Evaluation of amine-incorporated porous polymer networks (aPPNs) as sorbents for post combustion CO$_2$ capture

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Research Team

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• **Past Members:** Dr. Lanfang Zou, Dr. Mathieu Bosch, Dr. Xuan Wang, Dr. Yujia Sun, Dr. Ning Huang
• 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\textsubscript{2} capture that will approach the goal of 90% CO\textsubscript{2} capture rate with 95% CO\textsubscript{2} purity at a cost of electricity 30% less than baseline capture approaches
Amine-decorated Porous Materials

• Porous Polymer Networks (PPNs)

[Chemical structures and formulas]

McDonald, T. M.; Long, J. R., Nature 2015, 519 (7543), 303-308.
Initial PPN Candidate Materials

Yang, X. et al., *Polymer*. 2017
PPN-151-DEnviarname

**Cyanuric Acid (CA)**

\[ \text{Formaldehyde} + \text{Cyanuric Acid (CA)} \rightarrow \text{PPN-151} \]

\[ \text{PPN-151} + \text{Diethylenetriamine (DETA)} \rightarrow \text{PPN-151-D伊拉}}

**Conditions:**

DMSO, 150°C, 72hr

**References:**

PPN-151 Porosity Measurements

N\textsubscript{2} Isotherm PPN-151-DETA

<table>
<thead>
<tr>
<th>BET SA (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Average Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>804</td>
<td>0.784</td>
<td>67.3</td>
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</table>

PPN-151-DETA BJH Pore Size Desorption
PPN-151-DETA Fixed-bed Testing Long-term Wet Cycling

PPN-151-DETA CO₂ wet gas cycling

CO₂ Adsorption (wt%) vs Cycle Number
Regenerative Energy Demand

- Heat of adsorption at 150 mbar CO₂ and 40°C:
  - PPN-151-DETA: 1.40 MJ/kg CO₂

- Heat capacity increases exponentially with higher temperatures

- Regenerative energy demand at 85°C
  - PPN-151-DETA: 1.8 MJ/kg CO₂

(Typical MEA process: 3.8 MJ/kg CO₂)
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 Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>150°C</td>
</tr>
<tr>
<td>Time</td>
<td>5 day</td>
</tr>
<tr>
<td>Headspace</td>
<td>~80%</td>
</tr>
<tr>
<td>Melamine</td>
<td>201.62 g</td>
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<tr>
<td>Paraformaldehyde</td>
<td>108.00 g</td>
</tr>
<tr>
<td>Cyanuric acid</td>
<td>15.48 g</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide (DMSO)</td>
<td>2080 mL</td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>500</td>
</tr>
</tbody>
</table>
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

BET Surface Area of PPN-151

Granular CH₂O

Powder CH₂O

BET Surface Area (m²/g)

15 g (avg of 5 runs)

5-d

7-d

9-d Top

250 g

9-d bottom

900

800

700

600

500

400

300

200

100

0
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

BET Surface Area of Washed PPN-151

- *Full Wash*
- Acetone
- THF
- DCM
- MeOH
- MeOH x1
- MeOH x2

**Solvent Exchange**
1 kg Scale-Up Reactor
1 kg Scale-up at Vapor Point

Reaction Set-up

PPN Removal
Parameters and Performance of 1 kg Batch

1 kg batch of PPN-151

Quantity Adsorbed (cm$^3$/g STP) vs. Relative Pressure (P/P$_0$)

1 kg PPN-151-DETA Wet Gas Breakthrough Runs

CO$_2$ Uptake (wt%) vs. Cycle Number

Cycle Number: 1, 2, 3
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
• PPN-151-DETA can achieve $> 0.1 \text{ g/g CO}_2$ 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 *framergergy* and Vapor Point
  • 1 kg batch shows $> 0.12 \text{ g/g CO}_2$
• Final cycling tests will be performed
  • 1.5 L adsorber column has been ordered from Anton Paar
Acknowledgement and Disclaimer

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Acknowledgements

Publications


