Oxyfuel Pathways

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Oxyfuel Technology for CO$_2$ Capture - Definition:

- Fuel + oxygen + diluent (optional)
- Diluent can be H$_2$O or CO$_2$
  - i.e. Flue gas recycle
- Diluent controls combustion temperature
Oxyfuel Technology for CO₂ Capture - Characteristics:

- Minimises CO₂ impurities
  - N₂ and Ar from air ingress and oxygen impurities
  - O₂ excess from combustion

- Within the combustor all impurity concentrations derived from coal are increased
  - SO₂/SO₃, Hg, etc.

- Independent control of combustion temperature and excess oxygen level
Oxyfuel Applications

- Coal-fired boiler for power generation
- Oxyfuel gas turbine
- Oxyfuel high pressure steam generator – Clean Energy Systems
- Advanced Zero Emission Power Plant – Norsk Hydro
Pulverised Coal Supercritical Steam Boilers

There have been rapid advances in generation efficiency. Planned efficiency increases above 50% (LHV)
Design Study On Supercritical PF Coal Boiler With Oxyfuel

- Based on a study carried for the International Energy Agency Greenhouse Gas R and D programme
- Air fired boiler 677 MWe net output, Australian coal, new build, N. European location, SCR and flue gas desulphurisation
- Steam conditions 290 bar, 600°C/620°C, 40 mbar condenser 44.2% net efficiency (LHV)
- Oxyfuel system based on 95 mol% O₂ from 2 cryogenic air separation units each 5187 tonnes/day contained O₂ at 1.7 bara
- CO₂ purified to 98% and compressed to pipeline pressure of 110 bar
Schematic of Supercritical PF Oxyfuel Power Plant With CO₂ Capture

1 - IP STEAM BLEED
2 - HEAT FROM ASU ADIABATIC MAC
3 - CO2 COMPRESSOR STAGE HEAT
4 - FLUE GAS FEEDWATER HEATING

COAL

HP

ASU

MILL

NITROGEN

AIR

AIR INTAKE (START UP)

ID FAN

FD / RECYCLE FAN

ESP

COLD PA FAN

GAS / GAS HEATER

GAS COOLER & WATER REMOVAL

GAS DRIER

CO₂ PURIFICATION

INERTS

CO₂ PRODUCT FOR COMPRESSION

1234

PRIMARY RECYCLE

SECONDARY RECYCLE

HP HEATER

LP HEATER

DEAERATOR

HP PUMP

LP PUMP

CONDENSOR

1234

COLD PA FAN

OXYGEN
Schematic of Supercritical PF Oxyfuel Power Plant With CO₂ Capture

Capable of air or oxyfuel firing
Schematic of Supercritical PF Oxyfuel Power Plant With CO₂ Capture

Hot recycle gas for secondary flow
Cool primary recycle gas to ambient to minimise water content
Schematic of Supercritical PF Oxyfuel Power Plant With CO₂ Capture

Heat primary gas and pass through coal mill
Schematic of Supercritical PF Oxyfuel Power Plant With CO₂ Capture

Use of adiabatic compression of air and CO₂ to allow heat recovery to condensate and boiler feed water.
Supercritical PF Oxyfuel Power Plant With CO$_2$ Capture – Summary of Features

- Capable of air or oxyfuel firing
- Hot recycle gas for secondary flow
- Cool primary recycle gas to ambient to minimise water content
- Heat primary gas and pass through coal mill
- Use of adiabatic compression of air and CO$_2$ to allow heat recovery to condensate and boiler feed water
- Increased radiant heat transfer in the boiler
- 3 times higher SO$_2$ concentration due to flue gas recycle
- Can be retrofitted to existing PF coal fired power plants
### ASC PF Oxy-Combustion Power Plant – IEA GHG Study

- **ASU 12% of gross power output**
- **ASU Optimised for low power consumption**

<table>
<thead>
<tr>
<th></th>
<th>ASC PF Air Fired Power Plant Without CO₂ Capture</th>
<th>ASC PF Oxy-Combustion Power Plant With CO₂ Capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Input</td>
<td>kg/s</td>
<td>59.19</td>
</tr>
<tr>
<td>Fuel Heating Value</td>
<td>MJ/kg (LHV)</td>
<td>25.86</td>
</tr>
<tr>
<td>Fuel Heat Input</td>
<td>MWₗₜh (LHV)</td>
<td>1530.8</td>
</tr>
<tr>
<td>O₂ Input (contained)</td>
<td>tonne/day</td>
<td>-</td>
</tr>
<tr>
<td>Gross Power Output</td>
<td>MWₑ</td>
<td><strong>740</strong></td>
</tr>
<tr>
<td>ASU Power</td>
<td>MWₑ</td>
<td>-</td>
</tr>
<tr>
<td>CO₂ Compression &amp; Purification</td>
<td>MWₑ</td>
<td>-</td>
</tr>
<tr>
<td>Power Plant Auxiliaries</td>
<td>MWₑ</td>
<td>63</td>
</tr>
<tr>
<td>Net Power Output</td>
<td>MWₑ</td>
<td>677</td>
</tr>
<tr>
<td>Gross Efficiency</td>
<td>% LHV</td>
<td>48.3</td>
</tr>
<tr>
<td>Net Efficiency</td>
<td>% LHV</td>
<td><strong>44.2</strong></td>
</tr>
<tr>
<td>Efficiency Reduction</td>
<td>% points</td>
<td>-</td>
</tr>
</tbody>
</table>

- ASU 12% of gross power output
- ASU Optimised for low power consumption
Optimised Oxy-Combustion Power Plant

Efficiency 35.6% 36.1% 36.3% 36.4% 36.6%
Only Hot Recycle + Coal Drying + O₂ Preheat with IP Steam

Coal Drying

N₂ + H₂O

123°C to 70°C
Optimised Oxy-Combustion Power Plant

ASU PF Oxy-Combustion Boiler

1 - IP STEAM BLEED
2 - HEAT FROM ASU ADIABATIC MAC
3 - CO2 COMPRESSOR STAGE HEAT
4 - FLUE GAS FEEDWATER HEATING

Coal Drying

N₂ + H₂O → N₂

COAL

Nitrogen

ID FAN

ESP

GAS DRIER

CO₂ PURIFICATION

INERTS

GAS COOLER & WATER REMOVAL

CO₂ PRODUCT FOR COMPRESSION

AIR PRODUCTS
Optimised Oxyfuel Flowsheet

- Design of the station for air and oxygen or oxygen alone
- Option for coal drying with dry nitrogen from the ASU
- Allows total hot gas recycle, removal of 2 blowers, gas-gas exchanger and improves efficiency
- Dust removal in a closed cycle oxyfuel system – options for ESP operation at higher temperature
- First estimate for the duty of the boiler/steam turbine/auxiliary system following supercritical conversion. This will enable us to complete the overall process design of the oxyfuel and CO$_2$ compression system and its heat integration with the base case supercritical conversion project.
Oxyfuel Gas Turbine

- Pressurized oxygen
- Fuel
- Steam generator
- Gas turbine
- Steam turbine
- Electrical generator
- Cooler/condenser
- About 90% recycle

83% CO₂
15% H₂O
2% O₂

1 bar
Condenser
H₂O

CO₂ to compression

96% CO₂
2% H₂O
2.1% O₂
### NGCC Oxy-Combustion Power Plant – IEA GHG Study

<table>
<thead>
<tr>
<th></th>
<th>Typical NGCC Air Fired Power Plant Without CO₂ Capture</th>
<th>NGCC Oxy-Combustion Power Plant With CO₂ Capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Input</td>
<td>kg/s</td>
<td>14.77</td>
</tr>
<tr>
<td>Fuel Heating Value</td>
<td>MJ/kg (LHV)</td>
<td>46.90</td>
</tr>
<tr>
<td>Fuel Heat Input</td>
<td>MWₜₜ (LHV)</td>
<td>692.9</td>
</tr>
<tr>
<td>O₂ Input (contained)</td>
<td>tonne/day</td>
<td>-</td>
</tr>
<tr>
<td>Gross Power Output</td>
<td>MWₑ</td>
<td>400</td>
</tr>
<tr>
<td>ASU Power</td>
<td>MWₑ</td>
<td>-</td>
</tr>
<tr>
<td>CO₂ Compression &amp; Purification</td>
<td>MWₑ</td>
<td>-</td>
</tr>
<tr>
<td>Power Plant Auxiliaries</td>
<td>MWₑ</td>
<td>12</td>
</tr>
<tr>
<td>Net Power Output</td>
<td>MWₑ</td>
<td><strong>388</strong></td>
</tr>
<tr>
<td>Gross Efficiency % LHV</td>
<td></td>
<td>57.7</td>
</tr>
<tr>
<td>Net Efficiency % LHV</td>
<td></td>
<td>56.0</td>
</tr>
<tr>
<td>Efficiency Reduction % points</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
High Pressure Oxyfuel Steam Combustor – Clean Energy Systems

*CH₄, CO, H₂, etc.
Advanced Zero Emission Power Plant – AZEP, Norsk Hydro
Purification of Oxyfuel-Derived CO$_2$ for Sequestration or EOR

- CO$_2$ produced from oxyfuel requires purification
  - Cooling to remove water
  - Inerts removal
  - Compression

- Current design have limitations
  - SOx/NOx removal
  - Oxygen removal

- A new concept for purification has been developed
  - Includes SOx/NOx and oxygen removal
CO₂ Compression and Purification System – Inerts removal and compression to 110 bar

- Flue Gas Vent: 1.1 bar, 20°C, 25% CO₂, 75% inerts
- Flue Gas Expander: 28.9 bar, 300°C
- Flue Gas Heater: 20 bar
- Aluminium plate/fin exchangers
- Driers: 20 bar
- CO₂ product: 110 bar, 96% CO₂, 4% Inerts
- Condensate preheating: -60°C dp

30 bar Raw CO₂
Saturated 30°C
76% CO₂, 24% Inerts
### Raw and Product CO₂ Compositions
From IEA GHG Report – Assumed SO₂ passed through to the CO₂ Product

<table>
<thead>
<tr>
<th></th>
<th>Raw Flue Gas</th>
<th>CO₂ Product</th>
<th>Vent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ 35°C, 1.02 bara mol%</td>
<td>@ 35°C, 110 bar mol% Prior Art</td>
<td>@ 11°C, 1.1 bar mol% Prior Art</td>
</tr>
<tr>
<td>CO₂</td>
<td>71.5</td>
<td>95.8</td>
<td>24.6</td>
</tr>
<tr>
<td>N₂</td>
<td>14.3</td>
<td>2.0</td>
<td>48.7</td>
</tr>
<tr>
<td>O₂</td>
<td>5.9</td>
<td>1.1</td>
<td>19.4</td>
</tr>
<tr>
<td>Ar</td>
<td>2.3</td>
<td>0.6</td>
<td>7.1</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.4</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>NO</td>
<td>400 ppm</td>
<td>13 ppm</td>
<td>1180 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>10 ppm</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
## CO₂ Purity Issues

<table>
<thead>
<tr>
<th></th>
<th>Basic Design Case</th>
<th>EOR Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>&lt; 500 ppm</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>&gt; 90% mol</td>
<td>&gt; 90% mol</td>
</tr>
<tr>
<td>SO₂</td>
<td>From H&amp;MB</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>From H&amp;MB</td>
<td>From H&amp;MB</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt; 4% mol</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Ar + N₂ + O₂</td>
<td>&lt; 4% mol</td>
<td>&lt; 4% mol</td>
</tr>
</tbody>
</table>

- Regulations regarding onshore and off-shore disposal are being drafted world-wide.
- Co-disposal of other wastes (NOx, SOx, Hg) is a sensitive issue.
- Important that the CO₂ can be purified for disposal or EOR.
We realised that SO₂, NOx and Hg can be removed in the CO₂ compression process, in the presence of water and oxygen.

SO₂ is converted to Sulphuric Acid, NO₂ converted to Nitric Acid:

\[
\begin{align*}
NO + \frac{1}{2} O_2 & = NO_2 \quad (1) \text{ Slow} \\
2 NO_2 & = N_2O_4 \quad (2) \text{ Fast} \\
2 NO_2 + H_2O & = HNO_2 + HNO_3 \quad (3) \text{ Slow} \\
3 HNO_2 & = HNO_3 + 2 NO + H_2O \quad (4) \text{ Fast} \\
NO_2 + SO_2 & = NO + SO_3 \quad (5) \text{ Fast} \\
SO_3 + H_2O & = H_2SO_4 \quad (6) \text{ Fast}
\end{align*}
\]

Rate of Reaction 1 increases with Pressure to the 3rd power
- only feasible at elevated pressure

No Nitric Acid is formed until all the SO₂ is converted

Pressure, reactor design and residence times, and NO concentration are important
CO₂ Compression and Purification System – Removal of SO₂, NOx and Hg

- SO₂ removal: 100%
- NOx removal: 90-99%

1.02 bar
30°C
67% CO₂
8% H₂O
25%
Inerts
SOx
NOx

30 bar to Driers
Saturated 30°C
76% CO₂
24% Inerts
**SOx/NOx Removal – Key Features**

- **Adiabatic compression to 15 bar:**
  - No interstage water removal
  - All Water and SOx removed at one place

- **NO acts as a catalyst**
  - NO is oxidised to NO₂ and then NO₂ oxidises SO₂ to SO₃: The Lead Chamber Process

- **Hg will also be removed, reacting with the nitric acid that is formed**
## Corrected CO₂ Purity

<table>
<thead>
<tr>
<th></th>
<th>Raw Flue Gas @ 35°C, 1.02 bara mol%</th>
<th>CO₂ Product @ 35°C, 110 bar mol% Prior Art</th>
<th>Vent @ 11°C, 1.1 bar mol%</th>
<th>CO₂ Product @ 35°C, 110 bar mol% Corrected</th>
<th>Vent @ 11°C, 1.1 bar mol% Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>71.5</td>
<td>95.8</td>
<td>24.6</td>
<td>96.3</td>
<td>24.6</td>
</tr>
<tr>
<td>N₂</td>
<td>14.3</td>
<td>2.0</td>
<td>48.7</td>
<td>2.0</td>
<td>48.7</td>
</tr>
<tr>
<td>O₂</td>
<td>5.9</td>
<td>1.1</td>
<td>19.4</td>
<td>1.1</td>
<td>19.4</td>
</tr>
<tr>
<td>Ar</td>
<td>2.3</td>
<td>0.6</td>
<td>7.1</td>
<td>0.6</td>
<td>7.1</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.4</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO</td>
<td>400 ppm</td>
<td>13 ppm</td>
<td>1180 ppm</td>
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<tr>
<td>NO₂</td>
<td>10 ppm</td>
<td>0</td>
<td>0</td>
<td>&lt; 10 ppm</td>
<td>0</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
And Oxygen removal from the CO₂?

Replace simple phase separation with distillation.

Driers

30 bar Raw CO₂
Saturated 30°C
76% CO₂ 24% Inerts

99.89% CO₂
0.1% Ar
0.01% O₂
The Cost of Higher Purity CO$_2$

- Case 1: “Standard” dual flash system
- Case 2: Extra flash at cold end
- Case 3: Distillation at cold end
- Power is to 110 bar and uses adiabatic compression from 1 to 15 bar and from 20 to 110 bar
  - Heat is recovered to the steam system

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ Purity</th>
<th>Oxygen Content</th>
<th>CO$_2$ Recovery</th>
<th>Power kWhr/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>95.9 mol%</td>
<td>0.9 mol%</td>
<td>89.0%</td>
<td>168.5</td>
</tr>
<tr>
<td>Case 2</td>
<td>98 mol%</td>
<td>0.4 mol%</td>
<td>87.0%</td>
<td>166.5</td>
</tr>
<tr>
<td>Case 3</td>
<td>99.97 mol%</td>
<td>10 ppmv</td>
<td>87.4%</td>
<td>177.1</td>
</tr>
</tbody>
</table>
Summary of CO\(_2\) Purification

- FGD and DeNOx systems are not required to meet tight CO\(_2\) purity specifications
- Co-disposal of SO\(_2\) with CO\(_2\) is not possible
  - Compressing CO\(_2\) with NO + SO\(_2\) + O\(_2\) + Water will result in H\(_2\)SO\(_4\) production
- Low NOx burners are not required for oxyfuel combustion
- Oxygen can be removed for EOR-grade CO\(_2\)
- Large-scale demonstration is required
  - Further development is planned
FUTURE DEVELOPMENT OF OXYFUEL ASC BOILER SYSTEM

- Studies on retrofit to existing power stations
- Efficiency increase to 36.4% by improved coal drying using warm $N_2$, more $O_2$ preheat, higher temperature gas recycle
- Air firing option can be eliminated, system simplification boiler start system needs development
- Full scale burners must be demonstrated with flue gas recycle
- Ash characteristics/fouling tendency to be verified
- Materials of construction – corrosion
- Development and simulation of effective control systems
- Further optimisation, integration and cost reduction studies

LEADING TO

- Full scale boiler supercritical/oxyfuel conversion for system demonstration
Basic Cryogenic Air Separation Process

- Air Filter
- Main Air Compressor
- Steam Turbine or Electrical Drive
- DCAC
- TSAs
- Cold Box
- Oxygen Product
Large size single train plants – 3500 tonne/day for Qatar
Prefabricted modularised design
Proven Machinery Systems – Double-ended Steam Turbine
**Ion Transport Membranes (ITM): High-flux, High-purity Oxygen**

- Mixed-conducting ceramic membranes (non-porous)
- Typically operate at 800-900 °C
- Crystalline structure incorporates oxygen ion vacancies
- Oxygen ions diffuse through vacancies
- 100% selective for O\textsubscript{2}

\[
O_2 \text{Flux} \propto \frac{1}{L} \ln \left( \frac{P'_O}{P''_O} \right)
\]

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed air</td>
<td>( P'_O )</td>
</tr>
<tr>
<td>( \frac{1}{2}O_2 + 2e^- )</td>
<td>( O^2- )</td>
</tr>
<tr>
<td>Oxygen</td>
<td>( P''_O )</td>
</tr>
<tr>
<td>( O^2- )</td>
<td>( \frac{1}{2}O_2 + 2e^- )</td>
</tr>
</tbody>
</table>
Gas Turbine ITM Integration

- Oxygen
- Air
- HRSG
- Steam
- Exhaust Gas
- Electric Power
- Burners
- Fuel
- Heat Exchange
- ‘AIR’
- OXYGEN
- Ion Transport Membrane
Ion Transport Membrane For Low Cost Oxygen Production

- Vitiated compressed-air
- 800-900°C
- 15-20 bar
- Pure Oxygen

Thin membrane (A)
Porous membrane support (B)
Dense, slotted backbone (C)
Spacer ring
Product withdrawal tube
Thank you
tell me more

www.airproducts.com