Use of a Novel Process for Revolutionizing CO$_2$ Capture

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Project team

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Statement of Problems

- **Low CO₂ sorption and desorption kinetics**
  - \(-\text{NH}_2 + \text{CO}_2 + \text{H}_2\text{O} \underset{k_{R1}}{\overset{k_{-R1}}{\rightleftharpoons}} (-\text{NH}_3^+)(\text{HCO}_3^-)\)  
    - R1 and -R1
  - where \(k_{R1}\) and \(k_{-R1}\) are determined by their corresponding activation energies (\(E_{R1}\) and \(E_{-R1}\)) are the apparent rate constants of the CO₂ sorption and desorption steps, respectively.

  - \(\text{CO}_2 + \text{OH}^- \underset{k_{R2}}{\overset{k_{-R2}}{\rightleftharpoons}} \text{HCO}_3^-\)  
    - R2 and -R2
  - where \(k_{R2}\) and \(k_{-R2}\) determined by their corresponding activation energies (\(E_{R2}\) and \(E_{-R2}\)) are the apparent rate constants of CO₂ sorption and desorption steps, respectively.

- **High energy consumption**
Hypothesis

How can we accelerate both CO₂ sorption and desorption? Firstly, let us how catalysis can help CO₂ desorption. Based on the reported $E_a$ of CO₂ desorption in amine sorption system, 114.25 kJ/mol, the increase ratios of the reaction rate constant ($k$) in Arrhenius equation of CO₂ desorption at 80 °C due to the use of a catalyst is estimated according to:

$$\frac{k_{\text{with-catalyst}}}{k_{\text{without-catalyst}}} = \frac{A}{A} e^{-\frac{E_{\text{with-catalyst}} - E_{\text{without-catalyst}}}{RT}} = e^{\frac{m * E_{\text{without-catalyst}}}{RT}}$$  \hspace{1cm} (E1)

where $m$ is the activation energy reduction percentage due to the use of a catalyst and presented below.

<table>
<thead>
<tr>
<th>CO₂ desorption rate constant increase ratio due to use of catalyst</th>
<th>Assumed CO₂ desorption temperature</th>
<th>Activation energy decrease %</th>
<th>1%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{with-cat}}/k_{\text{without-cat}}$</td>
<td>T = 393 K</td>
<td>2</td>
<td>6</td>
<td>33</td>
<td>188</td>
<td>1,080</td>
<td></td>
</tr>
</tbody>
</table>
Hypothesis (continued)

Obviously, the catalytic potential for CO\textsubscript{2} desorption is significant. Also, reducing the activation energy of the CO\textsubscript{2} desorption reaction can lead to a decrease in the activation energy of the CO\textsubscript{2} sorption according to the relation

\[ \Delta H = E_{a,\text{desorption}} - E_{\text{sorption}} \]  

(E2)

where \( \Delta H \) is the heat of reaction, \( E_{a,\text{desorption}} \) is the activation energy of the CO\textsubscript{2} desorption, and \( E_{a,\text{-adsorption}} \) is the activation energy of CO\textsubscript{2} adsorption because \( \Delta H \) is constant for a given temperature according to thermodynamic theories, a reduction in \( E_{a,\text{desorption}} \) due to use of the catalyst means that \( E_{a,\text{-adsorption}} \) is also decreased. Thus, a catalyst can accelerate both CO\textsubscript{2} sorption and desorption.
Potential significance of the results of the work

- Economic significance – Overcoming the challenges
  - Lower CO$_2$ capture cost and make CO$_2$ capture acceptable in more industries
  - Generate high-quality CO$_2$ via relatively low temperature CO$_2$ capture via avoidance of amine oxidation
  - Increase employments through the commercialization of both CO$_2$ capture and utilization technologies
  - Reduce the cost of CO$_2$ utilization and thus improve CO$_2$ utilization-based economy
Potential significance of the results of the work

- Environmental benefits:
  - Capturing CO$_2$ is beneficial to environment. The additional benefits of this technology include
    - Lowering CO$_2$ emission resulting from CO$_2$ capture itself due to the lower energy demand of the new CO$_2$ capture technology
      - Lower energy consumption means lower CO$_2$ emission
    - Liquid waste discharge is reduced due to a higher CO$_2$ capture efficiency of the new technology (or higher amine utilization efficiency) and thus less demands for the solvent and water for capturing the same amount of CO$_2$
    - Secondary air pollution is reduced because
      - Any amines used for CO$_2$ captures could generate secondary pollution, resulting from the oxidation of amines
      - A higher CO$_2$ capture efficiency means less demand for amine
Relevancy to fossil energy

The new CO$_2$ capture technology can help DOE

- Meet its mission – ensuring America's access to and use of safe, secure, reliable, and affordable fossil energy resources and strategic reserves
- Realize its vision – improving the living standards of the American people with clean, efficient, and reliable energy
- Achieve its goal –
  - Develop secure and affordable fossil energy technologies
  - Enhance U.S. economic and energy security
  - Develop and maintain world-class organizational excellence
Statement of project objectives (SOPO)

Objectives

- Develop an innovative catalytic CO$_2$ capture technology (never reported in literature)
  - Dramatically increasing CO$_2$ sorption and desorption rates at $<100$ °C (especially CO$_2$ desorption rate)
  - So that the waste heat in industry can be well used
- Avoiding the need for state-of-the-art spent solvent regeneration at $>100$ °C
- Lowing CO$_2$ capture cost to <$30/tonne-CO$_2$
- Generating $>95\%$-purity CO$_2$
Statement of project objectives (SOPO)

- **Scope of work**
  - Preparation and characterization of catalyst
    - ChCl-C$_3$H$_3$AlO$_6$ (choline chloride-aluminum formate) or CCAF
  - Evaluation of the CO$_2$ capture performance of the catalytic solvent
  - Study on the thermodynamics, reaction kinetics, mass and heat transfer, reaction mechanism
  - Techno-economic analysis
Collaborative work with NETL

- Work with NETL’s Materials Engineering & Manufacturing Directorate (MEM) on
  - Task 1 - Catalyst preparation and characterization
  - Task 2 - Evaluation of the new CO$_2$ capture technology
  - Task 3 - Study on thermodynamics and reaction kinetics
  - Task 5 - Investigation of mass and heat transfer
  - Task 7 – Techno-economic analysis

- Work with System Engineering and Analysis (SEA) to quantify the potential advantages associated with the proposed novel CO capture technology via the performance of Task 7
Other relevant aspects of the project management plan (PMP)
- Project organization and structure
Project Status

- **CO₂ capture setup**

Project Status

- Pictures of CO₂ capture setup
CO₂ capture experiment

- **Absorption**: Piperidine solutions are prepared by mixing piperidine with deionized water. Predetermined amount of catalysts (ChCl-C₃H₃AlO₆) are added into the reactor. The mass flow controller is used to control flow rate of the simulated flue gas. H₂O is introduced into the inlet gas stream by a syringe pump. The simulated flue gas is bubbled into piperidine solution via a corrosion-resistant muffler (<100 microns). The CO₂ concentration of the outlet gas of the reactor is measured with an inline gas analyzer, and the measured concentration-time profile is recorded by a data recording unit.

- **Desorption**: CO₂ desorption is realized by heating the spent sorbent obtained from CO₂ sorption step to a desired desorption temperature. A vacuum pump can be added to promoted the desorption. The desorbed CO₂ goes through a check valve and mixed with carrier gas (N₂) with a flow rate of 500 mL/min. The CO₂ concentration of the gas mixture is measured by an in-line gas analyzer. The quantity of CO₂ desorbed can be calculated by integrating the recorded CO₂ sorption profiles.
Capture of 400 ppm CO₂

- Piperidine-based sorbent showed better CO₂ absorption performance than MEA-based sorbent, especially, the effective time for achieving 90% or 100% CO₂ absorption efficiency.
- Piperidine-based sorbent can keep achieving 100% CO₂ for 3200 min under tested conditions. MEA-based sorbent can not achieve 100% time.
- Piperidine-based sorbent can achieve >90% CO₂ absorption for 3300 min under tested conditions. MEA-based sorbent can achieve >90% CO₂ absorption 1600 min.

[Absorption conditions: Solution: 100 g; Piperidine/MEA concentration: 0.235mmol/g; 400 ppm CO₂; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]
Project status

Capture of 400ppm CO₂

1000 ppm is the optimal catalyst loading for 2 wt% piperidine-based sorbent.

[Absorption conditions: Solution: 100 g; Piperidine/MEA concentration: 0.235mmol/g; 400 ppm CO₂; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]
Capture of 10% CO₂

- Piperidine-based sorbent showed better CO₂ absorption performance than MEA-based sorbent, especially, the effective time for achieving 90% or 100% CO₂ absorption efficiency.

- Piperidine-based sorbent can keep achieving 100% CO₂ for 5150 sec under tested conditions. MEA-based sorbent can not achieve 100% time.

- Piperidine-based sorbent can achieve >90% CO₂ absorption for 5200 sec under tested conditions. MEA-based sorbent can achieve >90% CO₂ absorption 3000 sec.

Absorption conditions: Solution: 100 g; Piperidine/MEA concentration: 5.87mmol/g; 10% CO₂; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C
Project status

Capture of 10% CO$_2$

- 1wt% is the optimized catalyst loading for 50 wt% piperidine-based sorbent.

[Absorption conditions: Solution: 100 g; Piperidine concentration: 50 wt%; 10% CO$_2$; Catalyst with 1ChCl:1C$_3$H$_3$AlO$_6$; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]
**Project status**

Capture of 10% CO$_2$

- 1ChCl:$1\text{C}_3\text{H}_3\text{AlO}_6$ is the best ratio for Piperidine-based sorbent.

[Absorption conditions: Solution: 100 g; Piperidine concentration: 50 wt%; 10% CO$_2$; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]
Project Status

- FTIR based reaction mechanism study setup is ready
Project Status

- Other frequently used instruments for the project are ready

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- Carbon Capture Project Manager Dr Carl Laird at NETL
- Dr. Janice A. Steckel at all the people at NETL

for their guidance!

Questions? Please.