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

NETL Kick-Off Meeting

Hong-Cai “Joe” Zhou

Department of Chemistry

Texas A&M University
Outline

• Background

• Project Objectives

• Technical approach
  o Build amine-PPNs from anchors
  o Directly assemble amine-PPNs materials with alkyl amine groups

• Project progress

• Budget

• Risks
Outline

• Background

• Project Objectives

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• Project progress

• Budget

• Risks
Team Background - Dr. Zhou

• PhD from Texas A&M University 2000 under F.A. Cotton
• Post-doctoral fellow in the Holm lab at Harvard University 2000-2002
• Associate/Assistant Professor at Miami University 2002-2008
• Moved to TAMU in 2008 currently a Robert A. Welch Chair in Chemistry
• Previously led successful carbon capture grants with ARPA-e IMPACCT program for post-combustion capture and the Office of Naval Research for carbon capture from air
• Currently the Zhou group (37 total) has 26 graduate students, three post doctoral fellows, two visiting scholars, and four undergraduate researchers
• 200 publications, 19,533 citations, $h$-index of 66, and 5 patents
Team Background – framergy, Inc.

- An office space, a wet chemistry - materials synthesis laboratory and a materials testing laboratory located in the technology incubator space of Texas A&M University
- Availability for expansion to accommodate the project team (Chemical Technician, Engineering Technician) and required testing instrumentation
Team Background – Ray Ozdemir

• 12 Years of Technology and Product Development Experience

• Synthesis and Characterization of High Capacity CO\textsubscript{2} Adsorbents
  • Synthesized and tested interior surface modified mesoporous adsorbents for selective capture of CO\textsubscript{2} from flue gas streams
  • This work was funded under a performance based U.S. DOE SBIR contract
  • Successfully converted Phase I to Phase II (DOE Grant Contract No: DE-FG02-06ER84549)

• Inventor of a New Contactor Material for the Selective Capture of CO\textsubscript{2} from Atmosphere
  • This work was funded by U.S. DOD for the purpose of capturing atmospheric CO\textsubscript{2} as a feedstock for generating liquid hydrocarbon fuels (DOD Grant Contract No: W911QX-10-C-0070)
# Project Organization

**Project Team**
- **Prof. Hong-Cai 'Joe' Zhou**
  - Texas A&M University
  - Principal Investigator

**Lanfang Zhou**
- Texas A&M University
- Materials Synthesis Lead

**Jian Wang, Yujia Sun, Sai Che, Qi Wang, Xinyu Yang**
- Texas A&M University
- Graduate Research Assistants

**Carrie L. Frederiksen**
- Texas A&M University
- Report on Project Spending

**Zachary Perry**
- Texas A&M University
- Project Coordinator

**Mr. O.K. ‘Ray’ Ozdemir**
- framergy, Inc.
- Co-Principal Investigator

**TBD**
- framergy, Inc.
- Eng. Technician

**TBD**
- framergy, Inc.
- Chemical Technician

### Year 1 Role
- **Project Oversight**
- **Technical and Administrative Point of Contact (POC)**
- **New Materials Synthesis and Characterization**
- **Molecular Simulation Lab Scale Testing and Screening**
- **Coordinate Technical Progress**
- **Report on Project Spending**
- **Report on Resource Management**
- **Sorbent Synthesis Optimization – Projected Cost Analysis**
  - **framergy POC**

### Year 2 Role
- **Project Oversight**
- **Technical and Administrative Point of Contact**
- **New Materials Synthesis and Characterization**
- **Molecular Simulation Lab Scale Testing and Screening**
- **Coordinate Technical Progress**
- **Report on Project Spending**
- **Report on Resource Management**
- **Technical and Administrative Oversight**
  - **Sorbent Optimization – Cost Analysis**
  - **framergy POC**
- **Assist Initial Sorbent Scale-up**
- **Assist Attrition and Mechanical Hardness Tests**
- **Assist Initial Fixed Bed Testing**

### Year 3 Role
- **Project Oversight**
- **Technical and Administrative Point of Contact**
- **New Materials Synthesis and Characterization**
- **Molecular Simulation Lab Scale Testing and Screening**
- **Coordinate Technical Progress**
- **Report on Project Spending**
- **Report on Resource Management**
- **Technical and Administrative Oversight**
  - **Technology EH&I Assessment**
  - **framergy POC**
- **Sorbent Production**
- **Optimal Fixed Bed Testing**
Aqueous Alkanolamine Absorbents

Traditional “wet scrubbing” methods:
• High regeneration cost
• Fouling of the equipment
• Solvent boil-off

Basic Adsorptive-Separation Mechanisms

• **Size and/or shape exclusion**

• **Thermodynamic equilibrium effect** --- adsorbate-surface and/or adsorbate packing interactions

• **Kinetic effect** --- different diffusing rates

• **Quantum sieving effect** --- the quantum effect

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Normal BP/K</th>
<th>Liquid $V_{mol}$ at NBP/cm$^3$ mol$^{-1}$</th>
<th>$T_c$/K</th>
<th>$V_c$/cm$^3$ mol$^{-1}$</th>
<th>$P_c$/bar</th>
<th>Kinetic diameter/Å</th>
<th>Polarizability $\times^{10^{25}}$/cm$^3$</th>
<th>Dipole moment $\times^{10^{18}}$/esu cm</th>
<th>Quadrupole moment $\times^{10^{26}}$/esu cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.30</td>
<td>32.54</td>
<td>5.19</td>
<td>57.30</td>
<td>2.27</td>
<td>2.551</td>
<td>2.04956</td>
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<td>0.0</td>
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<tr>
<td>Ne</td>
<td>27.07</td>
<td>16.76</td>
<td>44.40</td>
<td>41.70</td>
<td>27.60</td>
<td>2.82</td>
<td>3.956</td>
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<tr>
<td>Ar</td>
<td>87.27</td>
<td>28.7</td>
<td>150.86</td>
<td>74.57</td>
<td>48.98</td>
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<td>Kr</td>
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<td>209.40</td>
<td>91.20</td>
<td>55.00</td>
<td>3.655</td>
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<td>Xe</td>
<td>165.01</td>
<td>42.91</td>
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<td>118.00</td>
<td>58.40</td>
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<tr>
<td>H$_2$</td>
<td>20.27</td>
<td>28.5</td>
<td>32.98</td>
<td>64.20</td>
<td>12.93</td>
<td>2.827–2.89</td>
<td>8.042</td>
<td>0</td>
<td>0.662</td>
</tr>
<tr>
<td>D$_2$</td>
<td>23.65</td>
<td>24.81</td>
<td>38.35</td>
<td>60.20</td>
<td>16.65</td>
<td>2.827–2.89</td>
<td>7.954</td>
<td>0</td>
<td>—</td>
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<tr>
<td>N$_2$</td>
<td>77.35</td>
<td>34.7</td>
<td>126.20</td>
<td>90.10</td>
<td>33.98</td>
<td>3.64–3.80</td>
<td>17.403</td>
<td>0</td>
<td>1.52</td>
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<td>O$_2$</td>
<td>90.17</td>
<td>27.85</td>
<td>154.58</td>
<td>73.37</td>
<td>50.43</td>
<td>3.467</td>
<td>15.812</td>
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<td>Cl$_2$</td>
<td>239.12</td>
<td>45.36</td>
<td>417.00</td>
<td>124.00</td>
<td>77.00</td>
<td>4.217</td>
<td>46.1</td>
<td>0</td>
<td>—</td>
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<td>Br$_2$</td>
<td>331.90</td>
<td>51.51</td>
<td>584.10</td>
<td>135.00</td>
<td>103.00</td>
<td>4.296</td>
<td>70.2</td>
<td>0</td>
<td>—</td>
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<td>CO</td>
<td>81.66</td>
<td>35.5</td>
<td>132.85</td>
<td>93.10</td>
<td>34.94</td>
<td>3.690</td>
<td>19.5</td>
<td>0.1098</td>
<td>2.50</td>
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<tr>
<td>CO$_2$</td>
<td>216.55</td>
<td>37.4</td>
<td>304.12</td>
<td>94.07</td>
<td>73.74</td>
<td>3.3</td>
<td>29.11</td>
<td>0</td>
<td>4.30</td>
</tr>
</tbody>
</table>


Metal-Organic Frameworks (MOFs)

• Crystalline inorganic-organic hybrid porous materials

• Properties:
  ✓ Defined crystalline structure
  ✓ Permanent porosity
  ✓ Extremely high surface area
  ✓ Tunable pore size and shape
  ✓ Adjustable functionalization

Inorganic clusters  Organic linkers

MOF-5

Porous Polymer Networks (PPNs)

- Networks connected by covalent bonds
  - Boronic acid condensation
  - Schiff-base reaction
  - Yamamoto coupling

- Properties:
  - High surface area
  - Extremely low density
  - High thermal and chemical stability

Amine-tethered PPN-6

Amine-tethered PPN-6

- Dramatic increases in CO$_2$ uptake capacities at low pressures and exceptionally high CO$_2$/N$_2$ adsorption selectivity
- Expensive bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) are required
- Purely serves as a support for amine chains, decreasing volumetric CO$_2$ uptake

High-throughput Energy Model

- Measurement
  - Heat Capacity Data
  - Adsorption Data

- Intermediate Calculation
  - Heating Enthalpy
  - Isosteric Heat of Adsorption
  - Adsorption Enthalpies
  - Langmuir Parameters

- Condensing of Information
  - Required Energy For Recovering
  - IAST Calculation
  - Working Capacity

- Final Result
  - Energy Efficiency: Captured CO\textsubscript{2} per used Energy

\[ q = \sum_{i=1}^{n} q_{i,\text{max}} \frac{b_i P}{1 + b_i P} \]

\[ b_i = b_{i,0} \exp\left(\frac{E}{RT}\right) \]

Outline

• Background

• Project Objectives

• Technical approach
  o Build amine-PPNs from anchors
  o Directly assemble amine-PPNs materials with alkyl amine groups

• Project progress

• Budget

• Risks
Project Objectives

• Global objective:

“The overall objective of the proposed work is to demonstrate the feasibility of the Recipient’s (Texas A&M University) amine-incorporated porous polymer networks (aPPNs) as sorbents for post-combustion carbon dioxide (CO₂) capture while demonstrating significant progress toward achievement of the overall fossil energy performance goals of 90% CO₂ capture rate with 95% CO₂ purity at a cost of electricity 30% less than baseline capture approaches.”
## Success Criteria

<table>
<thead>
<tr>
<th>Decision Point</th>
<th>Basis for Decision/Success Criteria</th>
</tr>
</thead>
</table>
| Completion of Budget Period 1    | Successful completion of all work proposed in Budget Period 1  
                                      Novel aPPN sorbent formulation retains a CO₂ adsorption capacity of at least 0.1 kg/kg after 30 cycles via TGA or physisorption testing  
                                      Produce ~50 grams of at least the two top-performing aPPN sorbent formulations                                                                                   |
| Completion of Budget Period 2    | 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  
                                      Top-performing aPPN sorbent formulation retains a CO₂ working capacity of at least 0.1 kg/kg after 30 cycles during automated fixed-bed testing |
| Completion of 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 CO₂ 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% CO₂ capture rate with 95% CO₂ purity at a cost of electricity 30% less than baseline capture approaches |
Outline

• Team Background

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• Technical approach
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  o Directly assemble amine-PPNs materials with alkyl amine groups

• Project progress(tasks. Milestones and success criteria)

• Budget

• Risks
Material Development

- Multiple reaction pathways are being investigated
  - Sequential assembly and amine incorporation
  - Nitrogen incorporation then activation
  - Direct amine incorporation

- Metrics for evaluation:
  - CO$_2$ Uptake
  - Scalability
  - Stability
  - Cost
Proposed Amine-PPNs: 1

\[ \text{X = C, Si, Admantane} \]

\[ \begin{align*}
 &\text{Br} \quad \text{Br} \quad \text{Br} \\
 &\text{Br} \quad \text{Br} \quad \text{Br}
\end{align*} \]

\[ + \]

\[ \begin{align*}
 &\text{HO} \quad \text{B} \quad \text{B} \quad \text{OH} \\
 &\text{HO} \quad \text{B} \quad \text{B} \quad \text{OH}
\end{align*} \]

\[ \xrightarrow{\text{Pd Catalyst}} \]

\[ \text{a} \]

\[ \begin{align*}
 &\text{R: Cl} \\
 &\text{R: Alkyl-amines}
\end{align*} \]

\[ \text{b} \]
Proposed Amine-PPNs: 2-3

Amine-PPNs
Proposed Amine-PPNs: 4-5

X = C, Si, Ge, Admantane

Dioxane/HCl(aq) 100 °C → Amine-PPNs

OCl⁻/TEA 100 °C  DETA 100 °C → Amine-PPNs

“Click”
Proposed Amine-PPNs: 6
Outline

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• Project progress

• Budget

• Risks
Directly Assemble Amine-PPNs

Resist to oxidation

Secondary amine–framework PPN - stable toward oxygen
Primary amine containing PPN - oxidized
Amine-tethered PPN-80

- Commercially available alkyl amine as starting materials
- Facile synthesis, catalyst-free, High density of secondary amines
- Limited crystallinity, amorphous

Directly assemble a-PPNs

- Schiff base reaction is utilized to synthesize high crystalline amine-functionalized PPNs (a-PPNs)
- Postsynthetic functionalization:
  ✓ Reduction
  ✓ Tautomerism

\[
\begin{align*}
\text{NH}_2 & \quad + & \quad \text{CHO} & \rightarrow & \text{a-PPN-1} \\
\text{NH}_2 & \quad + & \quad \text{HO-CHO} & \rightarrow & \text{a-PPN-2} \\
\text{NH}_2 & \quad + & \quad \text{Si-CHO} & \rightarrow & \text{a-PPN-3}
\end{align*}
\]
Outline

• Team Background

• Project Objectives

• Technical approach
  o Build amine-PPNs from anchors
  o Directly assemble amine-PPNs materials with alkyl amine groups

• Project progress(tasks. Milestones and success criteria)

• Budget

• Risks
# Project Progress - Budget Period 1 Milestones

<table>
<thead>
<tr>
<th>MS</th>
<th>Task</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
<th>Verification Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>2</td>
<td>Complete synthesis of least 5 novel aPPN sorbent formulations at small-scale (~100 milligrams)</td>
<td>1/31/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>d</td>
<td>3.0</td>
<td>Complete synthesis of two Gen 0 materials (PPN-6-DETA and MOF-74-Mg) for standardization of measurements</td>
<td>1/31/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>e</td>
<td>3.1</td>
<td>Complete initial CO₂ adsorption testing with at least five aPPN sorbent formulations and generate CO₂ loading isotherms</td>
<td>3/31/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>f</td>
<td>2</td>
<td>Complete synthesis of 5 or more additional aPPN sorbents (~100 mg)</td>
<td>5/31/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>g</td>
<td>3.2</td>
<td>Complete initial aPPN sorbent physical property characterization (heat capacity, heat of reaction, density, particle size, etc.)</td>
<td>6/30/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>h</td>
<td>3.3</td>
<td>Complete initial TGA testing with the top-performing aPPN sorbents (&gt;0.08 kg/kg CO₂ capacity) in the presence of moisture</td>
<td>6/30/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>i</td>
<td>3.3</td>
<td>Complete initial thermal and chemical stability (H₂O, SO₂) studies via TGA cycling and small breakthrough</td>
<td>8/30/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>j</td>
<td>2</td>
<td>Sorbent Synthesis Optimization – Projected Cost Analysis</td>
<td>8/30/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>k</td>
<td>2</td>
<td>Produce ~50 grams of at least the two top-performing aPPN sorbent formulations</td>
<td>9/30/2016</td>
<td>Results reported in the quarterly report</td>
</tr>
</tbody>
</table>
## Project Progress - Budget Period 2 Milestones

<table>
<thead>
<tr>
<th>MS</th>
<th>Task</th>
<th>Milestone Description</th>
<th>Planned Completion</th>
<th>Verification Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>6.0</td>
<td>Complete acquisition and installation of the temperature-controlled, fixed-bed test unit coupled with a mass spectrometer</td>
<td>1/31/2017</td>
<td>Description and photos provided in the quarterly report</td>
</tr>
<tr>
<td>m</td>
<td>4.0</td>
<td>Identify synthesis conditions (temperature, reaction time, monomer ratios, etc.) that yield optimal aPPN sorbent performance and cost</td>
<td>3/31/2017</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>n</td>
<td>5.0</td>
<td>Finalize scale-up procedure for top-performing aPPN sorbent formulations and prepare laboratory facilities</td>
<td>3/31/2017</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>o</td>
<td>5.0</td>
<td>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</td>
<td>7/31/2017</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>p</td>
<td>6.0</td>
<td>Complete initial fixed-bed cycling tests with the scaled-up aPPN sorbent formulations and maintain at least ≥0.1 kg/kg working capacity</td>
<td>9/30/2017</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>q</td>
<td>7.0</td>
<td>Complete attrition and mechanical hardness testing of the top-performing aPPN sorbent formulations</td>
<td>6/30/2017</td>
<td>Results reported in the quarterly report</td>
</tr>
</tbody>
</table>
## Project Progress - Budget Period 3 Milestones

<table>
<thead>
<tr>
<th>MS</th>
<th>Task</th>
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<th>Planned Completion</th>
<th>Verification Method</th>
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</thead>
<tbody>
<tr>
<td>r</td>
<td>8</td>
<td>Produce at least 1 kilogram of the top-performing aPPN sorbent formulation (≥0.12 kg/kg working capacity) for optimal fixed-bed cycling tests</td>
<td>3/31/2018</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>s</td>
<td>9</td>
<td>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</td>
<td>7/31/2018</td>
<td>Results reported in the quarterly report</td>
</tr>
<tr>
<td>t</td>
<td>10</td>
<td>Complete initial technical and economic feasibility study</td>
<td>9/30/2018</td>
<td>Results reported in Final Report</td>
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</tbody>
</table>
Subcontracted Cost Analysis and Testing Tasks

• Sensitivity Analysis
  - Preliminary data: Tornado diagram generated for sensitivity analysis – cost of aPPN is mostly impacted by the changes in the Ni (COD)\(_2\) reagent cost

• Mechanical Hardness Testing
  - As per ASTM D4179 and D6175
  - Crush strength – resistance of a solid sorbent to compression: Evaluate the mechanical failure modes of the developed sorbent material (different than loss of activity)

• Attrition in Fluidized Bed
  - As per ASTM D-5757-95
  - Attrition of powdered sorbents in fluidized beds
  - Air Jet Attrition (AJI) will be reported

Preliminary data: Tornado diagram generated for sensitivity analysis – cost of aPPN is mostly impacted by the changes in the Ni (COD)\(_2\) reagent cost
Subcontracted Testing Tasks (cont.)

• Tasks 6. Initial Fixed Bed Testing
  • ACES, LLC Instrument acquisition & training
  • Generate breakthrough data
  • Variable CO₂/N₂ (v/v) rates
  • Variable flow rates
  • Gas Analysis: Hiden Analytical HPR20 gas analysis system

• Task 9. Optimal Fixed Bed Testing
  • ACES, LLC Instrument acquisition & training
  • Cyclic testing of sorbents under simulated flue gas conditions
## Technical Risks

<table>
<thead>
<tr>
<th>Description of Risk</th>
<th>Probability (Low, Moderate, High)</th>
<th>Impact (Low, Moderate, High)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adequate sorbent working capacity</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Sorbent handling and attrition</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>Uniform process temperature control</td>
<td>Low</td>
<td>Moderate</td>
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<tr>
<td>Process energy demand</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Relating fixed-bed performance/desired sorbent attributes to fluidized bed</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>performance/desired sorbent attributes</td>
<td></td>
<td></td>
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<tr>
<td>Difficulty controlling particle size distribution</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Diffusion limitations and slow adsorption kinetics due to increased amine density</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>High sorbent costs due to high cost of reagents</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>High sorbent costs due to high cost of synthesis and wash solvents</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Resource Risks:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Timely acquisition of the fixed-bed test unit and required ancillary support</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>framergy™ is a start-up company with relatively few employees</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>framergy™ is a start-up company and relatively small (infrastructure and laboratory and office space) compared to TAMU</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Acknowledgement