Purification of Oxyfuel-Derived CO$_2$: Current Developments and Future Plans

1$^{st}$ OXYFUEL COMBUSTION CONFERENCE
8th - 11th September 2009
Radisson Hotel, Cottbus, Germany

Vince White and Kevin Fogash
Air Products
9$^{th}$ September 2009
Oxyfuel CO₂ Purification

- Oxyfuel combustion of coal produces a flue gas containing:
  - CO₂ + H₂O
  - Any inerts from air in leakage or oxygen impurities
  - Oxidation products and impurities from the fuel (SOₓ, NOₓ, HCl, Hg, etc.)

- Purification requires:
  - Cooling to remove water
  - Compression to 30 bar: integrated SOx/NOx/Hg removal
  - Low Temperature Purification
    • Low purity, bulk inerts removal
    • High purity, Oxygen removal
  - Compression to pipeline pressure
Air Products’ Oxyfuel CO₂ Capture Technology

Boiler Steam Cycle

Heat Recovery

Sour Compression

Condensate Collection

TSA Unit

CO₂ Compression

Auto-Refrigerated Inerts ( +O₂) Removal Process

Air Products PRISM® Membrane

Raw Flue Gas

O₂ and CO₂ Rich [To Boiler]

Inerts Vent [To Atmosphere]

Product CO₂
Air Products’ CO₂ Purification and Compression Technology for Oxyfuel

**Sour Compression**
- SOₓ/NOₓ removed in compression system
  - NO is oxidised to NO₂ which oxidises SO₂ to SO₃
  - The Lead Chamber Process
- FGD and DeNOₓ systems
  - Optimisation
  - Elimination
- Low NOx burners are not required for oxyfuel combustion
- Hg will also be removed, reacting with the nitric acid that is formed

**Auto-Refrigerated Inerts Removal**
- Ar, N₂, O₂
- Removal minimises compression and transportation costs.
- Optional O₂ removal for EOR-grade CO₂
- CO₂ capture rate of 90% with CO₂ purity >95%
- CO₂ capture rate depends on raw CO₂ purity which depends on air ingress

**Air Products’ PRISM® Membrane**
- For enhanced CO₂ + O₂ Recovery
- Inerts vent stream is clean, at pressure and rich in CO₂ (~25%) and O₂ (~20%)
- Polymeric membrane unit – selective for CO₂ and O₂ – in vent stream will recycle CO₂ and O₂ rich permeate stream to the boiler.
- CO₂ capture rate increases to >97% and ASU size/power reduced by ~5%
Chronicles of Air Products’ Proprietary Oxyfuel CO₂ Purification

- Path to commercialisation
  - Auto-refrigerated partial condensation for inerts removal considered prior art since 2004 (IEA GHG 2005/9 report)
  - Air Products give path to SOx/NOx removal in sour compression (June 2006 at GHGT8)
  - O₂ removal shown to be feasible (January 2007 – IEA GHG 2nd Oxyfuel Network Meeting)

Now we are advancing from lab to demonstration!
OXYCOAL-UK : Phase 1 : BERR 404 Oxyfuel Fundamentals

– WP1: Combustion Fundamentals
– WP2: Furnace Design & Operation
– WP3: Flue Gas Clean-up / Purification
– WP4: Generic Process Issues
Path to from Lab to Demo

Cylinder fed bench rig

160 kW\textsubscript{th} oxy-coal rig

Imperial College London

Renfrew, Scotland

Batch

6 kW\textsubscript{th} slip stream
The effect of Pressure on SO$_2$ and NO Conversion (1 sl/min, 7 and 14 barg)


### Table

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<th></th>
<th>14 bar g</th>
<th>7 bar g</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Inlet (Point A)</td>
<td>After Compressor &amp; Receiver (Point C)</td>
</tr>
<tr>
<td>ppm SO$_2$</td>
<td>900</td>
<td>20</td>
</tr>
<tr>
<td>ppm NO$_x$</td>
<td>520</td>
<td>50</td>
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Path to from Lab to Demo

Cylinder fed bench rig

160 kW$_{th}$ oxy-coal rig

15 MW$_{th}$ oxy-coal combustion unit

DOE Project
Host: Alstom, Windsor, CT

Imperial College
London

Renfrew, Scotland

Batch

6 kW$_{th}$ slip stream

0.3 MW$_{th}$ slip stream

Photo courtesy of Alstom Power
DOE Project: Air Products’ Sour Compression Process Development Unit (PDU)

- Focused on reactor parameters
  - Pressure
  - SOx Feed Levels
  - Residence Time
DOE Project: Air Products’ Sour Compression PDU

- Initiate Testing of Reactor System
  - Planned Date: September 30, 2009

- Evaluate Performance of Reactor Based Flue Gas
  - Planned Date: July 30, 2010
Path to from Lab to Demo

160 kW\textsubscript{th} oxy-coal rig

15 MW\textsubscript{th} oxy-coal combustion unit

30 MW\textsubscript{th} oxy-coal pilot plant

1 MW\textsubscript{th} slip stream

0.3 MW\textsubscript{th} slip stream

6 kW\textsubscript{th} slip stream

Batch

DOE Project
Host: Alstom, Windsor, CT

Cylinder fed bench rig

Photo courtesy of Imperial College

Photo courtesy of Alstom Power

Photo courtesy of Doosan Babcock

Photo courtesy of Vattenfall

Schwarze Pumpe, Germany

Imperial College
London

London

Doosan Babcock Energy

Renfrew, Scotland

AIR PRODUCTS
Air Products’ Proprietary Technology Joins World’s First Full Demonstration of Oxyfuel CO2 Capture and Sequestration at Vattenfall

LEHIGH VALLEY, Pa. (March 31, 2009) - Air Products (NYSE: APD) today announced it will play a key role in the world’s first full demonstration of oxyfuel carbon capture and sequestration with the signing of an agreement with Vattenfall AB, one of Europe’s leading energy companies. Air Products will install its proprietary carbon dioxide (CO2) capture, purification and compression system at Vattenfall’s research and development facility in Schwarze Pumpe, Germany, which is viewed globally as the preeminent CO2 oxyfuel project. Air Products will focus specifically on the purification and compression of oxyfuel combustion flue gas. The two companies also executed a joint research and development agreement related to the project. Air Products’ pilot plant is to be operational at Schwarze Pumpe in December 2010.
Air Products’ CO₂ Purification Unit (CPU) Pilot Plant at Vattenfall’s Schwarze Pumpe

Diagram:
- Raw Flue Gas
- Sour Compression
- Condensate Collection
- Process Condensate
- O₂ and CO₂ Rich [To OxPP]
- Inerts Vent [To OxPP]
- CO₂ Returned To OxPP
- Auto-Refrigerated Inerts + O₂ Removal Process
- TSA Unit
- Mercury Removal
- Air Products PRISM® Membrane
Flue Gas Condenser in a more acidic environment

The raw flue gas feed can be taken from two locations in the existing OxPP: upstream of the FGD to maximise SO₂ content and downstream of the FGD to ensure that impurity carry over from the FGD does not affect the rest of the downstream process.
Sulphur and Nitrogen Oxidation and Acid Removal

The "warm" part of the Air Products pilot plant will demonstrate the SOx/NOx removal process using 15 and 30 bar contacting columns.
Corrosion issues

With the acid streams that are formed throughout the process the design of the pilot plant must pay particular attention to corrosion. We will take the opportunity to test other materials.
Performance of TSA adsorbents

We will be monitoring the behaviour of the TSA

- Raw Flue Gas
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Mercury behaviour and distribution in the process

We need to understand: how much mercury exists, in what form, and at which locations in the process. A guard bed downstream of the dryers will remove elemental Hg to prevent attack on the Aluminium heat exchangers.
Confirm vapour/liquid equilibrium of the CO$_2$/Ar/N$_2$/O$_2$ stream that is flashed to remove inerts from the process and purified in the distillation column.
Performance depends on how tightly the main heat exchanger can be pinched. We need to understand the implications of operating so close to the triple point of CO$_2$: does solid CO$_2$ form and what is the consequence?

CO$_2$ Freeze-out

Auto-Refrigerated Inerts +O$_2$ Removal Process

Sour Compression

TSA Unit

Mercury Removal

Air Products PRISM® Membrane

Raw Flue Gas

Condensate Collection

Process Condensate

O$_2$ and CO$_2$ Rich [To OxPP]

Inerts Vent [To OxPP]
The performance the Air Products PRISM® membrane will be monitored since this is a new application for this type of membrane.
**Flexibility**

We can blend N\textsubscript{2} and CO\textsubscript{2} into the feed to simulate higher or lower air ingress. This could also be used to understand system dynamics by introducing a spike of N\textsubscript{2} or CO\textsubscript{2} into the feed.
Challenges

- Optimisation of SOx, NOx, & Hg removal
- Reaction kinetics / equilibrium
- Fouling / impurities effects
- Materials of construction
- Byproduct streams – H₂SO₄, HNO₃, Hg species,…
- Burners must be demonstrated with flue gas recycle
- Minimisation of parasitic power for O₂ supply and CO₂ compression / purification
Timeline to Commercialisation

2015
Demonstration Plant Onstream
(50-300MWe)
Acknowledgment: DOE/NETL

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