POSTCOMBUSTION TECHNOLOGY for CO$_2$ Capture

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MIT Energy Initiative
MITEI's Research Program

• MIT President called in 2005 for a renewed Institute commitment to energy-related research and education

• MITEI annual research volume of over $30 million (USD)
  – About 800 research projects since 2007, around 400 researchers
  – Spread across 22 of the 24 MIT academic departments, and 24 labs and centres

• The MITEI interdisciplinary research program focuses on:
  – Innovative technologies and underlying policy analysis that will improve conventional energy systems
  – Transformational technologies to develop alternative energy sources
  – Global systems through multidisciplinary systems approach that integrates policy design and technology development
  – Tools to enable innovation, transformation and simulation of global energy systems through strategic basic research
CC&ST Program

- **CC&ST** Program internationally recognized as a *world leader in CCS*

- Initiated in 1989

- **Carbon Sequestration Initiative** (July, 2000)

- **Key Activities**
  - Research
  - Annual Forum
  - Outreach

Presentation Outline

• Introduction: Post Combustion Capture
• Combustion technologies
  – Technology Overview
  – PC/CFB comparison
• Post Combustion Options
• Solvent Absorption Theory
• Solvents for Post Combustion Capture
• Membrane Technology
• Adsorbents
• Concluding remarks
Introduction

Postcombustion (PC)

Coal → Power & Heat → CO₂ Separation
Air

CO₂ ≈ 3-15%

Precombustion (IGCC)

Coal → Gasification
Air/O₂ → Shift, Gas Cleanup + CO₂ Separation → H₂ → Power & Heat
Steam

CO₂ ≈ 40%

Oxyfuel Combustion

Coal → Power & Heat
Air

CO₂ > 95%

Adapted from EPRI 2007
**Introduction**

- **Postcombustion (PC)**: Coal and air enter, producing power and heat. CO₂ is separated, with a purity of ≈3-15%.
- **Precombustion (IGCC)**: Coal and air/oxygen enter, producing power and heat. CO₂ is separated, with a purity of ≈40%.
- **Oxyfuel Combustion**: Air is separated, and oxygen is added to coal. CO₂ is produced and separated, with a purity of >95%.

Adapted from EPRI 2007
Combustion technologies

REACTANTS

OXYGEN

NITROGEN

CHLORINE

MINERAL MATTER

SULPHUR

HYDROGEN

OXYGEN

CARBON

PRODUCTS

CARBON DIOXIDE

WATER

FLY ASH

NITROGEN

NO

SO₂

NO₂
Combustion technologies

REACTANTS
- Chlorine
- Mineral matter
- Oxygen
- Sulfur
- Hydrogen
- Carbon
- Nitrogen
- Oxygen
- Nitrogen

PRODUCTS
- Carbon dioxide
- Water
- Nitrogen
- Fly ash
- Sulfur dioxide
- Nitrogen oxide (NO)
- Nitrogen dioxide (NO₂)
Coal Fired Power Plant - An Integrated Approach
Combustion technologies

Coal Fired Power Plant - An Integrated Approach
Combustion technologies
PC / FB Boilers
Combustion technologies
PC / FB Boilers

<table>
<thead>
<tr>
<th></th>
<th>SUBCRITICAL PC</th>
<th>SUPERCRITICAL PC</th>
<th>ULTRA SUPERCRITICAL PC</th>
<th>SUBCRITICAL CFB</th>
</tr>
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<tbody>
<tr>
<td>Performance</td>
<td>WOC</td>
<td>WC</td>
<td>WOC</td>
<td>WC</td>
</tr>
<tr>
<td>Efficiency (HHV)</td>
<td>34.3</td>
<td>25.1</td>
<td>38.5</td>
<td>29.3</td>
</tr>
<tr>
<td>CO2 emitted (g/KWh)</td>
<td>931</td>
<td>127</td>
<td>830</td>
<td>109</td>
</tr>
<tr>
<td>COE</td>
<td>4.84</td>
<td>8.16</td>
<td>4.78</td>
<td>7.69</td>
</tr>
</tbody>
</table>

Basis net output: 500 MWe, 61.2% wt C, HHV=25350 kJ/kg

Performance and economics for air-blown PC generating technologies

Adapted from The Future of Coal, Massachusetts Institute of Technology
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Why post-combustion capture?

- **Compatible with existing** power plant infrastructure (retrofit possibility)
- **Capture readiness** makes the post-combustion capture relatively easy to incorporate into power plants
- Leading candidate for **gas-fired power plants**. Neither pre- or oxy- approaches well suited for gas plants at this time
- Capture technologies are considered **available** and the solvent technologies are proven on a smaller scale
- Learning by doing will lead to **cost reductions** similar to experience with other capture processes (SOx)
- Learning by searching will lead to **better solvents** and **process integration**
Technology options for CO$_2$ capture
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Solvent Absorption Theory

Step 1  A gas mixture is contacted with a liquid to preferentially dissolve component(s) from the gas to form a solution in the liquid

Step 2  The 'loaded' solvent is exposed to alternate pressures and/or temperatures in order to re-release the absorbed gas. This operation is known as 'Stripping' and allows the solvent to be recovered for re-use
Solvent Absorption Theory

- **Absorber**
  - Feed Gas
  - Wash Water
  - Rich Solvent

- **Stripper**
  - Treated Gas
  - Lean Solvent
  - CO₂

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IEAGHG Summer School
July 22 - 26, 2013, Nottingham (UK)
Solvent Absorption Theory

Calculations in Solvent Absorption:

- Equilibrium relationship
- Mass and Energy Balances
- Mass transfer or efficiency equations (kinetics)
Solvent Absorption Theory

Equilibrium

The capacity of a solvent to take up CO$_2$ is given by an equilibrium relationship:

\[ X = \text{mols CO}_2 / \text{mols solvent} \]
\[ Y = \text{mols CO}_2 / \text{mols inert gas} \]

Equilibrium Line
Solvent Absorption Theory

Mass balance

Operating Line on an $X-Y$ diagram has a slope of $L/G$ and passes through $(X_1, Y_1)$ and $(X_2, Y_2)$.

\[
G(Y_1 - Y) = L(X_1 - X)
\]

$L$ – flowrate of solvent

$G$ – flowrate of inert gas

$L = \text{mols } \text{CO}_2 / \text{mols solvent}$

$Y = \text{mols } \text{CO}_2 / \text{mols inert gas}$

Equilibrium Line

$X = \text{mols } \text{CO}_2 / \text{mols solvent}$
Solvent Absorption Theory

Issues for carbon capture

- **Low** total flue gas pressure
- **Low** CO$_2$ concentrations
- Very high flowrates (**big columns**)
- High **energy demand** in the reboiler (25-35% of power plant output)

- Impurities cause solvent degradation, loss of performance and equipment corrosion
- Solvent can be lost from the **top of the absorber**

![Solvent Absorption Diagram]

**Diagram Image Description:**
- **Treated Gas**
- **Wash Water**
- **Feed Gas**
- **Rich Solvent**
- **Lean Solvent**
- **CO$_2$**

**Diagram Legend:**
- **ABSORBER**
- **STRIPPER**

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Solvents for Post Combustion

Amine Solvents

**Primary and Secondary Amines**

\[ 2(R-NH_2) + CO_2 \leftrightarrow R-NH-COO^- + R-NH_3^+ \]

- Two solvent molecules required for each CO2 molecule sorbed
- Carbamates form

**Examples:**
- MEA
- Ammonia

**Tertiary and Hindered Amines**

\[ R_3-N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \]

- One solvent molecule required for each CO2 molecule sorbed, but slower rate
- Carbonates form

**Examples:**
- AMP
- MDEA

*Increasing reaction rate*  
*Increasing capacity*
Solvents for Post Combustion
Primary and Secondary amines

Monoethanolamine (MEA)

- Fluor Daniel ECONAMINE FG, Kerr-McGee/ABB Lummus
  - Commercially successful
  - BUT:
    - High energy consumption 25-35% of power plant output
    - Amine degradation caused by $O_2$, $SO_x$ and $NO_x$
    - Degradation products cause corrosion
    - Solvent volatility leads to loss to atmosphere
Ammonia

$2\text{NH}_3 + \text{CO}_2 \leftrightarrow \text{NH}_2\text{COO}^- + \text{NH}_4^+$

- Alstom/EPRI, Powerspan/NETL; UK CAER/E-ON,CSIRO
- Less degradation, more O2, SOX and NOX admissible
- BUT
  - Solvent volatility means high losses unless low temperatures are used

Example: Chilled Ammonia
Solvents for Post Combustion
Tertiary and Hindered Amines

**Hindered amines**
- Mitsubishi KS-1, Exxon Flexsorb PS
  - Less solvent required
  - Slightly lower energy consumption
  - Lower rates of solvent degradation

**Methyldiethanolamine (MDEA)- tertiary amine**
- DOW, Huntsman, BASF
  - Used industrially for H$_2$S removal in particular
  - Slower kinetics which leads to greater tower height
  - Improved through the use of promoters
Solvents for Post Combustion

**Amino Acid Salts**

- Non-volatile
- Non-toxic and biodegradable
- Resistant to degradation by $O_2$, $SO_X$ and $NO_X$
- BASF Puratreat, Siemens/TNO

**Potassium Carbonate**

- Non-volatile
- Non-toxic and biodegradable
- Resistant to degradation by $O_2$, $SO_X$ and $NO_X$
- Slower kinetics which gives greater tower height. Improved through the use of promoters
- DOE/University of Illinois, CO2CRC
Solvents for Post Combustion
Comparison of Solvent Properties

<table>
<thead>
<tr>
<th></th>
<th>Cost (US$/lb)</th>
<th>Volatility (atm x 10^3 at 40C)</th>
<th>Degradation</th>
<th>Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>40</td>
<td>0.1</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>MDEA</td>
<td>300</td>
<td>0.003</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Ammonia</td>
<td>5</td>
<td>200</td>
<td>None</td>
<td>High</td>
</tr>
<tr>
<td>Potassium Carbonate</td>
<td>40</td>
<td>0</td>
<td>None</td>
<td>High</td>
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Membrane Gas Absorption

Absorption liquid on one side of the membrane and the gas stream on the other side of the membrane

- Size of the pores:
  - Large enough so that the CO$_2$ can easily pass through the membrane
  - Small enough so that the liquid will not wet the pores
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Adsorption Theory

- Utilizes a solid (usually granular, beads, pellets) material, selective for one or more components in the gas phase
- Proportional to the amount of surface: very porous solids are used (up to 3000 m$^2$/g)
Adsorption Theory

Adsorption Processes

• PSA – *pressure swing adsorption* – pressure is varied

• VSA – *vacuum swing adsorption* – pressure is varied from a vacuum to some value above atmospheric pressure

• TSA – *temperature swing adsorption* – temperature is varied

• ESA – *electrical swing adsorption* – a current is applied cyclically to a conducting adsorbent such as a carbon
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Summary

- **Chemical absorption** currently most feasible technology for post combustion

- **Commercially available**, although not at large scale (>500 MW_e)

- **Energy penalty** and **additional costs** high with current solvents: R&D focus on process integration & solvents

- CO₂ capture between **80-90%**

- **Retrofit possibility**
Summary

Post Combustion Where to Focus!!?

- **Perfect solvent**: Higher capacity, lower regeneration energy, stable and cheaper

- **Heat integration** with the power plant

- **Heat recovery** (top of stripper, heat exchangers)

- **Cheaper equipments**
Thank you!!!

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