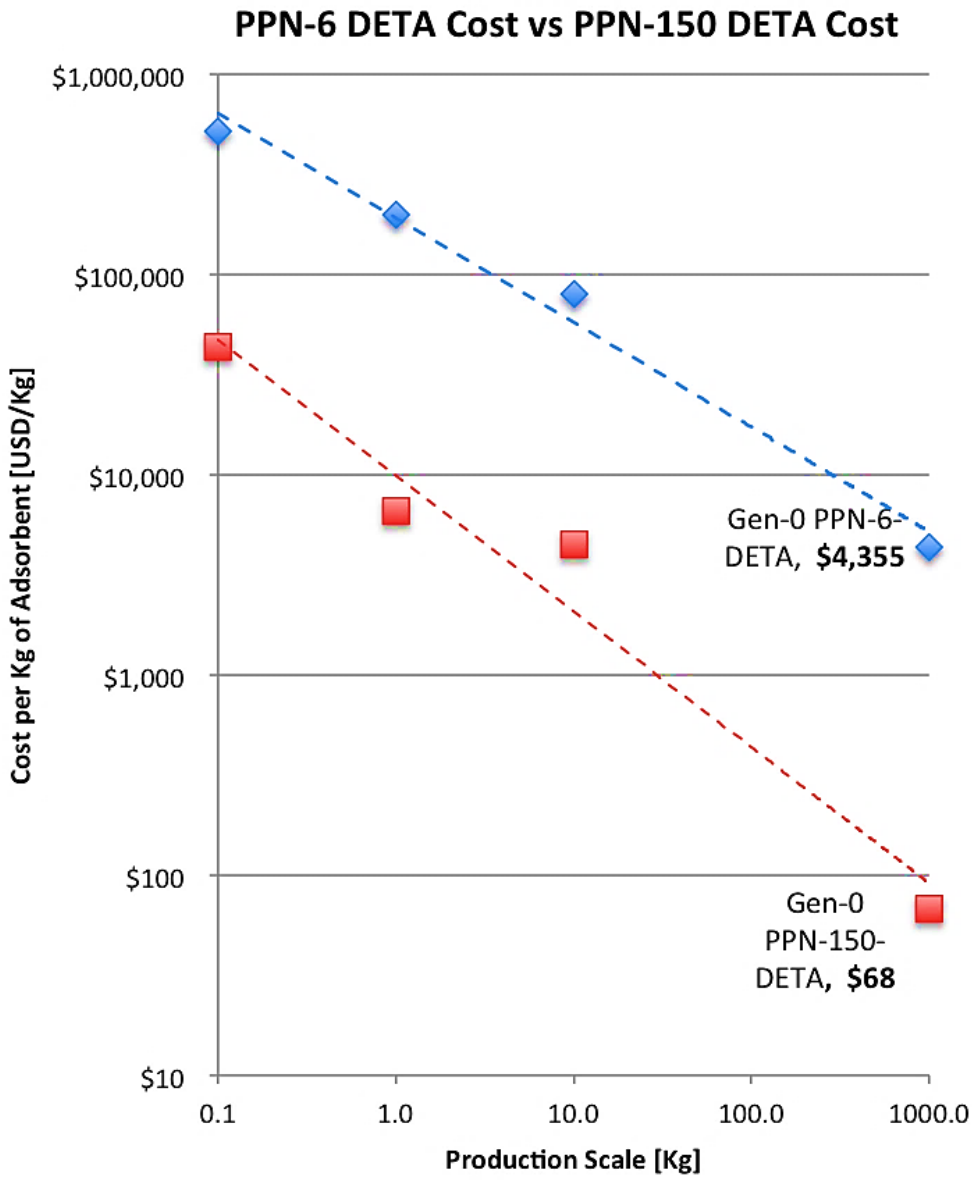
Initial ~50g scale-up proved unsuccessful

PPN-150 Series



Initial Cost Analysis

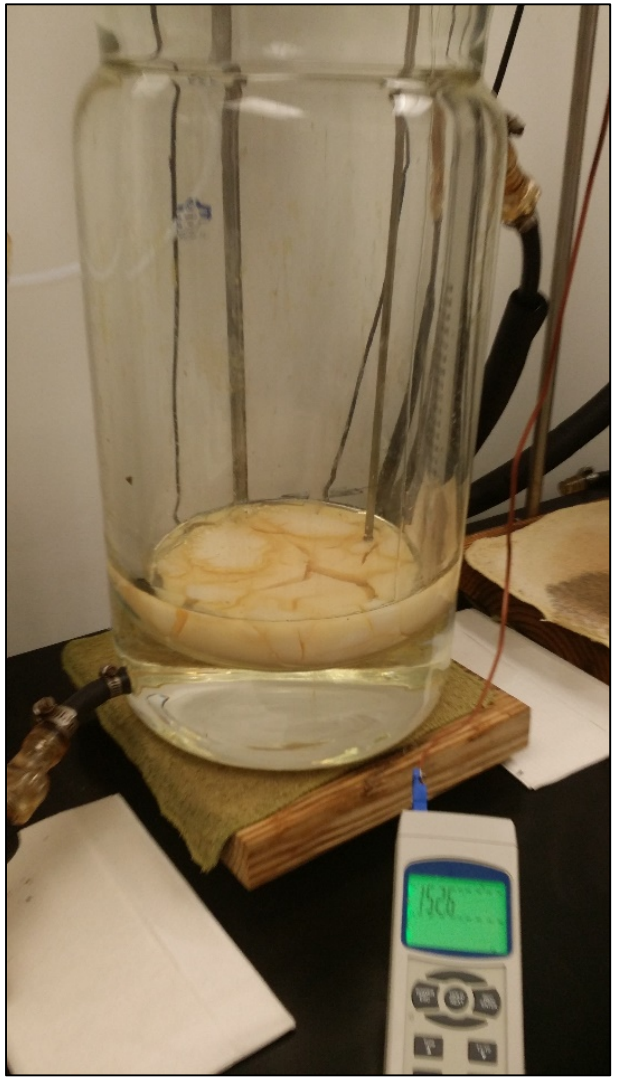
- Initial cost analysis shows increasing cost reduction as synthesis scales-up
- Further cost reduction predicted if improved solvent reduction/recycling is explored

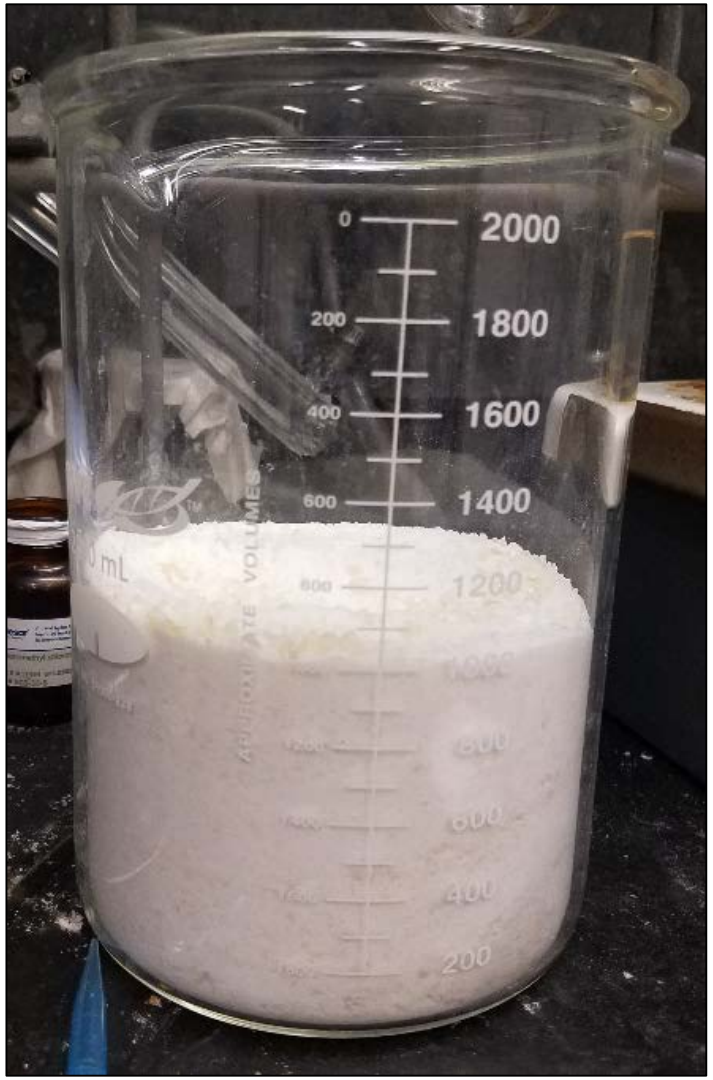


Initial 50g Scale-up

- The team utilized *Framergy*'s 10L jacketed solvothermal reactors to scale-up the sorbent synthesis

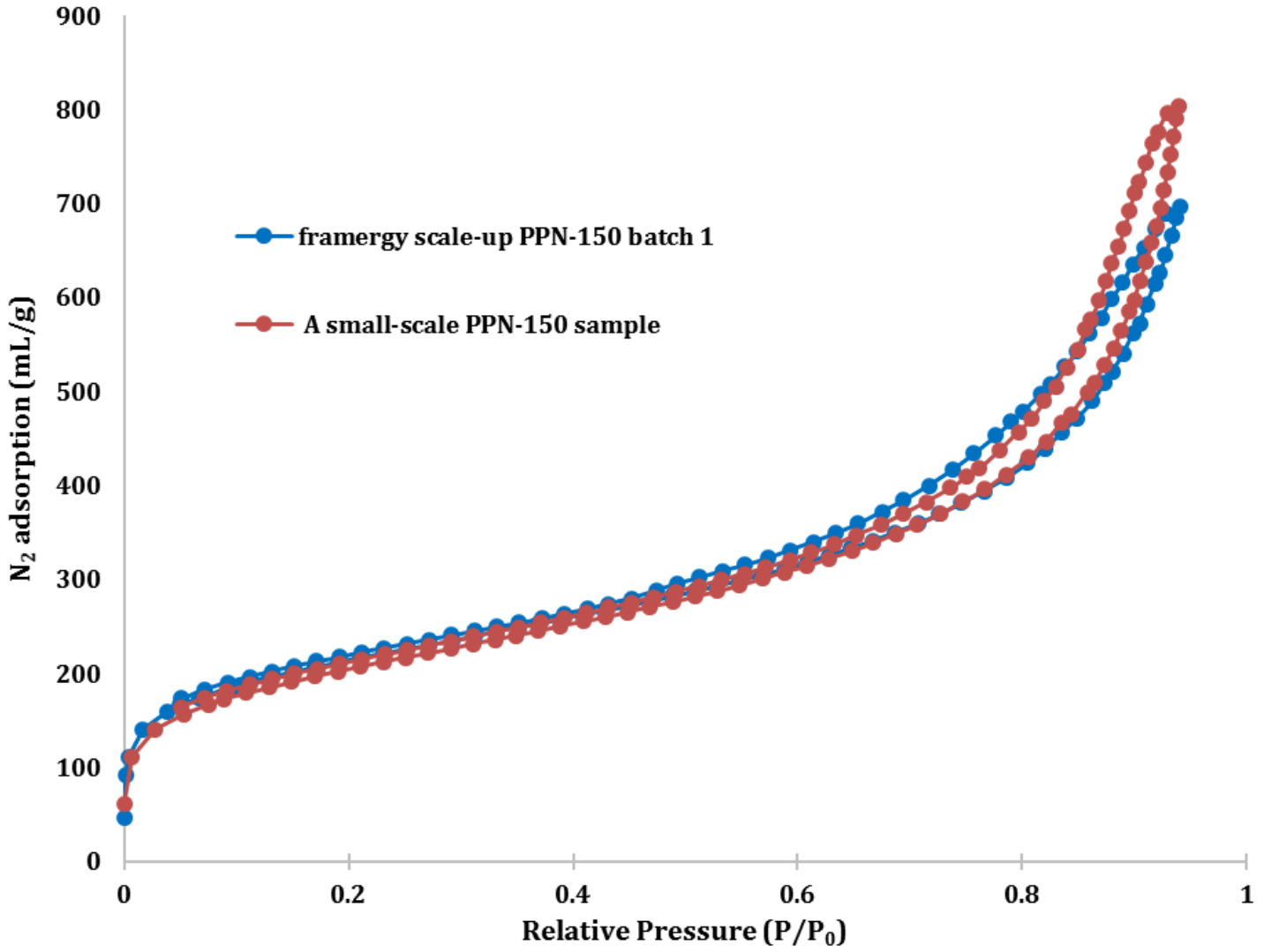
- Real-time monitoring with webcams



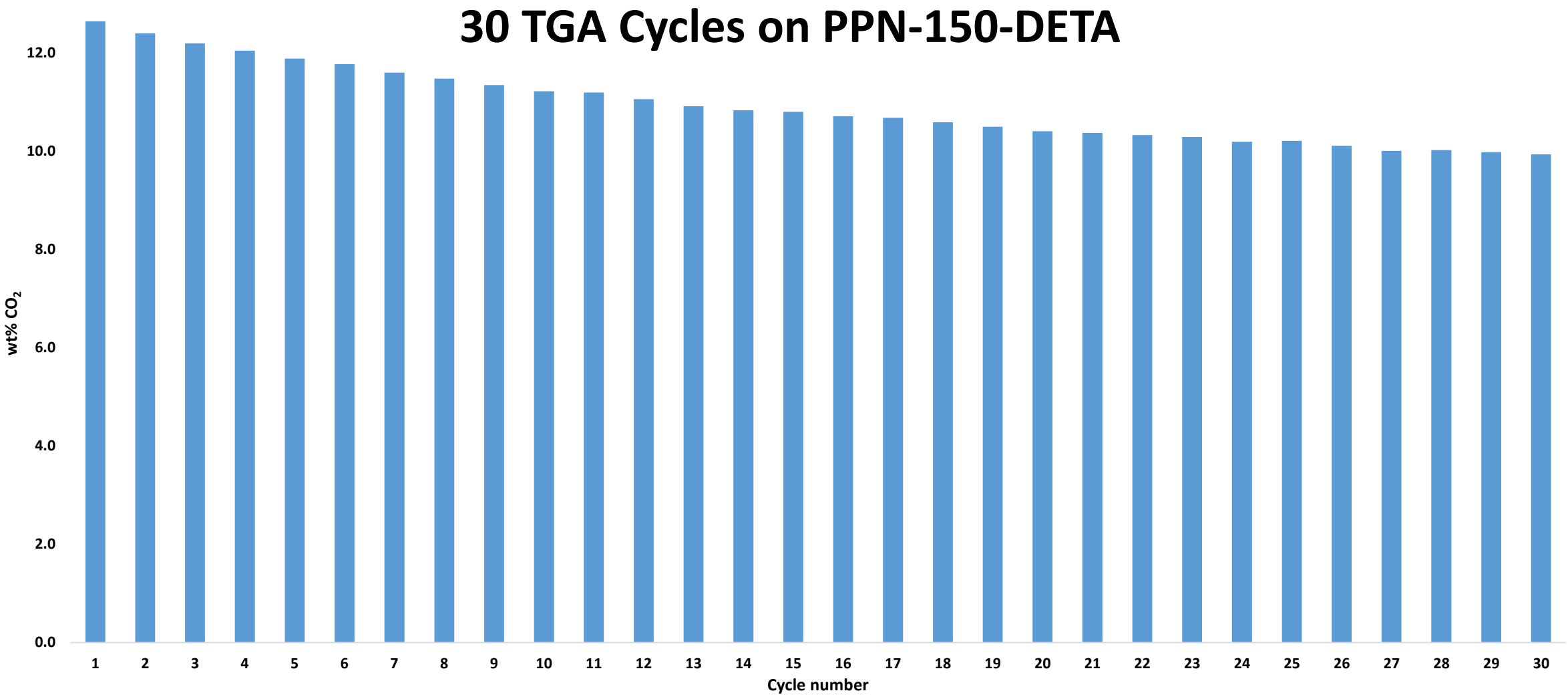


Initial 50g Scale-up

- Comparable BET isotherms between small and large batches



50g Scale-up – TGA Cycling



BP1 Success Criteria

Decision Point	Basis for Decision/Success Criteria	Status
Completion of Budget Period 1	Successful completion of all work proposed in Budget Period 1	Completed.
	Novel aPPN sorbent formulation retains a CO_2 adsorption capacity of at least 0.1 kg/kg after 30 cycles via TGA or physisorption testing	Complete. PPN-150-DETA retained a CO_2 adsorption capacity of 0.099 kg/kg after 30 cycles via TGA
	Produce ~50 grams of at least the two top-performing aPPN sorbent formulations	Complete. Two top-performing aPPN sorbent formulations (PPN-150-DETA and PPN-151-DETA) were produced in excess of 50g
	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified, including quotes and budget justification for service contractors and major equipment items	The BP2 Continuation Application was submitted on July 12, 2016

Outline

- Introduction
  - Carbon capture
  - Amine-materials
  - Objectives
  - Budget
- BP1 Milestones
- BP2 Milestones
  - Synthesis optimization
  - Scale-up
  - Breakthrough
  - Pelletization, Attrition, and mechanical hardness
- BP3
  - Overview
  - Budget

BP2 Milestones

ID	Task	Milestone Description	Planned Completion	Actual Completion	Percentage Complete	Verification Method
l	6.0	Complete acquisition and installation of the temperature-controlled, fixed-bed test unit coupled with a mass spectrometer	1/31/2017	6/30/17	100%	Results reported in the quarterly report
m	4.0	Identify synthesis conditions (temperature, reaction time, monomer ratios, etc.) that yield optimal aPPN sorbent performance and cost	3/31/2017	3/31/17	100%	Results reported in the quarterly report
n	5.0	Finalize scale-up procedure for top-performing aPPN sorbent formulations and prepare laboratory facilities	3/31/2017	3/31/2017	100%	Results reported in the quarterly report
o	5.0	Produce ~200 grams of at least the two top-performing aPPN sorbent formulations ($\geq$0.1 kg/kg working capacity) for initial fixed-bed cycling tests	7/31/2017	8/31/2017*	90%	Results reported in the quarterly report
p	6.0	Complete initial fixed-bed cycling tests with the scaled-up aPPN sorbent formulations and maintain at least ≥0.1 kg/kg working capacity	9/30/2017	9/30/2017*	80%	Results reported in the quarterly report
q	7.0	Complete attrition and mechanical hardness testing of the top-performing aPPN sorbent formulations	6/30/2017	9/30/2017*	50%	Results reported in the quarterly report

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, 1h shaker, hexane solvent, THF wash**

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	856.5698	77.81	0.68497
50.0%	Pressure Tube	838.3735	79.22	0.886095
11.6%	Pressure Tube	722.4549	78.201	0.802089

- 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	356.2916	98.37	0.761238
DMSO	854.0684	87.148	1.114849
Ethylene glycol	365.0005	107.755	0.854695
Ethylene glycol/Ethanol	251.5467	103.683	0.542143
DMSO/H_2O	113.9345	84.674	0.135036
Ethylene glycol/H_2O	298.0362	107.049	0.653072
Ethylene glycol/Methanol	278.5665	104.21	0.597119
DMSO/Methanol	518.2893	92.136	0.508379

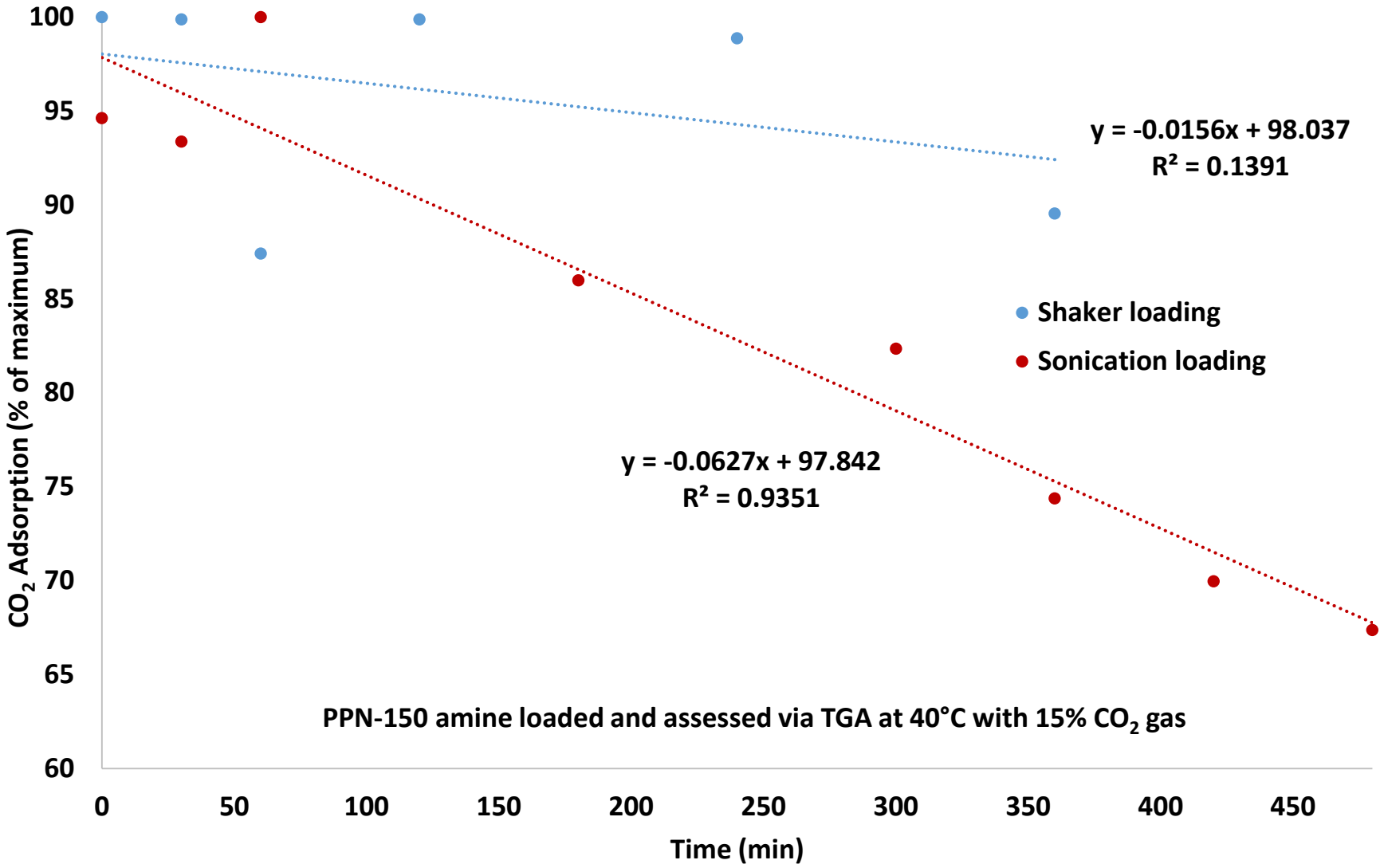
- Neat DMSO yields highest surface area

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	0.296	9.6%
5	640	0.281	9.2%
7	1014	1.042	5.3%

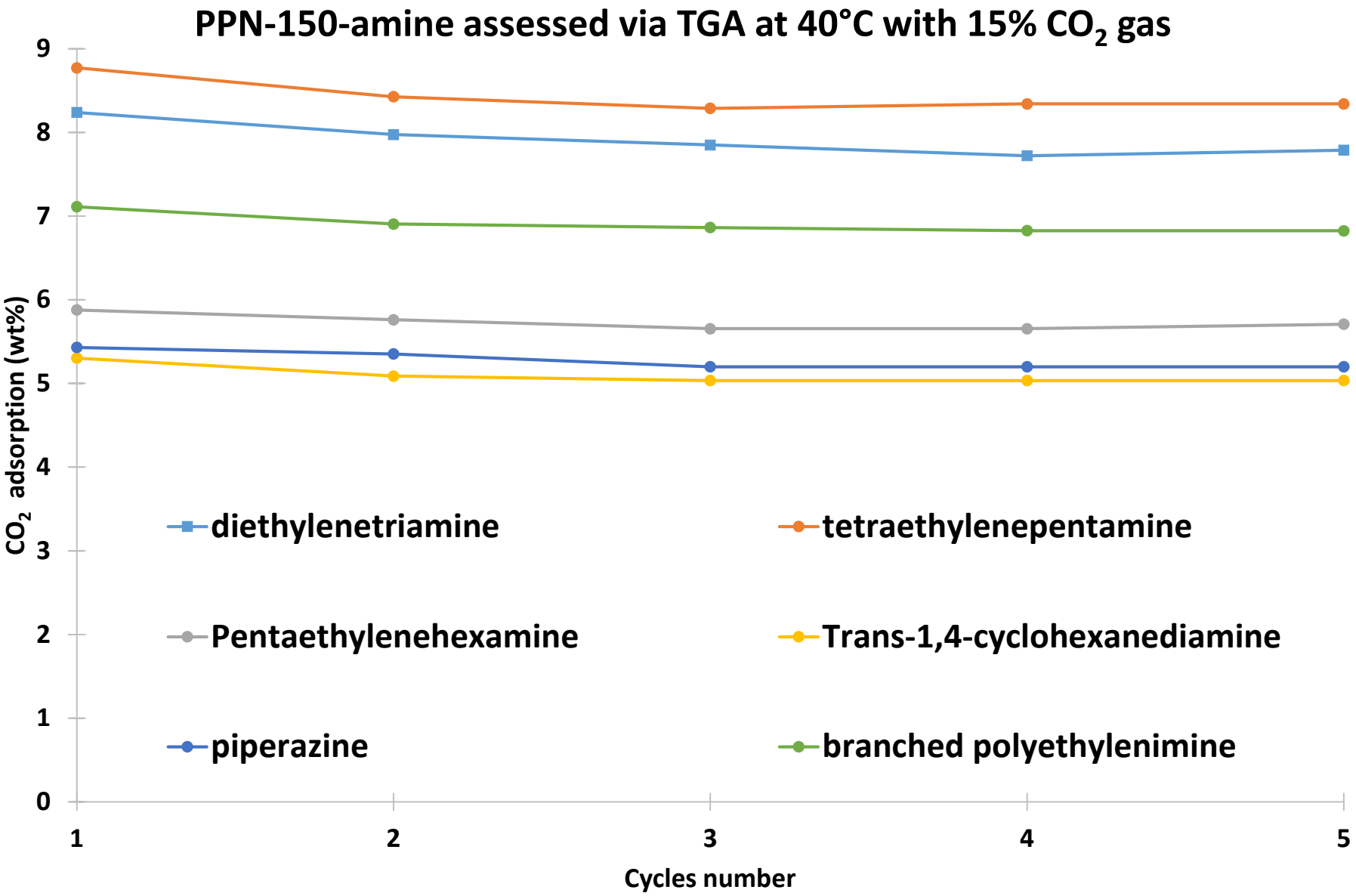
- 3-5 days yields sorbent with highest microporosity

Amine Loading Optimization



Shaker shows more consistent loading

Amine Optimization



200g Scale-up

- The team utilized *framergy*'s 10L jacketed solvothermal reactors to scale-up the sorbent synthesis

- ~250g batches of the sorbent were produced

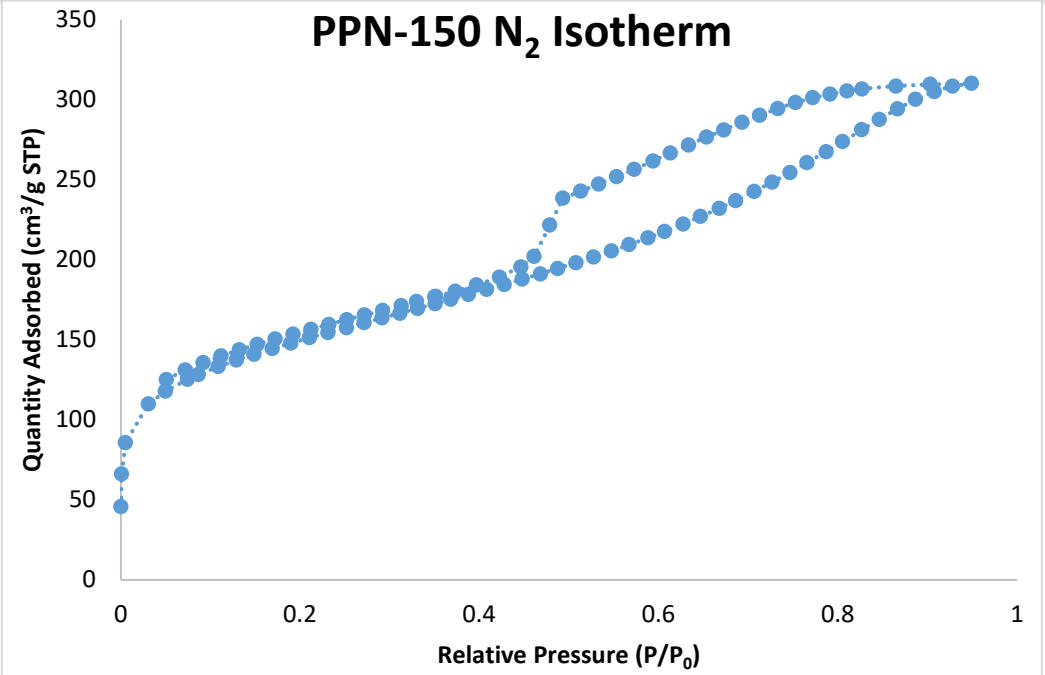
Parameter	Value
Temperature	150°C
Time	5 day
Headspace	~80%
Melamine	201.62g
Paraformaldehyde	108.00g
Cyanuric acid	15.48g
Dimethyl Sulfoxide (DMSO)	2080mL

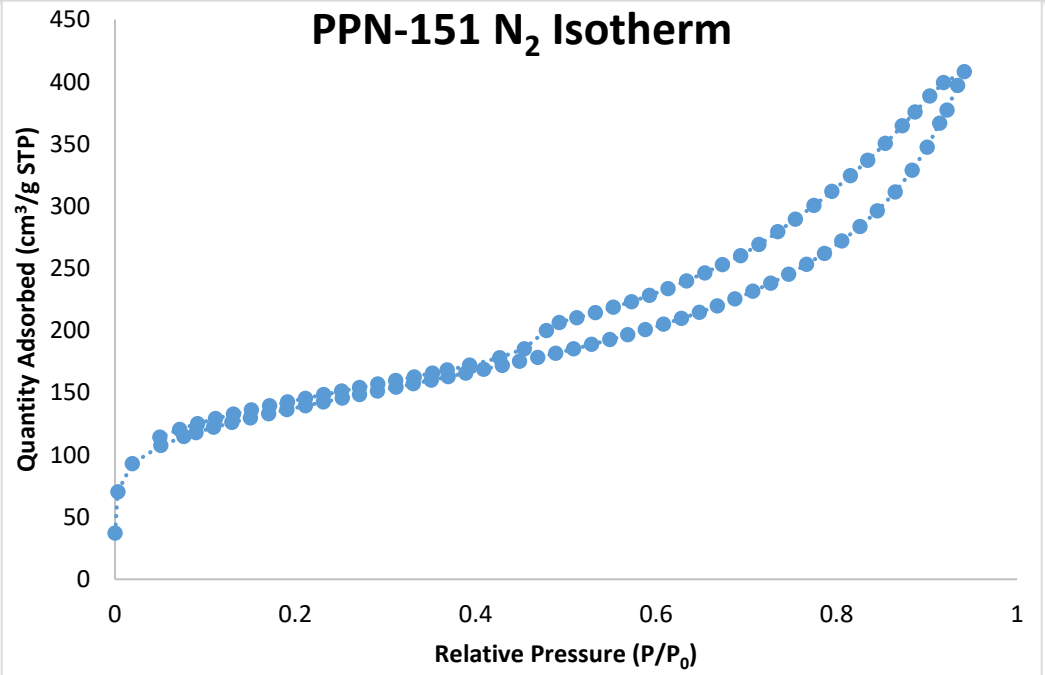
200g Scale-up

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

- Sorbent dried under vacuum before amine-incorporation

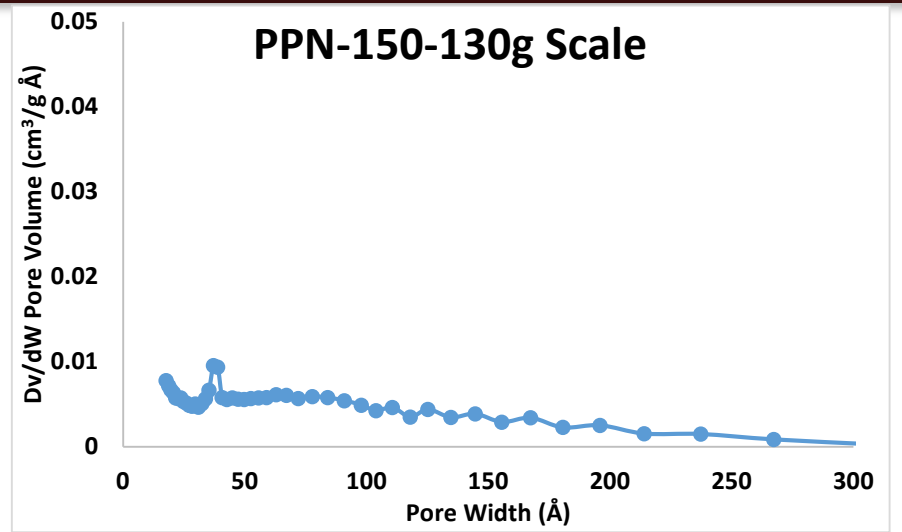
200g Scale Evaluation

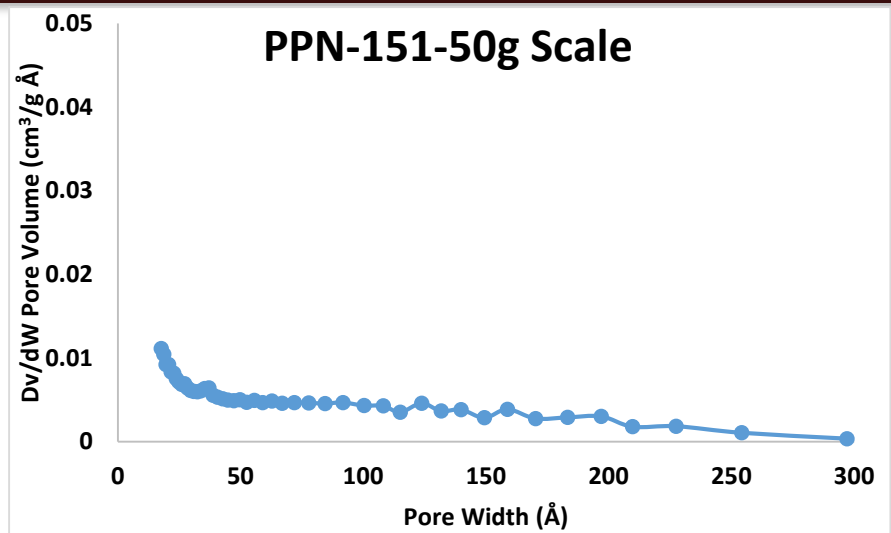


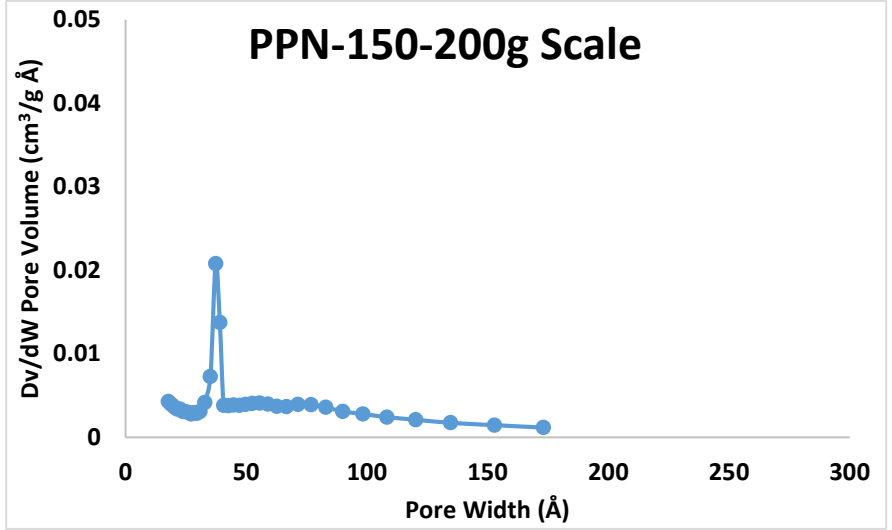


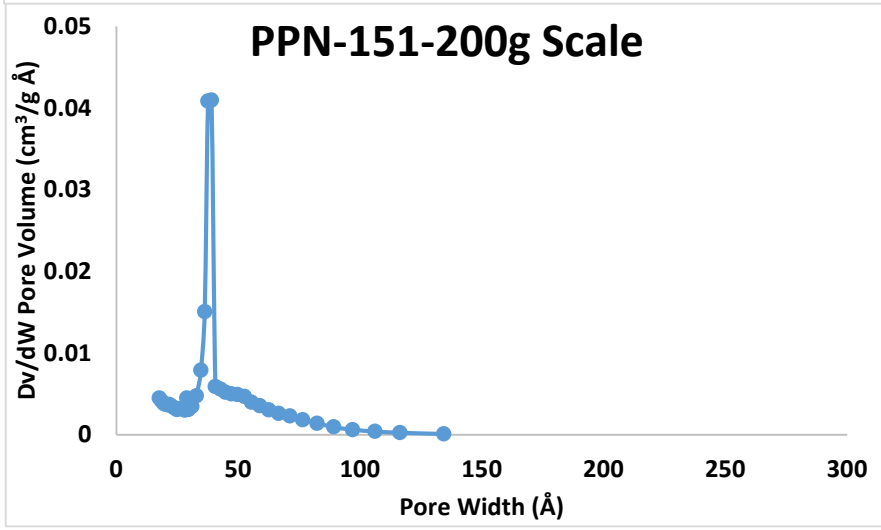
Sorbent	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)	CO_2 Uptake for DETA loaded sorbent at 40°C & 150mbar (kg/kg) (BET)
PPN-150-130g	778.1	0.897	79.1	0.033
PPN-151-50g	898.4	0.748	68.1	0.036
PPN-150-200g	538.1	0.365	10.5	0.020
PPN-151-200g	499.7	0.427	10.2	0.071

Comparison of Pore Size Distribution



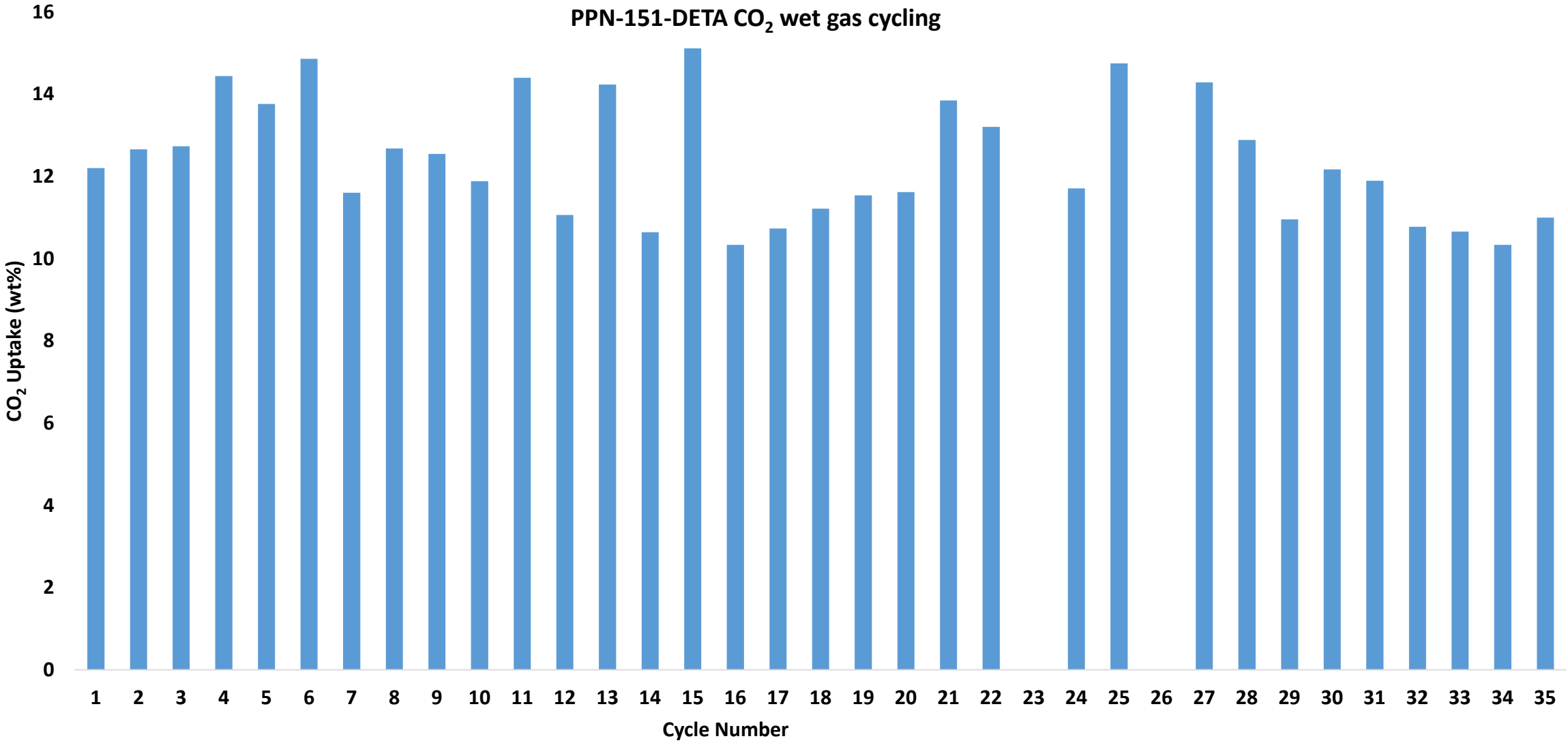




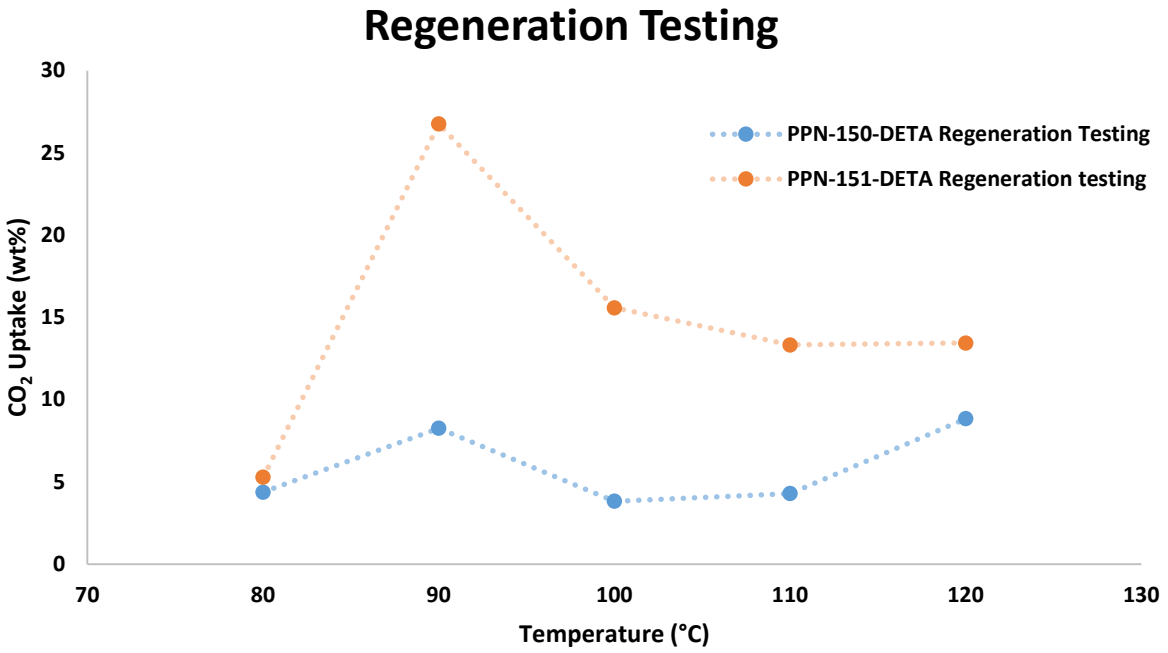


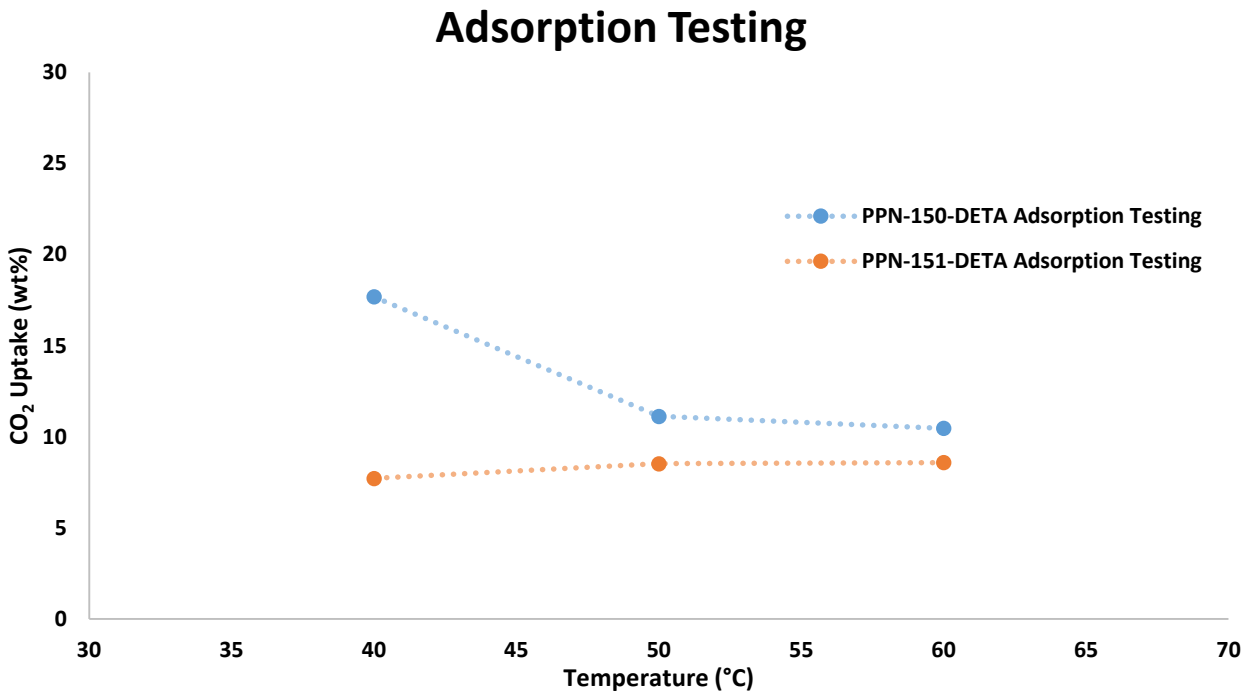
200g batches are predominantly microporous and lack much pore volume at higher pore sizes, reducing overall pore volume but not necessarily effecting CO_2 uptake which still predominantly takes place in the microporous regime.

Fixed-bed Testing Long-term Cycling



Fixed-bed Testing Adsorption and Regeneration





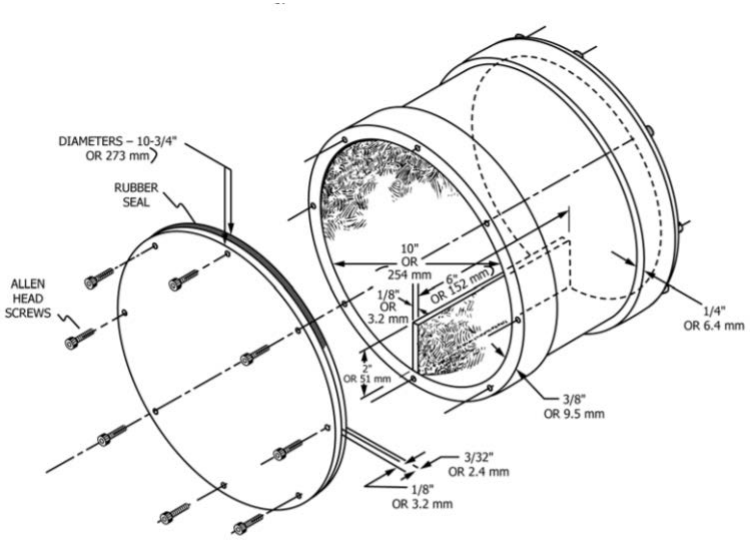
Fixed-bed Testing BP3 Testing

- As part of the purchase of the dynaSorb BT fixed-bed test unit, a 100mL adsorption column was also acquired
  - Current Testing plans for BP3 involve repeating previous breakthrough runs using the larger column

Test	Sample Size (mL)	Cycle (#)	Adsorption Temperature (°C)	H_2O	Regeneration Temperature (°C)
Stepped breakthrough	100	3	40-60, 10°C steps	Yes	120
Stepped regeneration	100	>5	40	Yes	80-120, 10°C steps
Long-term cycling 1	100	100	40	Yes	80-120
Long-term cycling 2	100	100	40	Yes	80-120

Attrition Testing

ASTM D4058 will determine the attrition pellets of sorbent sorbent materials



Material will be evaluated based off of a percentage of fine particles removed from pellets.

$$\textbf{Loss on Attrition}, \% = \frac{m_a - mb}{m_a} x\ 100$$

m_a = initial mass of pellet

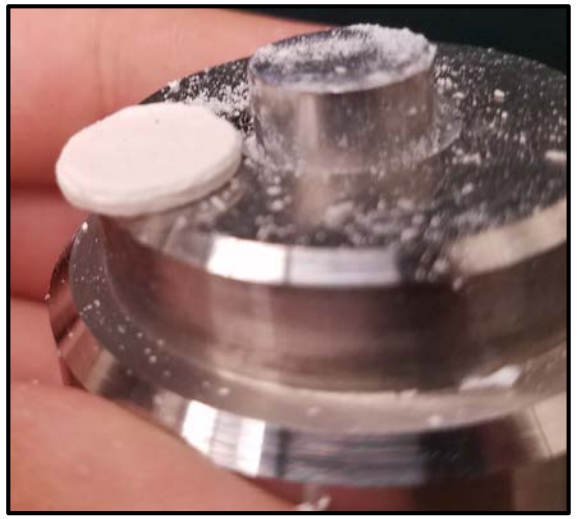
m_b = mass of pellet after attrition testing

ASTM D4058-96(2015) Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers, ASTM International, West Conshohocken, PA, 2015, https://doi.org/10.1520/D4058-96R15

Attrition Testing

- Pelletization performed by contractor LFA Machines did not produce a pelletized material

- Pelletization has been successful using the TAMU press. The appropriate amount of material will be produced on site and run using ASTM D4058 with contractor assistance



BP2 Success Criteria

Decision Point	Basis for Decision/Success Criteria	Status
Completion of Budget Period 2	Successful completion of all work proposed in Budget Period 2	All work on track for completion in BP2
	Produce ~200 grams of at least the two top-performing aPPN sorbent formulations (≥0.1 kg/kg working capacity) for initial fixed-bed cycling tests	90% complete. 250g batches of each PPN-150 and PPN-151 have been synthesized. Amine loaded samples from these batches are undergoing analysis to ensure their performance matches samples from medium scale batches 10-100g.
	Top-performing aPPN sorbent formulation retains a CO_2 working capacity of at least 0.1 kg/kg after 30 cycles during automated fixed-bed testing	100% complete based on current results for PPN-151-DETA. Fixed-bed testing will be repeated in the coming month.
	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified, including quotes and budget justification for service contractors and major equipment items	Submitted July 28, 2017 Updated August 14, 2017

Outline

- Introduction
  - Carbon capture
  - Amine-materials
  - Objectives
  - Budget
- BP1 Milestones
- BP2 Milestones
  - Synthesis optimization
  - Scale-up
  - Breakthrough
  - Pelletization, Attrition, and mechanical hardness
- BP3
  - Overview
  - Budget

BP3 Milestones

ID	Task	Milestone Description	Planned Completion	Verification Method
r	8.0	Produce at least 1 kilogram of the top-performing aPPN sorbent formulation (≥0.12 kg/kg working capacity) for optimal fixed-bed cycling tests	3/31/2018	Results reported in the quarterly report
s	9.0	Complete optimal fixed-bed cycling tests with the top-performing aPPN sorbent formulation and maintain at least ≥0.12 kg/kg working capacity in the presence of moisture and sulfur dioxide	7/31/2018	Results reported in the quarterly report
t	10.0	Complete initial technical and economic feasibility study	9/30/2018	Results reported in the quarterly report
FR	1	Draft Final Report	10/31/2018	Draft Final Report file

BP3 Success Criteria

Decision Point	Basis for Decision/Success Criteria
Completion of Budget Period 3	Successful completion of all work proposed in Budget Period 3
	Produce at least 1 kilogram of the top-performing aPPN sorbent formulation (≥0.12 kg/kg working capacity) for optimal fixed-bed cycling tests
	Optimal aPPN sorbent formulation retains a CO_2 working capacity of at least >0.12 kg/kg after 50 cycles in the presence of moisture and sulfur dioxide and <10% parasitic energy loss due to regeneration
	Results of the initial technical and economic feasibility study show significant progress toward achievement of the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches
	Submission of an updated state-point data table for the optimal sorbent based on the results of lab-scale testing
	Submission of a Final Report

framergy's Role in BP3 - NETL

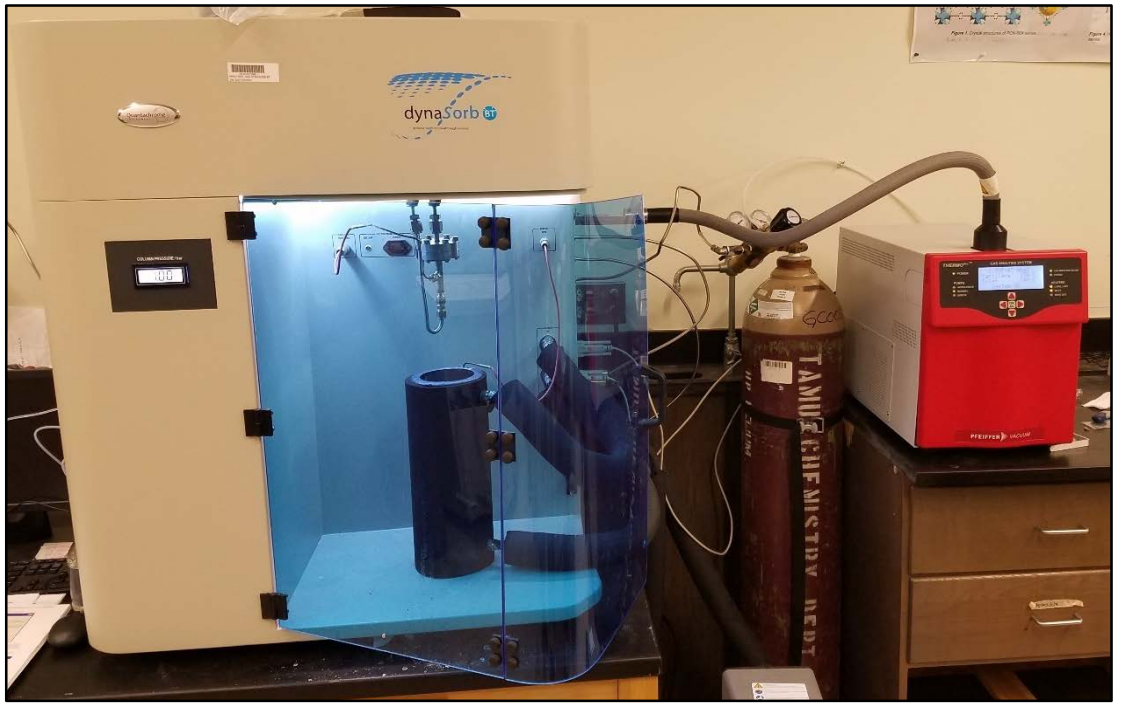
- Design and implement 20L synthesis system with temperature and pressure control
  - Integrate filtration unit for seamless processing
- Implement custom 1.5L fixed-bed device for assessment
  - Integrate 1.5L column and supporting equipment into Quantachrome automated fixed-bed instrument for kilogram-scale for breakthrough analysis
- Comprehensive technology assessment
  - EH&S risk assessment
  - Sorbent life-cycle assessment
  - Technical and economic feasibility study

framergy™

Fixed-bed Testing

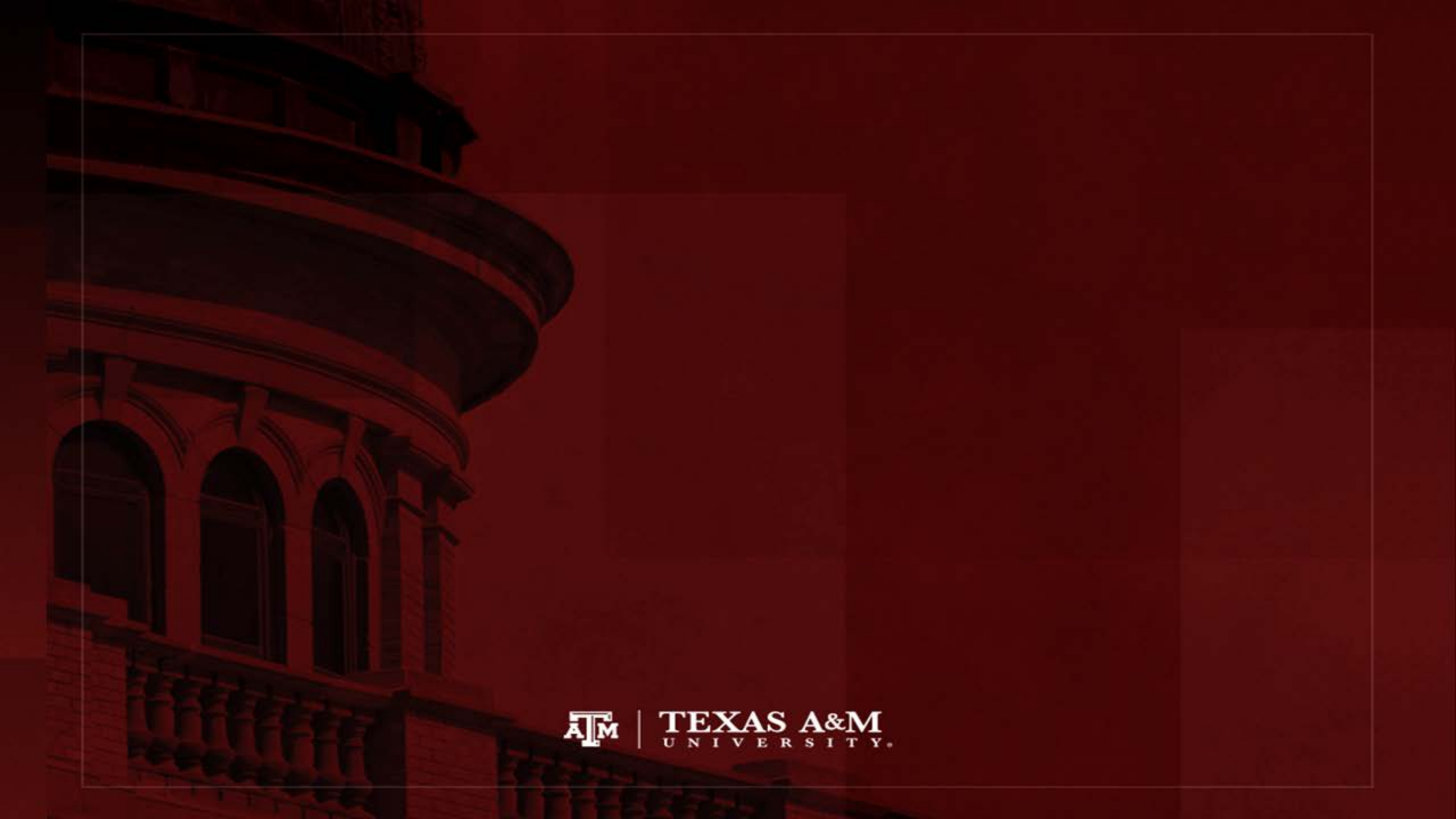
- Praxair has produced a custom gas mixture for us that contains 20ppm SO_2. This gas mixture will be used for fixed-bed testing
- Moving between lab and bench scale will require the ability to perform fixed-bed testing in greater than 100mL scales
- Quantachrome has been contracted to develop a 1.5L column
  - Current cost estimate is $42,000
    - The installation of a new mass flow controller could be performed at the same time as a previously scheduled service visit, saving ~$10,000
  - Fabrication will likely take several months

Quantachrome dynaSorb BT fixed-bed test unit



Acknowledgement and Disclaimer

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


TEXAS A&M
UNIVERSITY