Flue Gas Purification Utilizing SOx/NOx Reactions During Compression of CO_2 Derived from Oxyfuel Combustion (Oxy – T – Fired)

(NETL Cooperative Agreement No. DE-NT0005309)

Kevin Fogash

Air Products and Chemicals, Inc.

Who Is Air Products?

- **Global atmospheric, process and specialty gases, performance materials, equipment and services provider**
  - **Serving industrial, energy, technology and healthcare markets worldwide**
- **Fortune 500 company**
- **Known for our innovative culture and operational excellence**
- **Safety leader in the chemical industry**
- **Capture techniques**
  - **Based upon wide experience in ASU, HyCO, combustion applications, cryogenic separations, compression & CO_2 handling**
  - **Promising proprietary developments point to reductions in cost of CO_2 capture**

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Agreement Period of Performance & Cost Share

- **Period of Performance:**
  - **1 October 2008 – 30 September 2010**

Air Products	**$ 251,000 (20%)**
NETL Cost Share:	**$ 1,003,995 (80%)**
Overall Project Total:	**$ 1,254,995**

- **Project Participants: Air Products**
- **Host Site: Alstom Power - Power Plant Laboratories - Boiler Simulation Facility in Windsor, CT.**

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Technology Fundamentals

- **What is the technology?**
- **Design for the PDU (process development unit)**
- **Current status of technology**

Oxyfuel CO_2 Purification

- **Oxyfuel combustion of coal produces a flue gas containing:**
  - **$CO_2 + H_2O$**
  - **Any inerts from air in leakage or oxygen impurities**
  - **Oxidation products and impurities from the fuel (SO_x, NO_x, 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**

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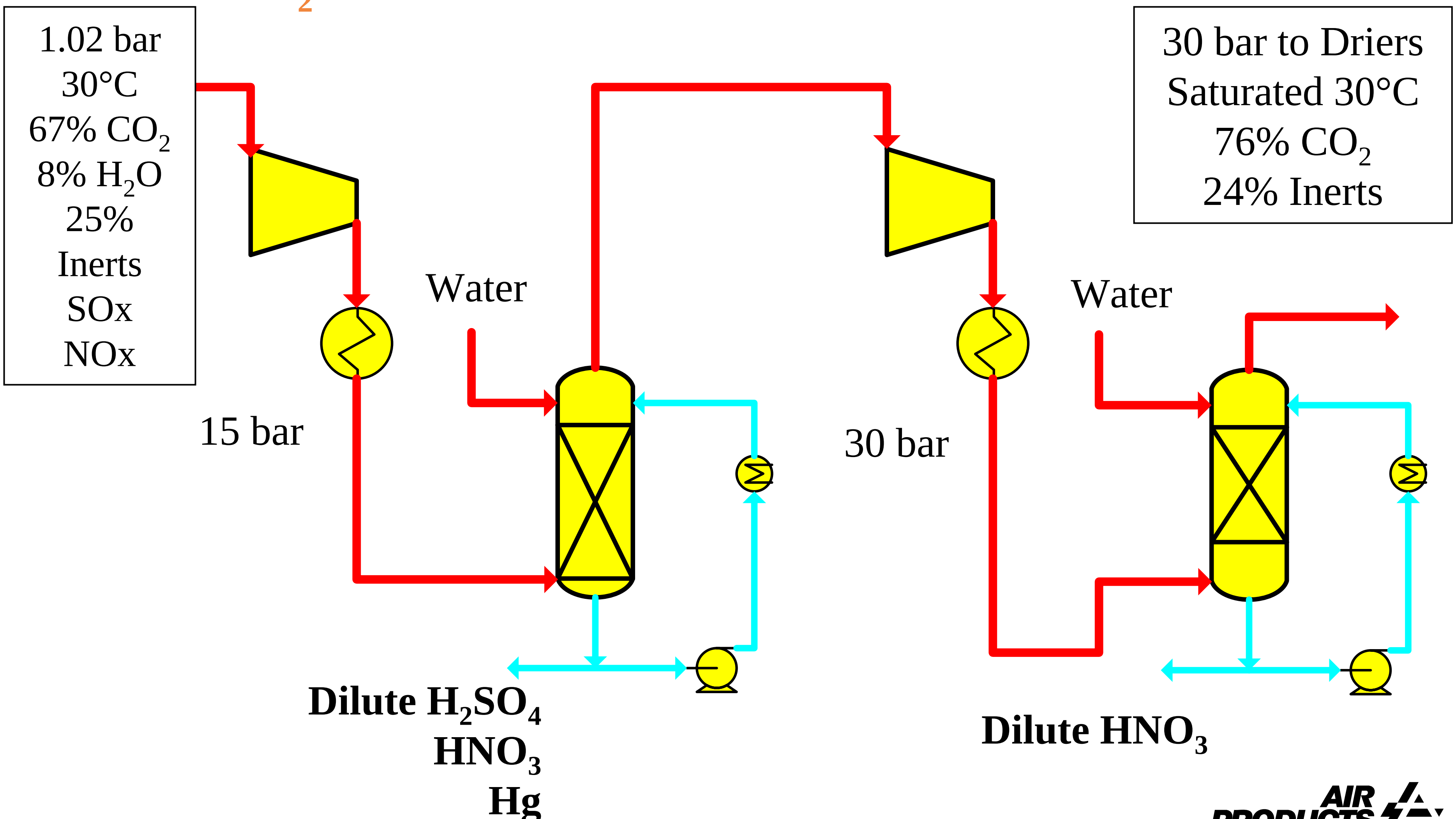
NOx SO_2 Reactions in the CO_2 Compression System

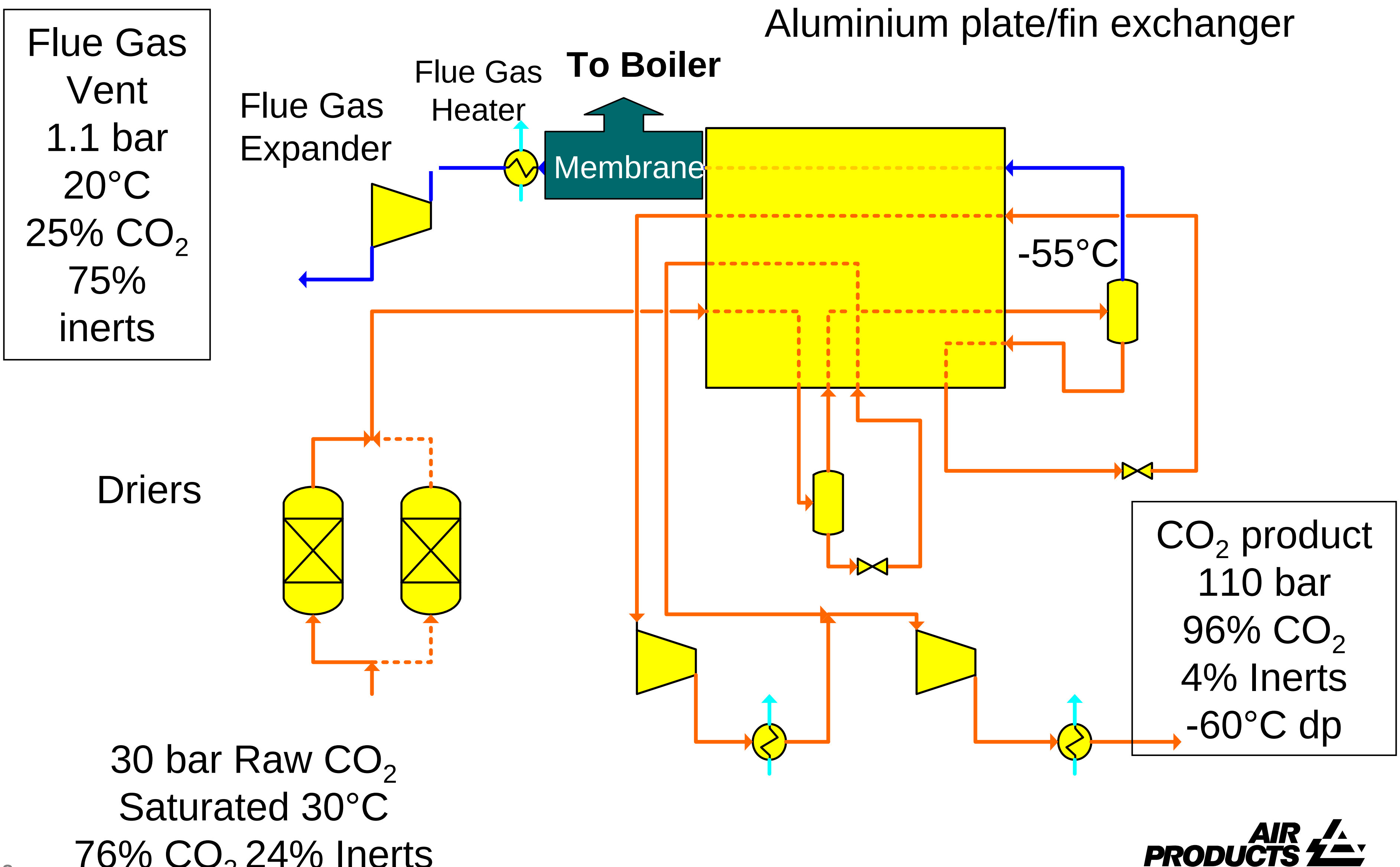
- We realized that SO_2, NOx and Hg can be removed in the CO_2 compression process, in the presence of water and oxygen.
- SO_2 is converted to Sulfuric Acid, NO_2 converted to Nitric Acid:
  - $NO + \frac{1}{2} O_2 = NO_2$ (1) Slow
  - $2 NO_2 = N_2O_4$ (2) Fast
  - $2 NO_2 + H_2O = HNO_2 + HNO_3$ (3) Slow
  - $3 HNO_2 = HNO_3 + 2 NO + H_2O$ (4) Fast
  - $NO_2 + SO_2 = NO + SO_3$ (5) Fast
  - $SO_3 + H_2O = H_2SO_4$ (6) Fast
- Rate increases with Pressure to the 3rd power
  - only feasible at elevated pressure
- Little Nitric Acid is formed until all the SO_2 is converted
- Pressure, reactor design and residence times, are important.

Air Products' CO_2 Compression and Purification System: Removal of SO_2, NOx and Hg

- **SO_2 removal: 100%** **NOx removal: 90-99%**



Air Products' System: Inerts removal and compression to 110 bar



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 oxidized to NO_2 and then NO_2 oxidizes SO_2 to SO_3: The Lead Chamber Process
- Hg will also be removed, reacting with the nitric acid that is formed
- FGD and DeNOx systems are not required for emissions or CO_2 purity
  - SOx/NOx removed in compression system
  - Low NOx burners are not required for oxyfuel combustion

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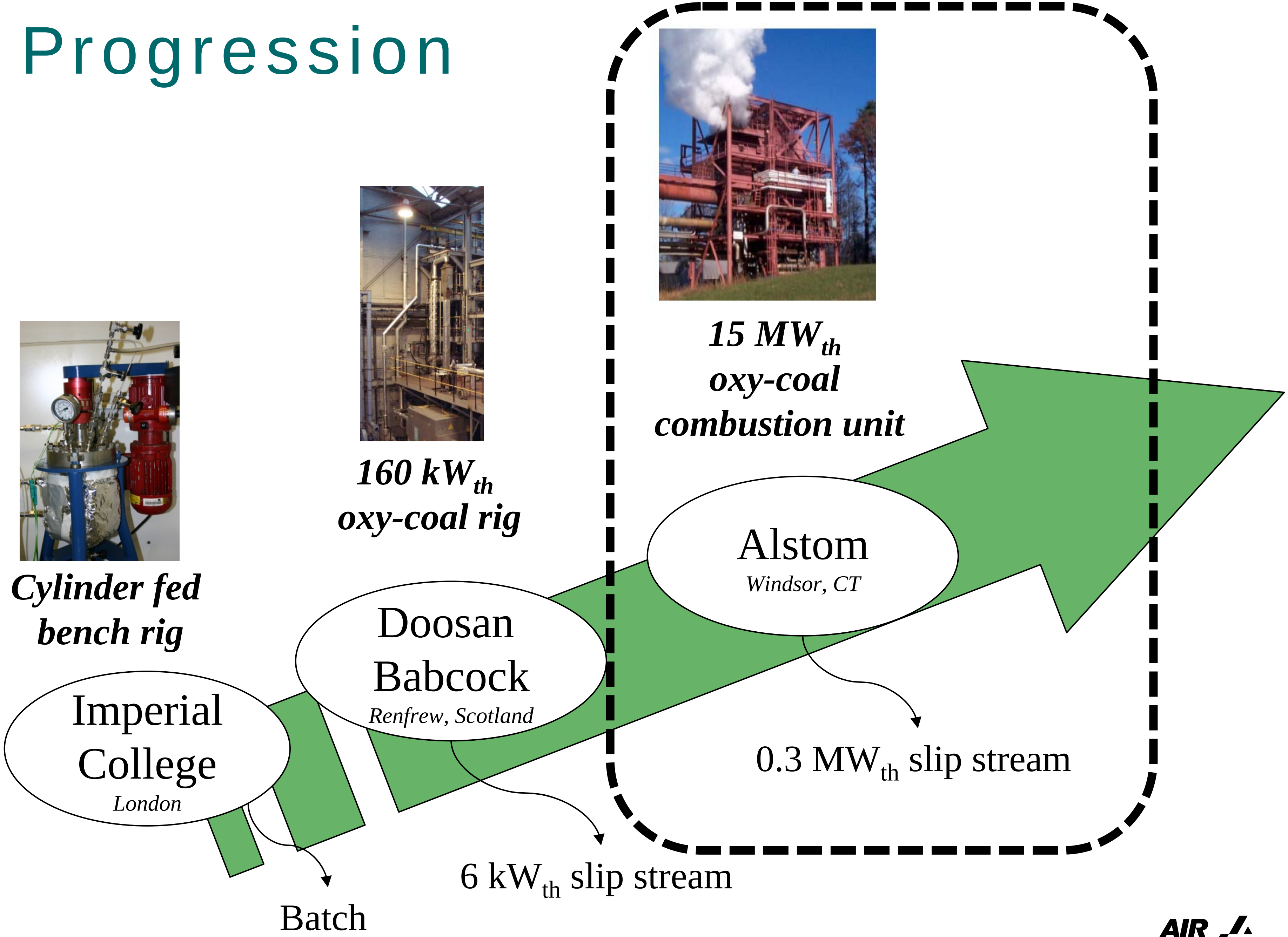
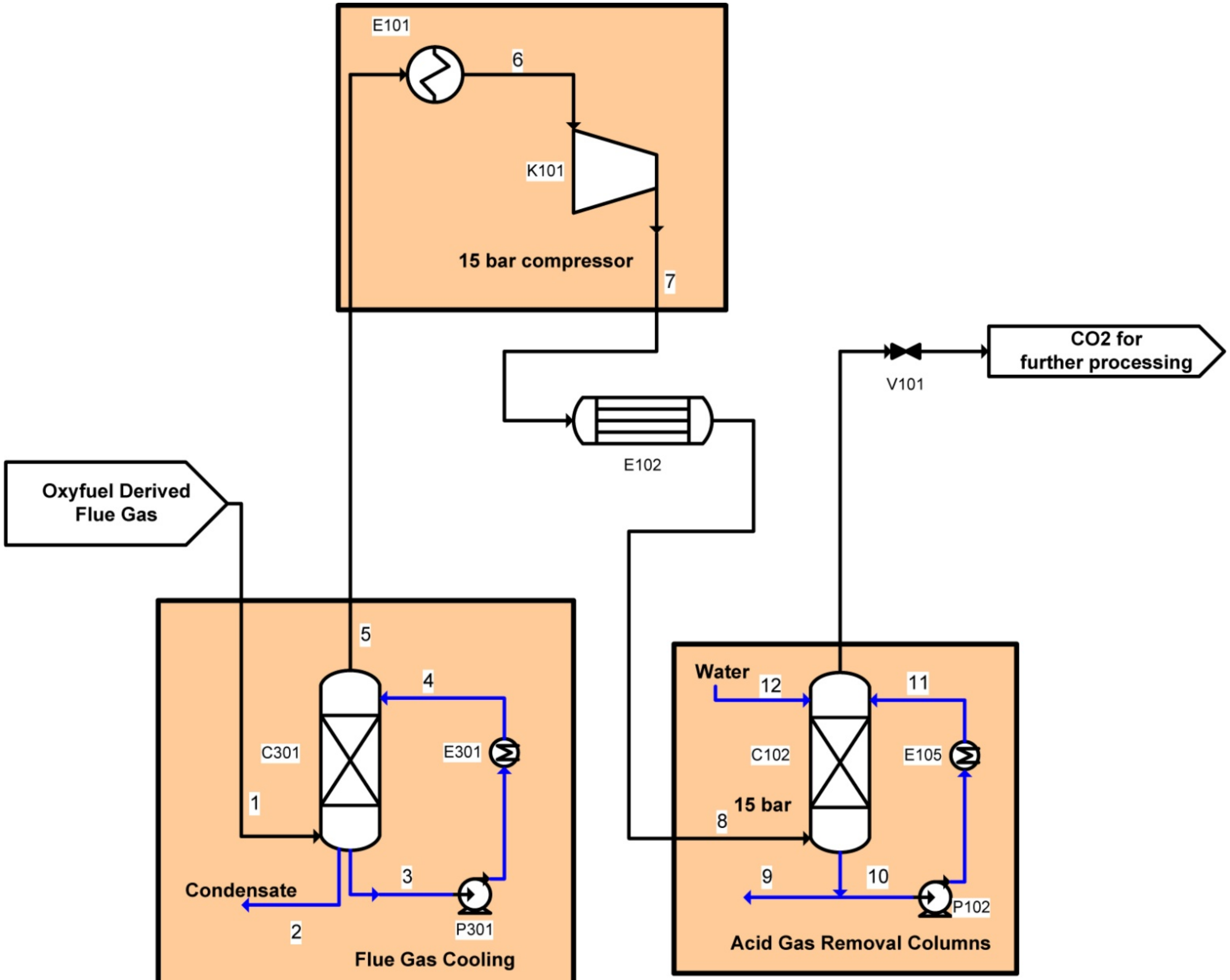
Progression



Current Process Flow Diagram



PDU (process development unit)

Previous Results

Cylinder fed bench rig

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

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

Imperial College
London

Batch

Doosan Babcock
Renfrew, Scotland

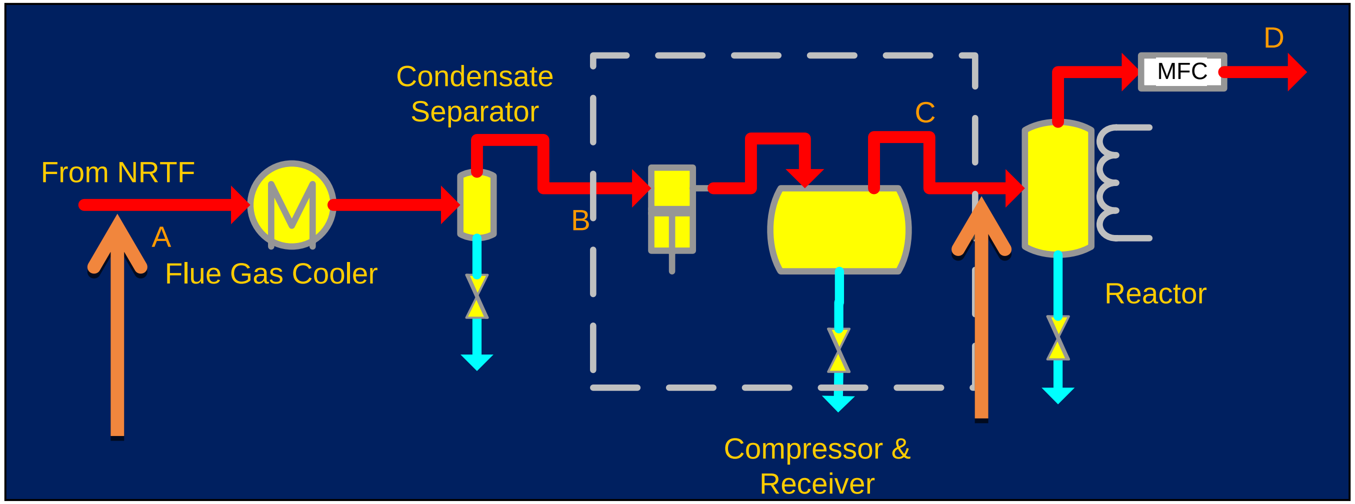
6 kW$_{th}$ slip stream

Alstom
Windsor, CT

0.3 MW$_{th}$ slip stream

The effect of Pressure on SO_2 and NO Conversion (1 sl/min, 7 and 14 barg)

Presented at the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9) "Purification of Oxyfuel-Derived CO_2", Vince White, Laura Torrente-Murciano, David Sturgeon, and David Chadwick, Washington, D.C., November 2009



	14 bar g			7 bar g		
	Inlet (Point A)	After Compressor & Receiver (Point C)	Conversion	Inlet (Point A)	After Compressor & Receiver (Point C)	Conversion
ppm SO2	900	20	98%	950	150	84%
ppm NOx	520	50	90%	390	120	68%

Doosan Babcock Energy

Imperial College London

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Advantages

- FGD and DeNOx systems are not required for emissions or CO_2 purity
  - SOx/NOx removed in compression system
  - Low NOx burners are not required for oxyfuel combustion
- Oxygen can be removed to produce EOR-grade CO_2
- No penalty if CO_2 is required as a liquid
- Vent stream is clean, at pressure and rich in CO_2 (~25%) and O_2 (~20%)
  - Polymeric membrane unit – selective for CO_2 and O_2 – in vent stream will recycle CO_2 and O_2 rich permeate stream to boiler.
  - CO_2 Capture increase to >97%
  - ASU size/power reduced ~5%

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Challenges

- **Optimization of SOx, NOx, & Hg removal**
- **Reaction kinetics / equilibrium**
- **Fouling / impurities effects**
- **Materials of construction**
- **Byproduct streams – H_2SO_4, HNO_3, Hg species,…**
- **Burners must be demonstrated with flue gas recycle**
- **Minimization of parasitic power for O_2 supply and CO_2 compression / purification**

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Project objectives

- **To purify the CO_2 derived from oxy-coal combustion by utilizing the SOx / NOx reactions that will occur during CO_2 compression**

Phase 1

Design and Construction of Reactor System for Purification of CO_2 from Oxy-Coal Combustion

- **The Phase I objectives include the design, construction, and commissioning of a 15 bar reactor system for removal of SOx /NOx from actual oxy-coal derived, CO_2-rich flue gas.**
- **The system will be designed to cool an oxy-coal combustion flue gas slip stream(~0.35 MW_{th} flow rate equivalent), compress from 1 bar to 15 bar and react within a 15 bar column the SOx/NOx present in the CO_2 rich flue gas.**

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Project objectives (continued)

Phase II

Evaluate Robustness of Reactor Performance for Purification CO_2 from Oxy-Coal Combustion

- **The Phase II objectives include further evaluations of the reaction process using oxy-coal derived flue gas generated by the host site (Alstom).**
  - **Evaluate the performance of the reactor based on the reactor effluents for different reactor pressures as well as water recycle rates**
  - **Characterize the reactor effluents (both liquid and gaseous) to assess any change in reactor performance**
- **Air Products will develop an engineering model to describe the 15 bar purification reactor performance.**
  - **Perform a sensitivity analysis using said model to elucidate those parameters most critical to performance**

Milestones / Schedule

- **Initiate Construction of Reactor System**
  - **Planned Date: March 30, 2009**
- **Initiate Testing of Reactor System**
  - **Planned Date: September 30, 2009**
- **Evaluate Performance of Reactor Based Flue Gas**
  - **Planned Date: July 30, 2010**
- **Develop Engineering Model and Perform Sensitivity Analysis**
  - **Planned Date: September 30, 2010**

Next Steps

- **Continue PDU / small scale testing of SOx/NOx removal in 2009+**
- **Finalize step up to pilot scale for CO_2 purification and compression**

- **Scale up to Pilot: 2009-2012**
- **Demonstration on stream: 2015**
- **Commercialization: 2017-2020**

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Thank you

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