CO$_2$ Separation – State of the Art and Future Prospects

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Director of Technology
Overview

- This presentation covers CO₂ capture techniques
  - Flue gas scrubbing
  - Precombustion CO₂ capture
  - Oxyfuel

- CO₂ separation technologies
  - adsorption
  - membrane
  - absorption
  - Low temperature (primarily purification and liquefaction)

- We will deal with options using existing technology together with new techniques requiring further development
Carbon Dioxide Management
Reducing CO₂ Emissions
Carbon Dioxide Management
Reducing CO₂ Emissions

- Enhanced Oil Recovery
- Enhanced Coal Bed Methane
- Old Oil/Gas Fields
- Saline Formations

Flue Gas Scrubbing

Amine Absorption

CO₂ Compression & Dehydration

Sky

CO₂

N₂

O₂

Power & Heat

Fuel

Air
Carbon Dioxide Management
Reducing CO$_2$ Emissions

- Enhanced Oil Recovery
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Carbon Dioxide Management
Reducing CO₂ Emissions

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Flue Gas Scrubbing
Precombustion Decarbonisation
Oxyfuel
# CO₂ Separation Technologies

## Capabilities

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Membrane</th>
<th>Absorption</th>
<th>Cryogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Pressure</td>
<td>Low to High</td>
<td>Medium to High</td>
<td>Low to High</td>
<td>Medium to High</td>
</tr>
<tr>
<td>CO₂ Pressure</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low to Medium</td>
</tr>
<tr>
<td>CO₂ Purity</td>
<td>Medium to High</td>
<td>Low to Medium</td>
<td>Medium to High</td>
<td>High</td>
</tr>
<tr>
<td>CO₂ Recovery</td>
<td>Medium to High</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
CO₂ Separation Technologies
Commercial Applications

- **Adsorption**
  - Hydrogen Production
  - ASU Air Clean-up

- **Membrane**
  - Natural Gas Purification
  - Enhanced Oil Recovery

- **Absorption**
  - Syngas Purification
  - CO₂ Recovery from Flue Gas

- **Low Temp**
  - CO₂ Liquefaction
# Flue Gas Scrubbing

- **Typical CO₂ Compositions…**

<table>
<thead>
<tr>
<th>Source</th>
<th>CO₂ Range</th>
<th>Impurities</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas Turbine Exhaust</td>
<td>3-4%</td>
<td>low SOₓ and NOₓ levels, 12-15% O₂</td>
<td>1 atm</td>
</tr>
<tr>
<td>Coal/Oil Fired Boilers</td>
<td>11-14%</td>
<td>high SOₓ and NOₓ levels, 2-5% O₂</td>
<td>1 atm</td>
</tr>
<tr>
<td>IGCC Syngas Turbine Exhaust</td>
<td>4.5-6%</td>
<td>Low SOₓ and NOₓ</td>
<td>1 atm</td>
</tr>
<tr>
<td>Blast Furnace Gas (after combustion)</td>
<td>25-30%</td>
<td>SOₓ and NOₓ present</td>
<td>1 atm</td>
</tr>
<tr>
<td>Cement Kiln off-gas</td>
<td>15-35%</td>
<td>Could have many impurities</td>
<td>1 atm</td>
</tr>
</tbody>
</table>
Flue Gas Scrubbing

- Uses aqueous amine solvents
  - Sensitive to acidic impurities such as \( \text{NO}_2, \text{SO}_2, \text{SO}_3 \) and \( \text{HCl} \)
  - Pretreatment requirement to achieve low levels of \( \text{NO}_2, \text{SO}_2, \text{SO}_3 \) and \( \text{HCl} \)

- Commercial systems available e.g.
  - Kerr-McGee / ABB Lumus Crest
  - Fluor Daniel ECONAMINE
  - MHI

- Utilities required
  - Low pressure steam for regeneration
  - Power for pumping
Flue Gas Scrubbing – Current Developments

- Advanced amine formulations
  - More resistant to acid gas impurities and oxygen
  - Lower regeneration energy
- New contacting devices
  - Hybrid membrane absorption systems
- High temperature regenerable solid sorbents
  - Lithium and Calcium Oxide based
General Arrangement For CO\textsubscript{2}-free Hydrogen Production
Precombustion CO₂ Capture – Natural Gas Based Systems

- Conventional hydrogen production
  - SMR, POX, ATR
  - Convective Reforming Combined with the above

- Conventional CO₂ removal
  - Chemical or physical absorption system
  - Adsorption using a PSA system

Comparative economics at 42 MM SCFD H₂(1986)

<table>
<thead>
<tr>
<th></th>
<th>Gemini System</th>
<th>Amine/PSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital (M$)</td>
<td>9800</td>
<td>13300</td>
</tr>
<tr>
<td>Operating (M$/yr)</td>
<td>550</td>
<td>590</td>
</tr>
</tbody>
</table>
Precombustion CO₂ Capture – Natural Gas Based Systems

Concept
Combine reforming or water gas shift reaction with high temperature CO₂ removal to decarbonise gas turbine fuel

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2
\]

Process goals
● Shift CO to low levels and simultaneously remove CO₂
● Produce decarbonised H₂ fuel at high T/P
  – No steam condensation
  – Higher electrical generation efficiency

drive reaction this way
remove by adsorption
A closer look at the SER process

- Multiple adiabatic fixed beds containing mixture of shift catalyst and high temperature CO₂ adsorbent such as hydrotalcites
- Cyclic operation, reaction step and regeneration steps
- Regeneration by lowering pressure and purging with steam (Pressure Swing Adsorption, or PSA mode)
- Specific process cycle developed to achieve 90+% carbon recovery, 97+% CO₂ purity, and 99+% H₂ recovery

**Diagram:**
- **Reaction**
- **CO₂ Rinse**
- **Depressurisation**
- **Purge**
- **Equalisation**
- **Pressurisation**

Decarbonised H₂ product

Packed with catalyst and adsorbent

Feed (syngas)

CO₂ rinse

CO₂ product

CO₂ product

Steam

Recycle

Equalisation

Feed (syngas)
O₂ ATR – with SER

O₂ Feed
Natural Gas
Steam

preheat
ATR
WHB
HTS
SER

100 bar CO₂
Steam
N₂

Condenser
Steam

H₂
Steam

Power

Air Feed

Steam

100 bar

Steam

Power

Steam Turbines

Water

Water

HRSG

HRSG
Aspen simulation results with MDEA & SER systems

<table>
<thead>
<tr>
<th>MDEA SER</th>
<th>Air ATR</th>
<th>Air ATR SD</th>
<th>O₂ ATR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon removal</td>
<td>94.2%</td>
<td>94.6%</td>
<td>96.2%</td>
</tr>
<tr>
<td></td>
<td>99.3%</td>
<td>99.3%</td>
<td>97.9%</td>
</tr>
<tr>
<td>Efficiency</td>
<td>42.6%</td>
<td>41.8%</td>
<td>41.8%</td>
</tr>
<tr>
<td></td>
<td>48.9%</td>
<td>46.6%</td>
<td>47.3%</td>
</tr>
<tr>
<td>$/tonne CO₂</td>
<td>$34.85</td>
<td>-</td>
<td>$30.29</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>$24.02</td>
</tr>
</tbody>
</table>
Ion Transport Membrane

- Hot Compressed Air
- Oxygen Product
- Oxygen
- Pure Oxygen
- Porous membrane support
- Dense, slotted backbone
- Product Withdrawal Tube
- 800-900°C
- 200-300 psig
- Vitiated compressed-air
- Thin membrane

Diagram showing the process of ion transport in a membrane, with arrows indicating the flow of oxygen, electrons, and vitiating air.
Commercial ITM Oxygen Vessel Concept: 350 tons/day
CO₂-Free Power and Hydrogen From Coal Fuelled System

Coal → Coal Gasification → Quench/Heat Recovery → Shift reactors → CO₂/H₂S Physical Absorption System → H₂ Product

100 bar CO₂

100 bar H₂

4,000 tonne/day CO₂ @ 100 bar

220,000 Nm³/hr H₂

Power 380 MW

H₂ Purification

Air Feed → Air

Steam → Gas Turbine → Power → Heat Recovery

N₂ → Shift reactors

Water/N₂ → Quench/Heat Recovery

Oxygen → Shift reactors

Ash/Slag → Coal Gasification

Steam → Power

Steam → Steam Turbines → Power

Water
Oxyfuel CO$_2$ Capture

- Eliminates N$_2$ from the flue gas by burning the fuel in oxygen
- Recycle of flue gas can be used to vary the flame temperature
- Combustion products contain:
  - CO$_2$ + H$_2$O
  - Any inerts from air inleakage or oxygen impurities
  - Oxidation products and impurities from the fuel (SO$_x$, NO$_x$, HCl, Hg, etc.)
Oxyfuel Boiler Conversion
(CCP Grangemouth System)

Steam

ID Fan

Boiler

FGR Fan

Air

FD Fan

Steam Heater

O₂ from ASU 15.08 kg/s

Fuel 4.12 kg/s

O₂ from ASU 15.08 kg/s

Steam 63.0 kg/s

Not required for Oxyfuel firing but retained for air firing backup

Air Infiltration

Local CO₂ Drying and Compression

Stack

20.50 kg/s

74.51 kg/s

231°C

4.35 kg/s

74.51 kg/s

231°C

41.06 kg/s

220°C

Air

77.6 %w/w

1.6 %w/w

9.2 %w/w

CO₂

H₂O

O₂

N₂

Inerts

69.1 %w/w

29.6 %w/w

59.6 %w/w

17.4 %w/w

5.5 %w/w
Raw CO$_2$ Treatment

- **Cooling water return**: 2704 tonne/hr, 44°C
- **Cooling water**: 2617 tonne/hr, 24°C
- **Boiler feed water**: 12.2 tonne/hr
- **Direct Contact Cooler**
- **Compression**: 14.5 MW
- **Water knockout**: 2.4 tonne/hr
- **Flue gas**: (collected from local heaters or boilers)
  - CO$_2$: 40.77 mol%
  - O$_2$: 1.67 mol%
  - Ar: 2.10 mol%
  - N$_2$: 8.08 mol%
  - H$_2$O: 47.28 mol%
  - SO$_2$: 0.08 mol%

**Total, kmol/hr**: 4,577

**T, °C**: 30.00
**P, bara**: 32.06

**To central purification system**
Central CO₂ Purification and Compression System
(CCP Grangemouth System)

<table>
<thead>
<tr>
<th>Gases</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>30 bara</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.6 bara</td>
</tr>
<tr>
<td>O₂</td>
<td>19.6 bara</td>
</tr>
<tr>
<td>SO₂</td>
<td>9.8 bara</td>
</tr>
<tr>
<td>CO₂</td>
<td>221 bara</td>
</tr>
</tbody>
</table>

- CO₂ product for sequestration
- CO₂ from local drying and compression areas
- Flue Gas Expander
- Warm Exchanger
- Cold Exchanger

| CO₂  | 25.1 mol% |
| N₂   | 47.8 mol% |
| Ar   | 13.6 mol% |
| O₂   | 13.5 mol% |
| SO₂  | 0.0 mol%  |

| CO₂  | 96.2 mol% |
| N₂   | 1.9 mol%  |
| Ar   | 1.1 mol%  |
| O₂   | 0.7 mol%  |
| SO₂  | 0.1 mol%  |
Progression of Supercritical PF

- Proven
  - Spiral furnace 540°C/560°C
- For demonstration now
  - Vertical ribbed tubes 600°C/620°C
- Requires materials development
  - ISB 2000
- Requires materials & layout development
  - COST 522
- Novel layouts
  - 700°C/720°C/720°C
- THERMIE 700
Oxyfuel PF Coal Fired Power Station

<table>
<thead>
<tr>
<th></th>
<th>AIR</th>
<th>OXYFUEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal flow kg/sec (dry ash free)</td>
<td>47.9</td>
<td>47.9</td>
</tr>
<tr>
<td>Heating value MW(LHV)</td>
<td>1554</td>
<td>1554</td>
</tr>
<tr>
<td>Power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam turbines MW</td>
<td>652</td>
<td>718</td>
</tr>
<tr>
<td>Auxiliaries MW</td>
<td>-26</td>
<td>-28</td>
</tr>
<tr>
<td>Oxygen plant MW</td>
<td>-</td>
<td>-103</td>
</tr>
<tr>
<td>CO₂ compression MW</td>
<td>-</td>
<td>-76.5</td>
</tr>
<tr>
<td>Total net power MW</td>
<td>626</td>
<td>511</td>
</tr>
<tr>
<td>Net efficiency %</td>
<td>40.3</td>
<td>32.9</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow tonne/day</td>
<td>0</td>
<td>11000</td>
</tr>
<tr>
<td>Purity %</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow tonne/h</td>
<td>0</td>
<td>480</td>
</tr>
<tr>
<td>Pressure bara</td>
<td>-</td>
<td>220</td>
</tr>
<tr>
<td>Purity %</td>
<td>-</td>
<td>99.99</td>
</tr>
<tr>
<td>Recovery %</td>
<td>-</td>
<td>91.3</td>
</tr>
</tbody>
</table>

- Cryogenic Air Separation Unit uses adiabatic air compressor
- CO₂ compressor has two adiabatic stages
- Heat for condensate and boiler feedwater preheating
- Supercritical and Oxyfuel are suitable for retro-fit or new build
- Supercritical/Oxyfuel efficiency ~38% (approximately the same as IGCC)
Natural Gas Fired Oxyfuel Gas Turbine Combined Cycle

<table>
<thead>
<tr>
<th>Net Power</th>
<th>226 MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>~45% LHV</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3400 tonne/day</td>
</tr>
</tbody>
</table>
A Water Quenched Direct Fuel Oxygen Combustion (CES Cycle)

- No limit on steam temperature
- Efficiencies >50% possible

*CH₄, CO, H₂, etc.
The Chemical Looping Combustion Principle

- Metal oxides of transition metals
- Reactor Temperatures 800-1200°C
- Either Brayton or Rankine steam cycle

No oxygen plant required
Thank you
tell me more
www.airproducts.com