

**MIT Carbon Sequestration Forum VII**  
**Pathways to Lower Capture Costs**  
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# Oxyfuel Pathways

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# Oxyfuel Technology for CO<sub>2</sub> Capture - Definition:

- Fuel + oxygen + diluent (optional)
- Diluent can be H<sub>2</sub>O or CO<sub>2</sub>
  - i.e. Flue gas recycle
- Diluent controls combustion temperature

# Oxyfuel Technology for CO<sub>2</sub> Capture - Characteristics:

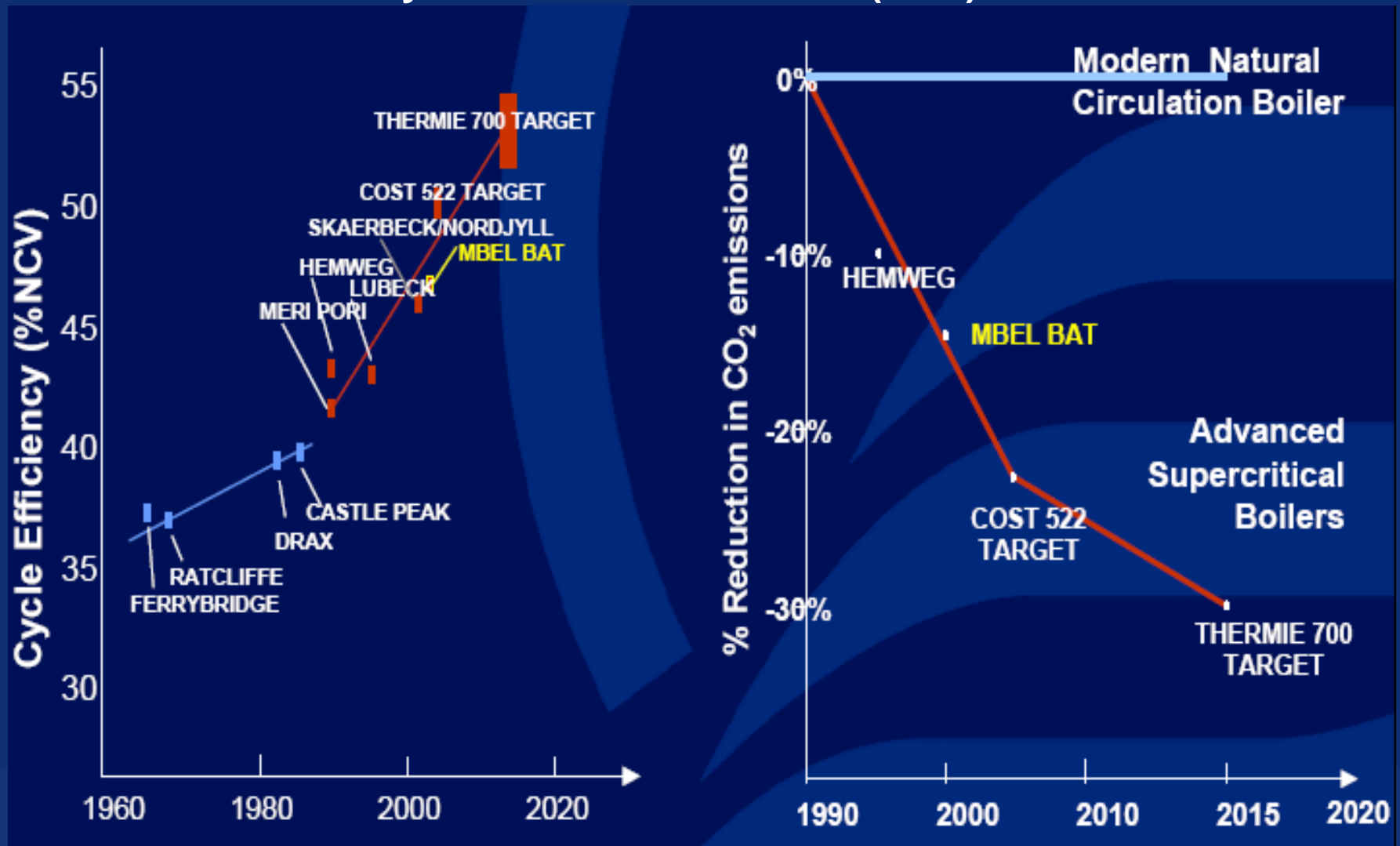
- **Minimises CO<sub>2</sub> impurities**
  - N<sub>2</sub> and Ar from air ingress and oxygen impurities
  - O<sub>2</sub> excess from combustion
- **Within the combustor all impurity concentrations derived from coal are increased**
  - SO<sub>2</sub>/SO<sub>3</sub>, Hg, etc.
- **Independent control 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

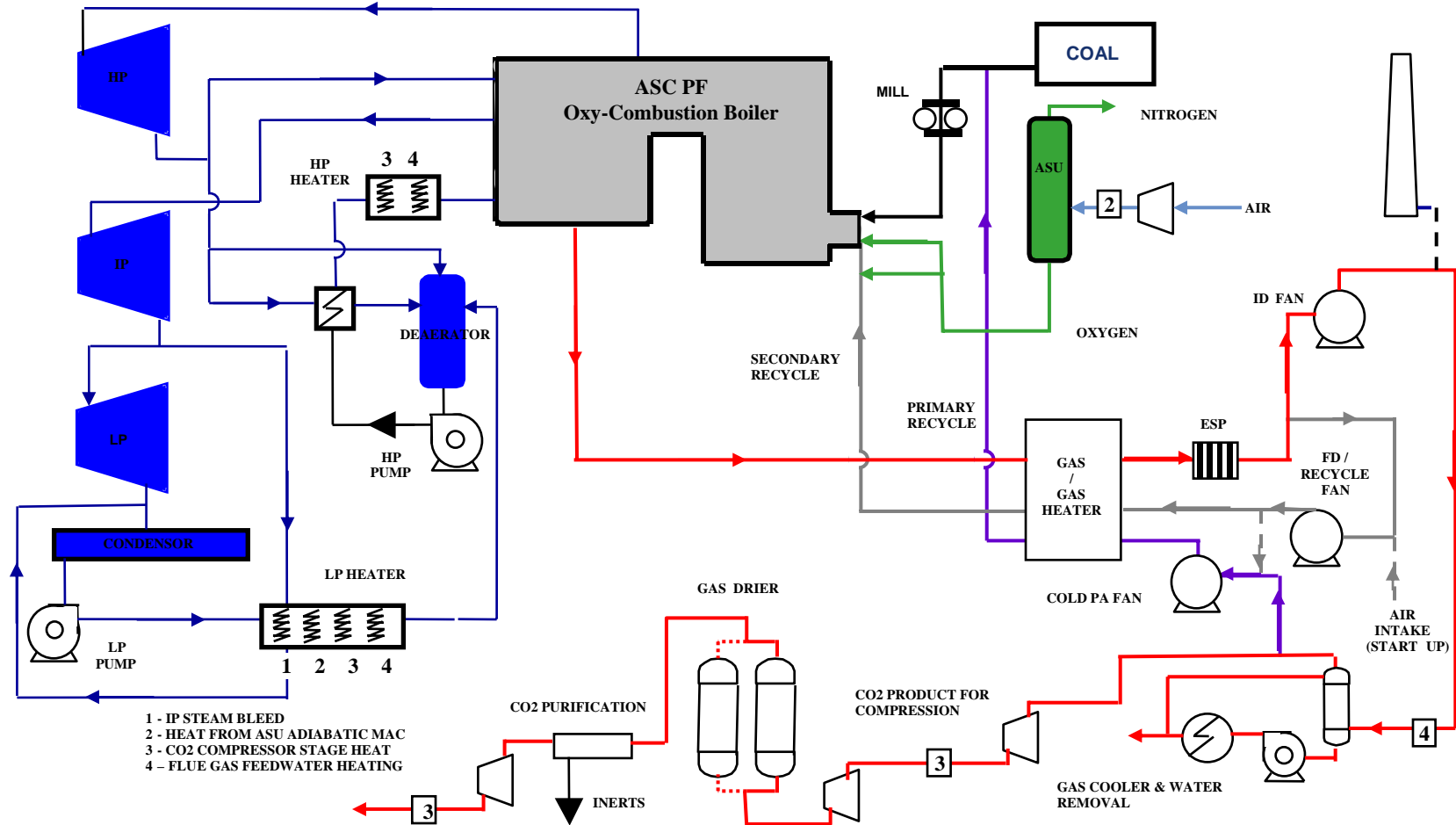
There have been rapid advances in generation efficiency.  
Planned efficiency increases above 50% (LHV)



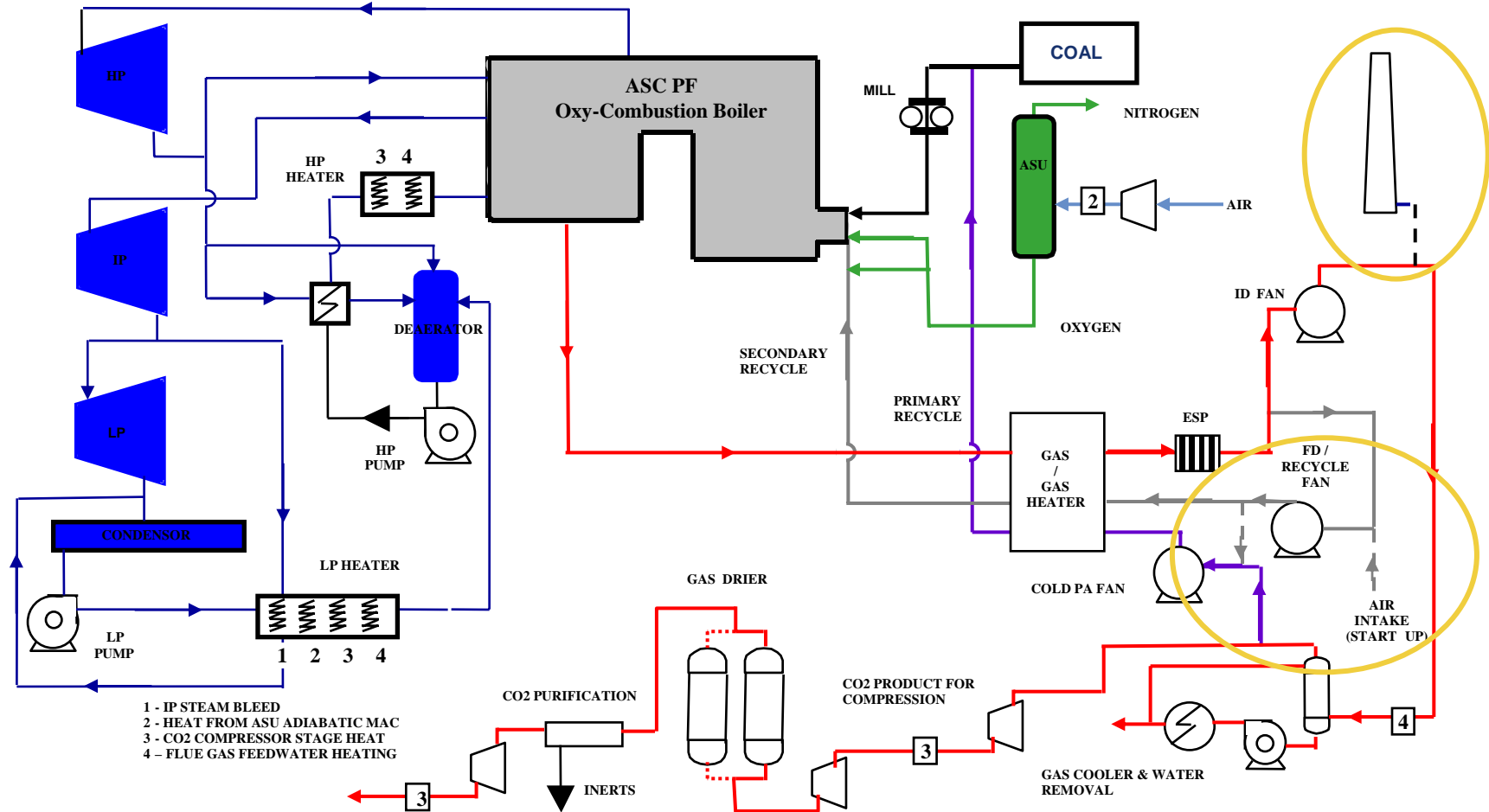
# Design Study On Supercritical PF Coal Boiler With Oxyfuel

- 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% O<sub>2</sub> from 2 cryogenic air separation units each 5187 tonnes/day contained O<sub>2</sub> at 1.7 bara
- CO<sub>2</sub> purified to 98% and compressed to pipeline pressure of 110 bar

# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture

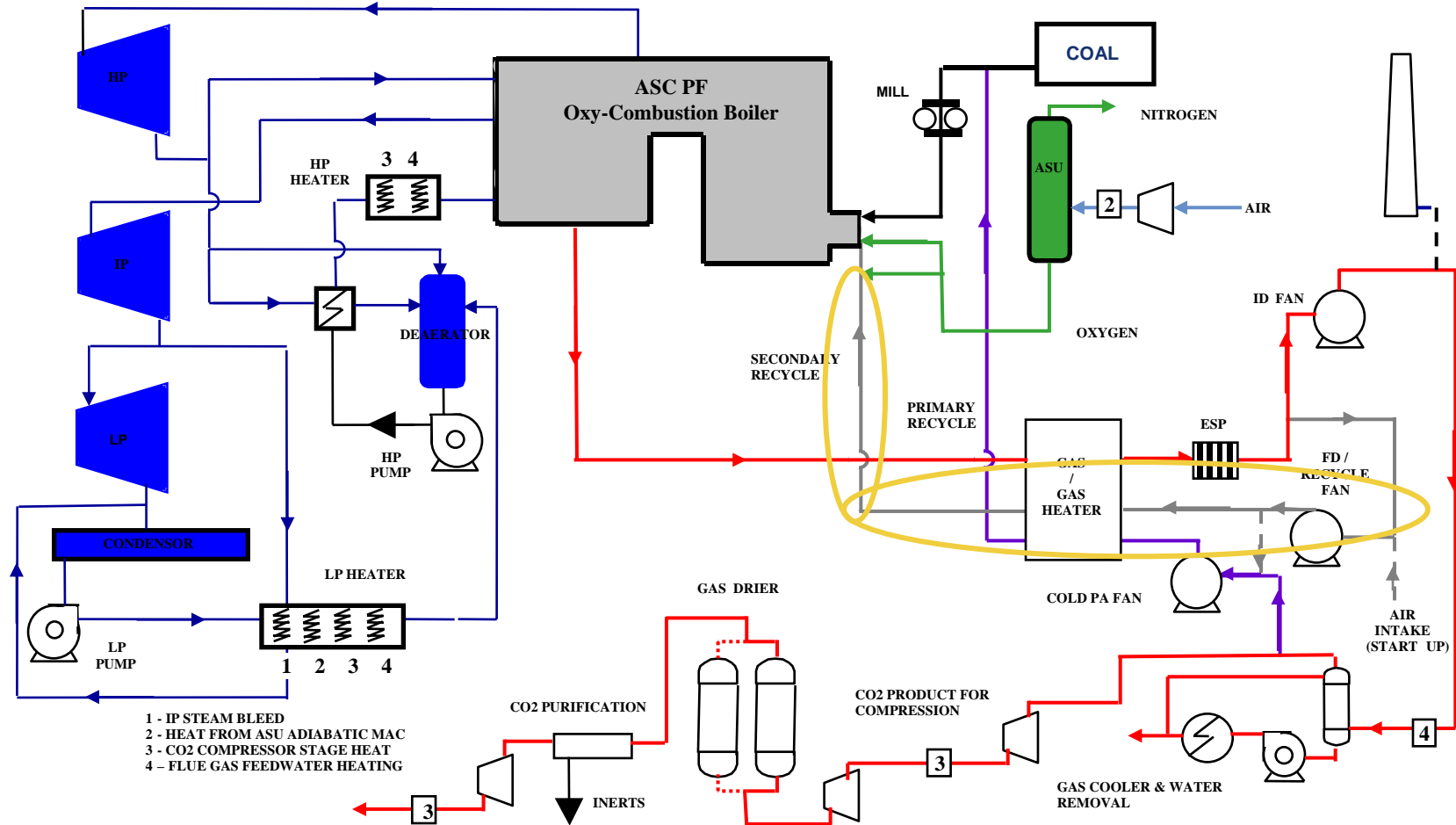


# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture



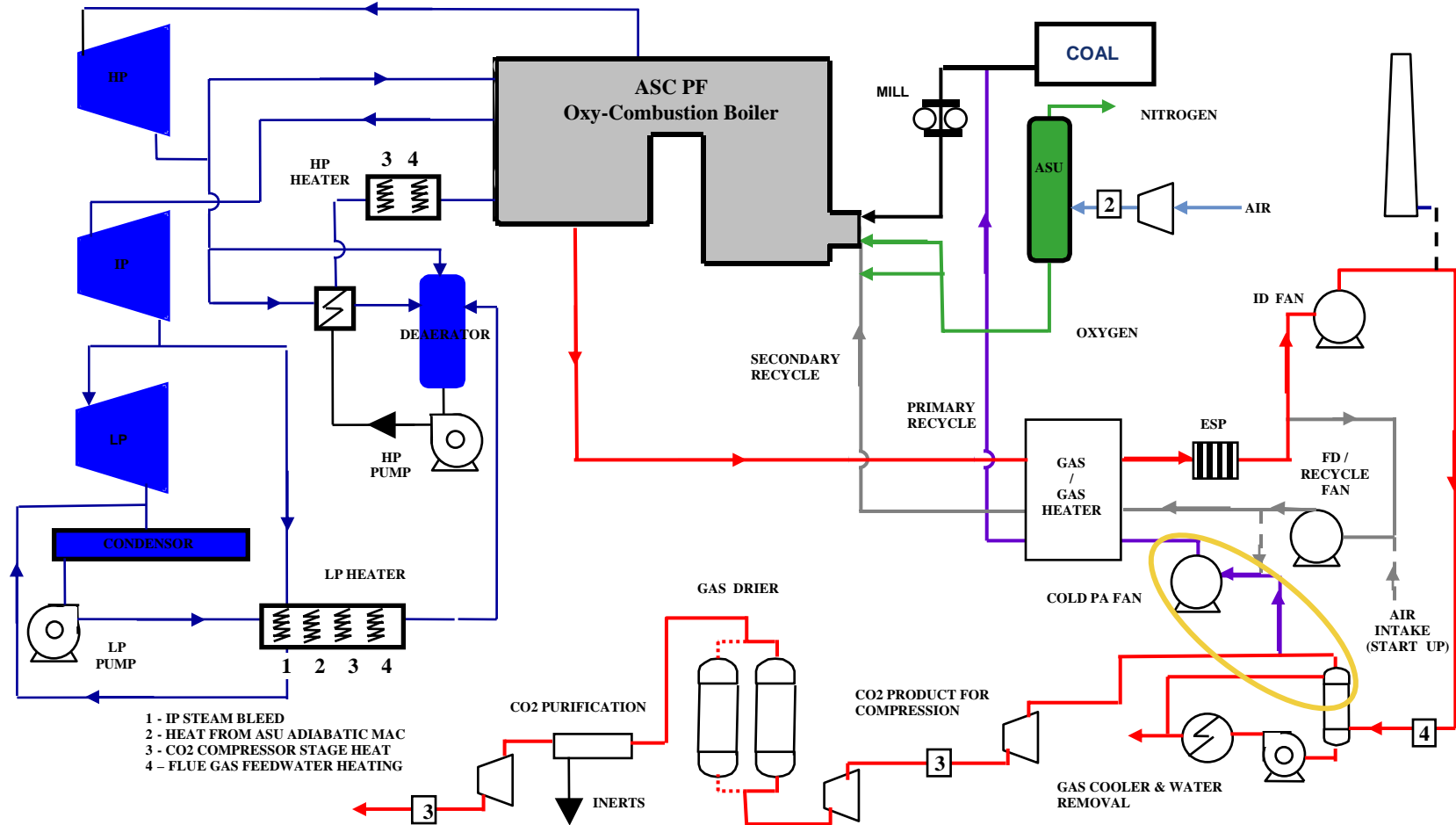
Capable of air or oxyfuel firing

# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture



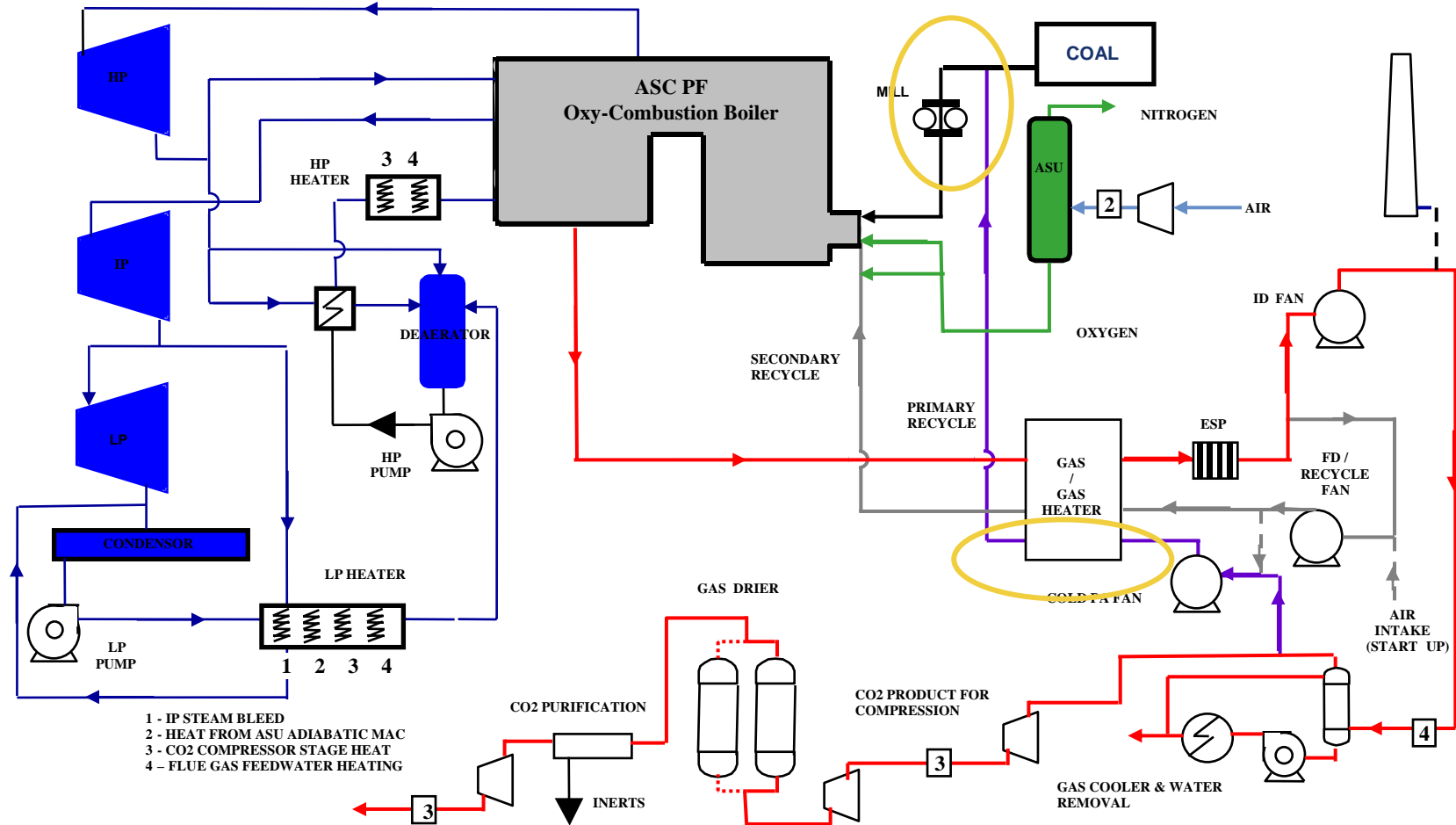
Hot recycle gas for secondary flow

# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture



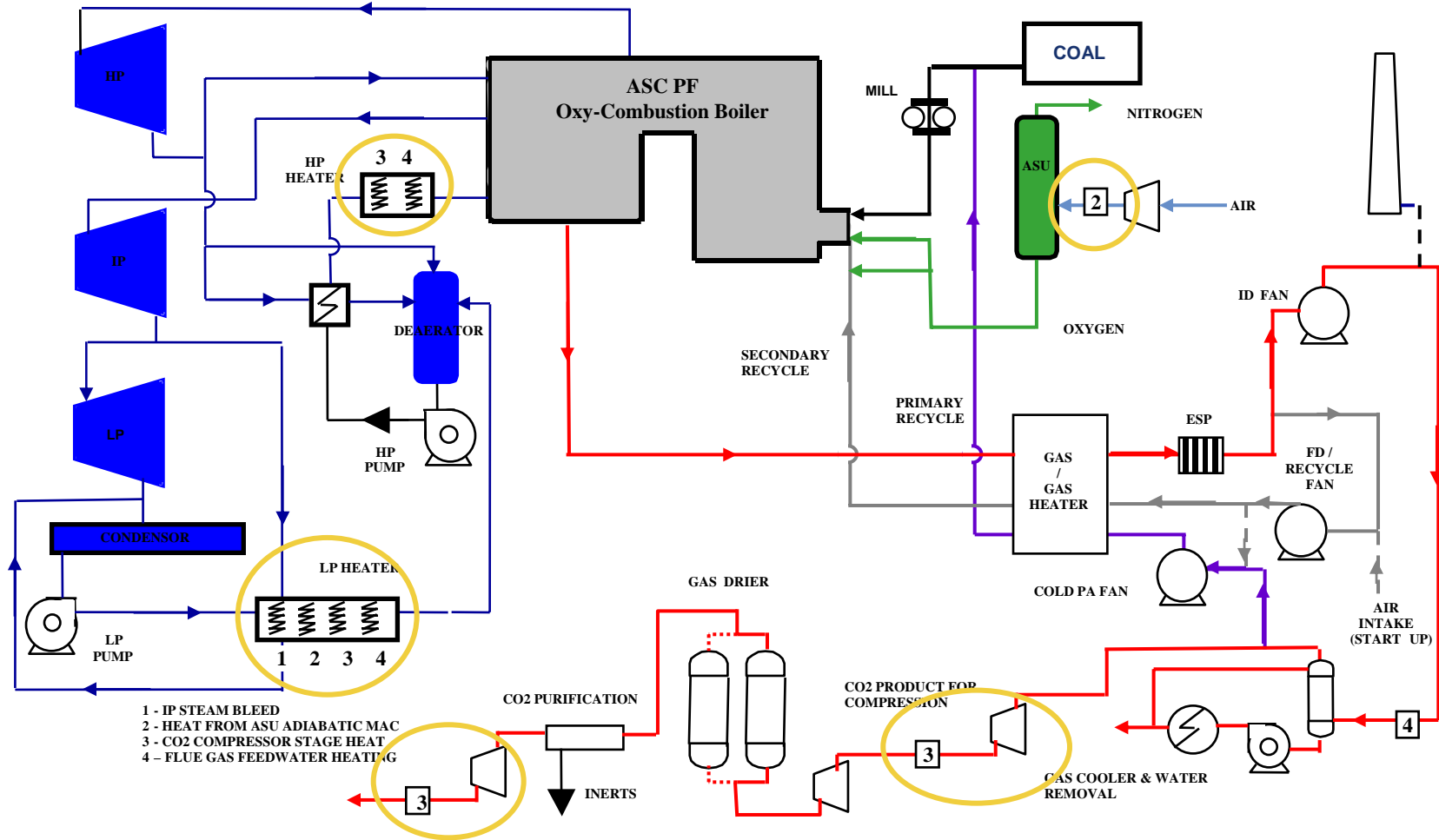
Cool primary recycle gas to ambient to minimise water content

# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture



Heat primary gas and pass through coal mill

# Schematic of Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture



Use of adiabatic compression of air and CO<sub>2</sub> to allow heat recovery to condensate and boiler feed water

# Supercritical PF Oxyfuel Power Plant With CO<sub>2</sub> Capture – Summary of Features

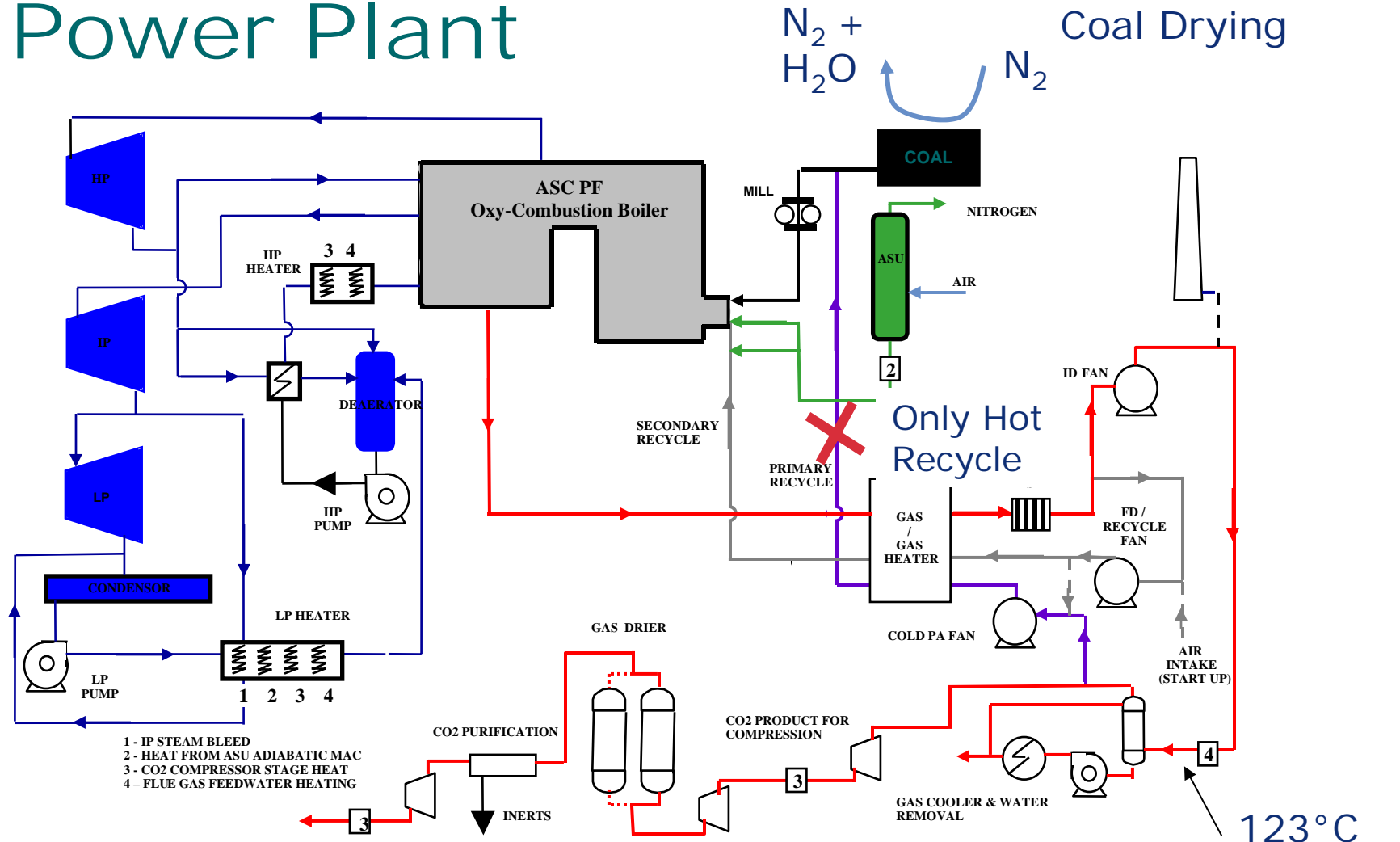
- Capable of air or oxyfuel firing
- Hot recycle gas for secondary flow
- Cool primary recycle gas to ambient to minimise water content
- Heat primary gas and pass through coal mill
- Use of adiabatic compression of air and CO<sub>2</sub> to allow heat recovery to condensate and boiler feed water
- Increased radiant heat transfer in the boiler
- 3 times higher SO<sub>2</sub> 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

		ASC PF Air Fired Power Plant Without CO <sub>2</sub> Capture	ASC PF Oxy- Combustion Power Plant With CO <sub>2</sub> Capture
Fuel Input	kg/s	59.19	58.09
Fuel Heating Value	MJ/kg (LHV)	25.86	25.86
Fuel Heat Input	MW <sub>th</sub> (LHV)	1530.8	1502.2
O <sub>2</sub> Input (contained)	tonne/day	-	10,373
Gross Power Output	MW <sub>e</sub>	<b>740</b>	<b>737</b>
ASU Power	MW <sub>e</sub>	-	87
CO <sub>2</sub> Compression & Purification	MW <sub>e</sub>	-	65
Power Plant Auxiliaries	MW <sub>e</sub>	63	53
Net Power Output	MW <sub>e</sub>	677	<b>532</b>
Gross Efficiency	% LHV	48.3	49.06
Net Efficiency	% LHV	<b>44.2</b>	<b>35.4</b>
<b>Efficiency Reduction</b>	<b>% points</b>	-	<b>8.8</b>

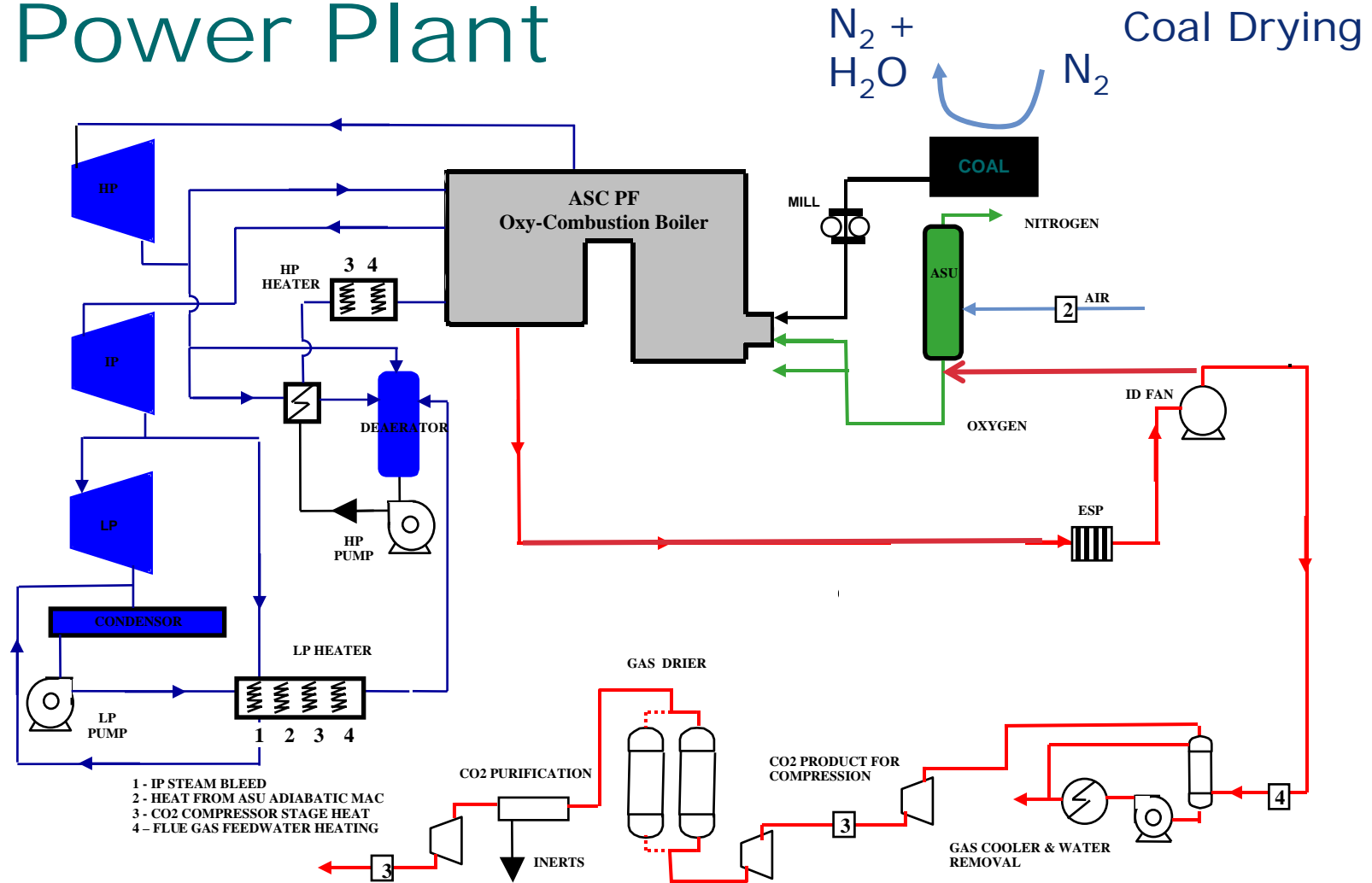
# Optimised Oxy-Combustion Power Plant



Efficiency	35.6%	36.1%	36.3%	36.4%	36.6%	to 70°C
	Only Hot Recycle	+ Coal Drying	+ O <sub>2</sub> Preheat with IP Steam			



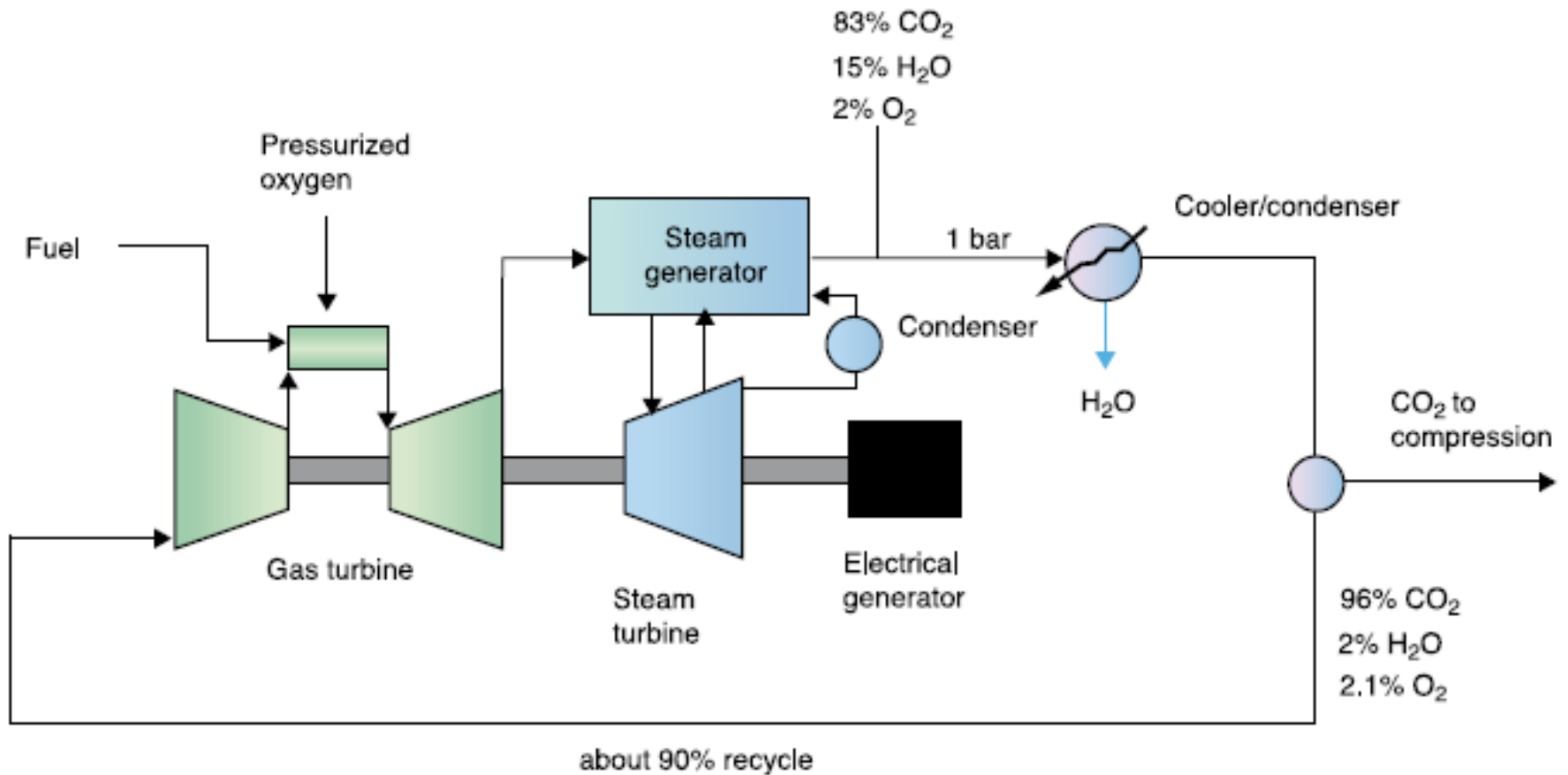
# Optimised Oxy-Combustion Power Plant



# 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<sub>2</sub> compression system and its heat integration with the base case supercritical conversion project.**

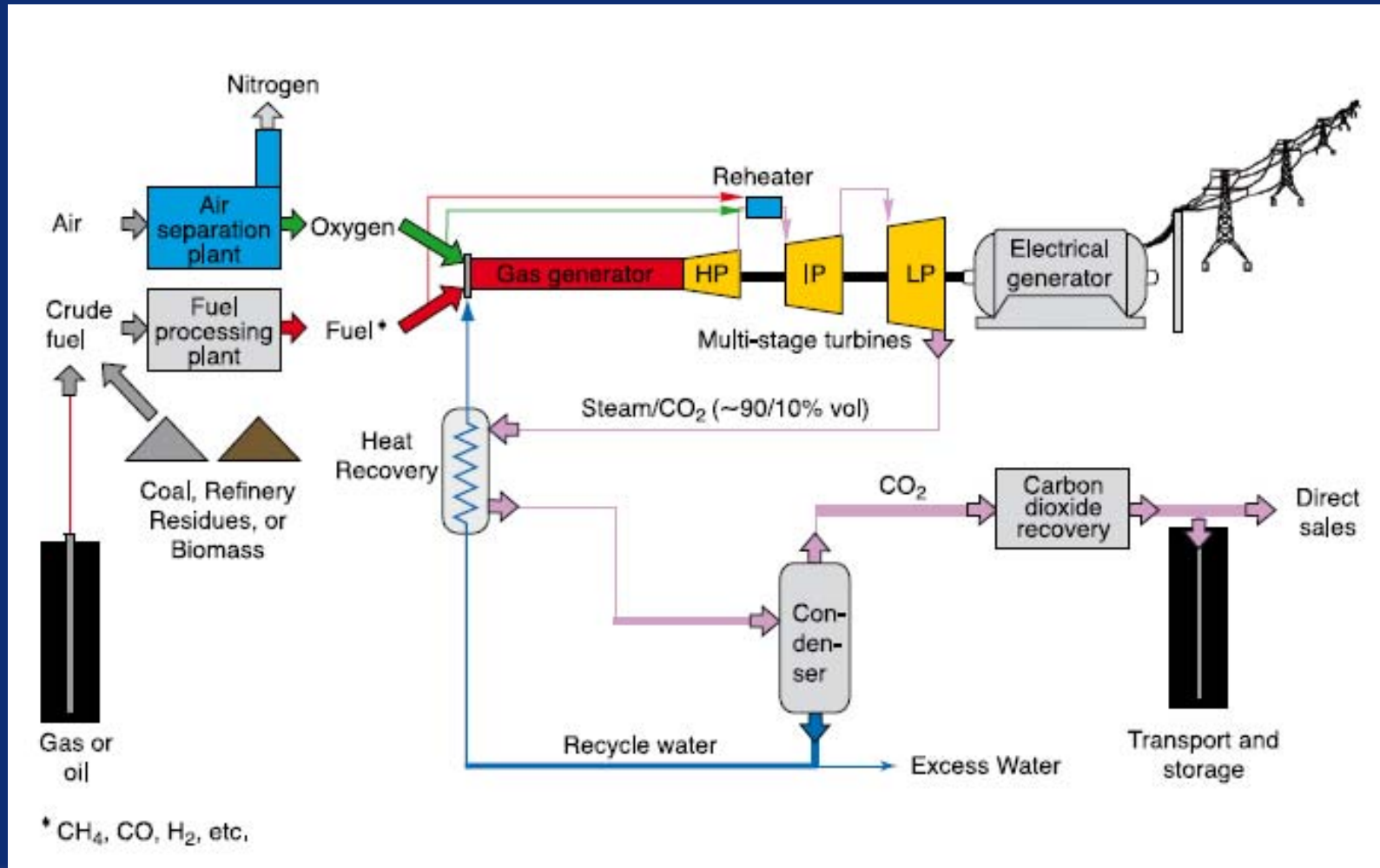
# Oxyfuel Gas Turbine



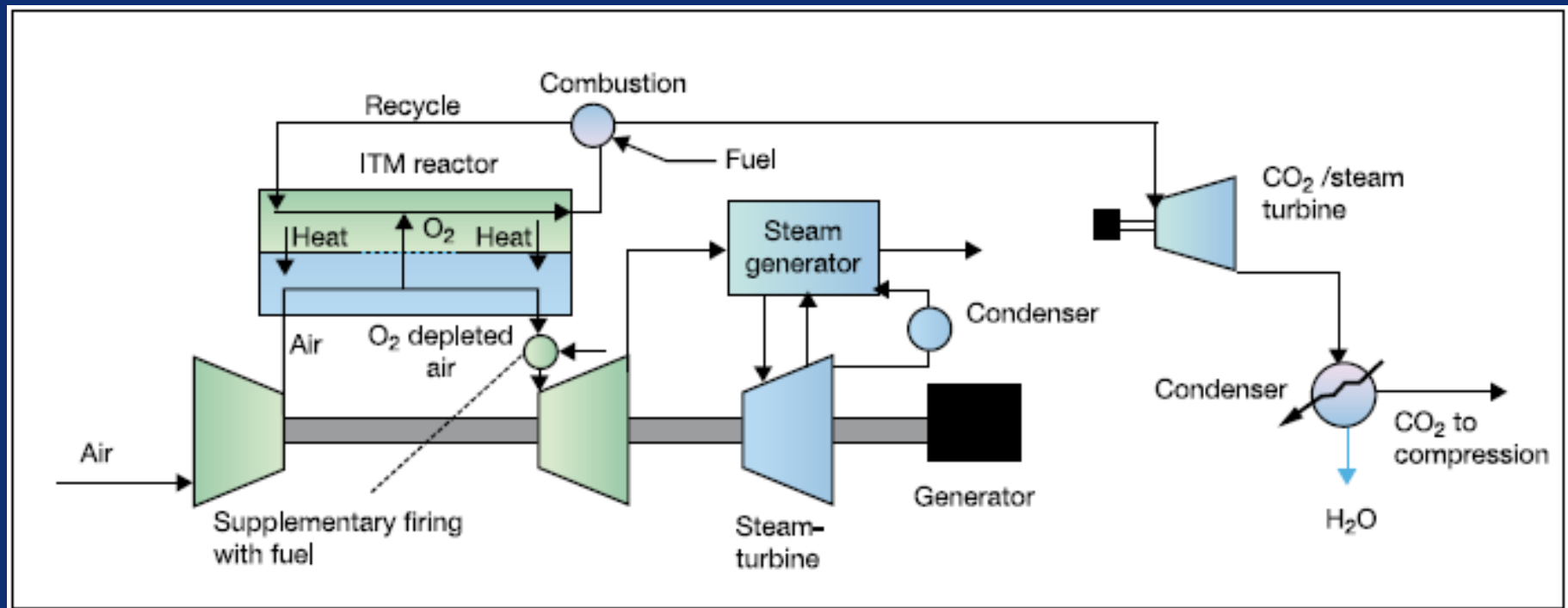
# NGCC Oxy-Combustion Power Plant – IEA GHG Study

		Typical NGCC Air Fired Power Plant Without CO <sub>2</sub> Capture	NGCC Oxy- Combustion Power Plant With CO <sub>2</sub> Capture
Fuel Input	kg/s	14.77	20.32
Fuel Heating Value	MJ/kg (LHV)	46.90	48.45
Fuel Heat Input	MW <sub>th</sub> (LHV)	692.9	984.5
O <sub>2</sub> Input (contained)	tonne/day	-	6,840
Gross Power Output	MW <sub>e</sub>	400	575
ASU Power	MW <sub>e</sub>	-	70
CO <sub>2</sub> Compression & Purification	MW <sub>e</sub>	-	49
Power Plant Auxiliaries	MW <sub>e</sub>	12	18
Net Power Output	MW <sub>e</sub>	<b>388</b>	<b>440</b>
Gross Efficiency	% LHV	57.7	58.4
Net Efficiency	% LHV	<b>56.0</b>	<b>44.7</b>
Efficiency Reduction	% points	-	<b>11.3</b>

# High Pressure Oxyfuel Steam Combustor – Clean Energy Systems



# Advanced Zero Emission Power Plant – AZEP, Norsk Hydro

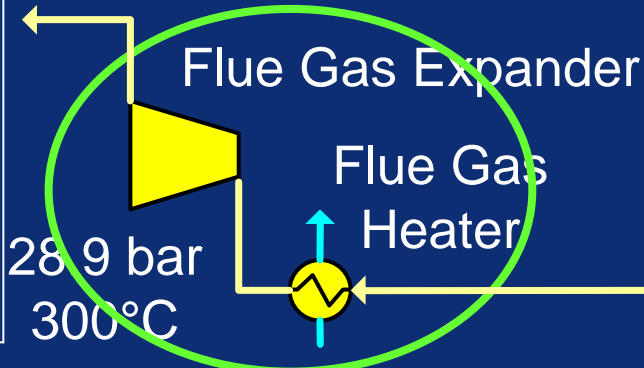


# Purification of Oxyfuel-Derived CO<sub>2</sub> for Sequestration or EOR

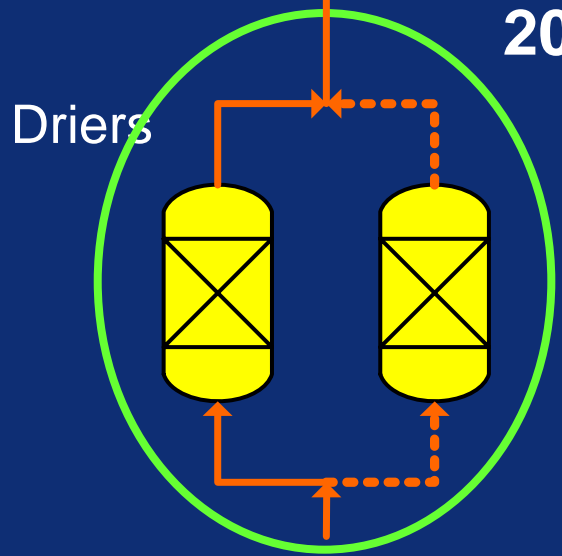
- **CO<sub>2</sub> produced from oxyfuel requires purification**
  - Cooling to remove water
  - Inerts removal
  - Compression
- **Current design have limitations**
  - SO<sub>x</sub>/NO<sub>x</sub> removal
  - Oxygen removal
- **A new concept for purification has been developed**
  - Includes SO<sub>x</sub>/NO<sub>x</sub> and oxygen removal

# CO<sub>2</sub> Compression and Purification System – Inerts removal and compression to 110 bar

Flue Gas Vent  
1.1 bar  
20°C  
25% CO<sub>2</sub>  
75% inerts



Aluminium plate/fin exchangers



30 bar Raw CO<sub>2</sub>  
Saturated 30°C  
76% CO<sub>2</sub> 24% Inerts

20 bar

10 bar

110 bar

Condensate preheating

CO<sub>2</sub> product  
110 bar  
96% CO<sub>2</sub>  
4% Inerts  
-60°C dp



# Raw and Product CO<sub>2</sub> Compositions From IEA GHG Report – Assumed SO<sub>2</sub> passed through to the CO<sub>2</sub> Product

	Raw Flue Gas  @ 35°C, 1.02 bara mol%	CO <sub>2</sub> Product  @ 35°C, 110 bar mol%  Prior Art	Vent  @ 11°C, 1.1 bar mol%  Prior Art
CO <sub>2</sub>	71.5	95.8	24.6
N <sub>2</sub>	14.3	2.0	48.7
O <sub>2</sub>	5.9	1.1	19.4
Ar	2.3	0.6	7.1
SO <sub>2</sub>	0.4	0.5	0
NO	400 ppm	13 ppm	1180 ppm
NO <sub>2</sub>	10 ppm	0	0
H <sub>2</sub> O	5.6	0	0

# CO<sub>2</sub> Purity Issues

	Basic Design Case	EOR Case
H <sub>2</sub> O	< 500 ppm	< 50 ppm
CO <sub>2</sub>	> 90% mol	> 90% mol
SO <sub>2</sub>	From H&MB	< 50 ppm
NO	From H&MB	From H&MB
O <sub>2</sub>	< 4% mol	100 ppm
Ar + N <sub>2</sub> + O <sub>2</sub>	< 4% mol	< 4% mol

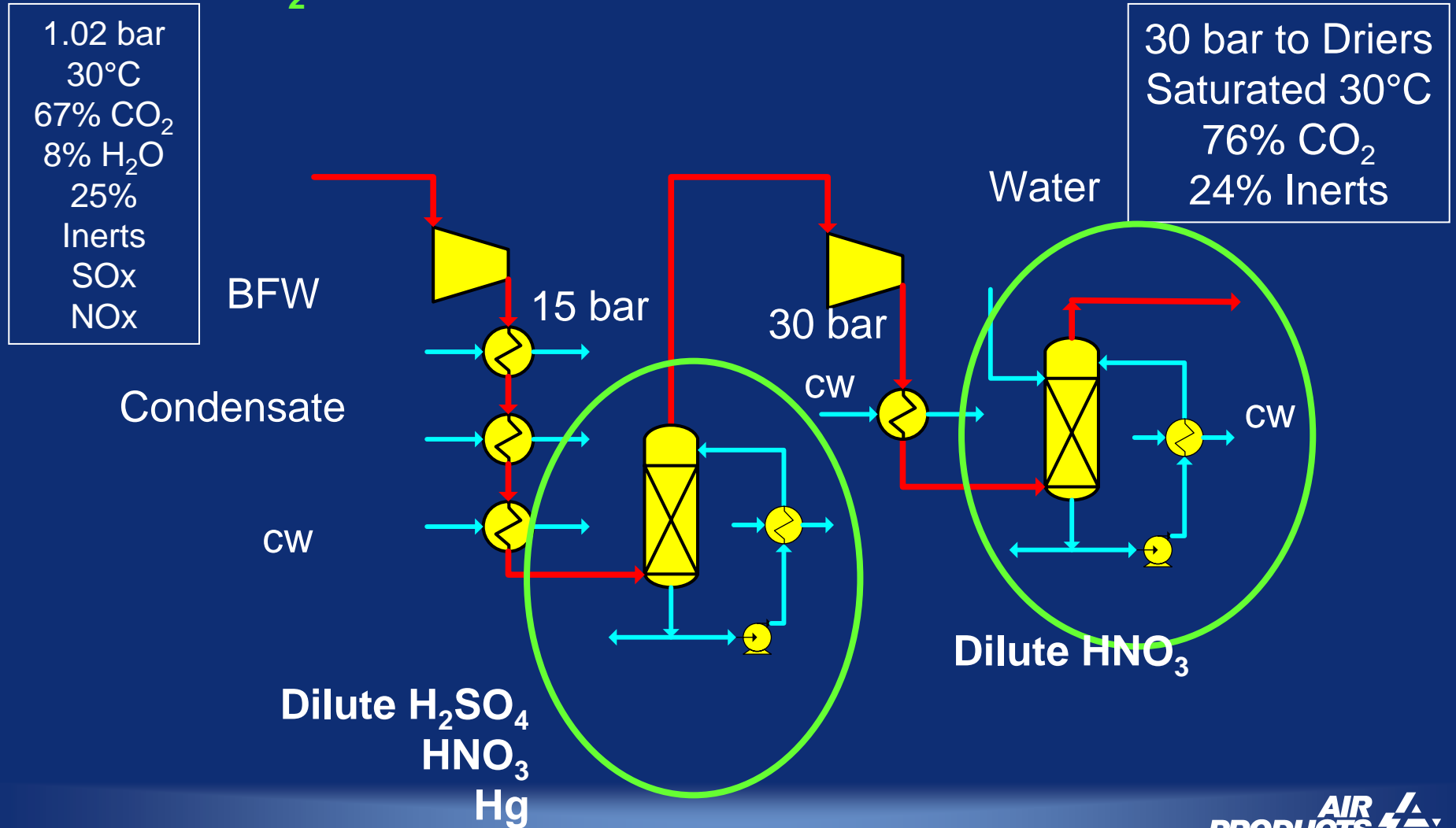
- Regulations regarding onshore and off-shore disposal are being drafted world-wide
- Co-disposal of other wastes (NO<sub>x</sub>, SO<sub>x</sub>, Hg) is a sensitive issue
- Important that the CO<sub>2</sub> can be purified for disposal or EOR

# NO<sub>x</sub> SO<sub>2</sub> Reactions in the CO<sub>2</sub> Compression System

- We realised that SO<sub>2</sub>, NO<sub>x</sub> and Hg can be removed in the CO<sub>2</sub> compression process, in the presence of water and oxygen.
- SO<sub>2</sub> is converted to Sulphuric Acid, NO<sub>2</sub> converted to Nitric Acid:
  - NO + ½ O<sub>2</sub> = NO<sub>2</sub> (1) Slow
  - 2 NO<sub>2</sub> = N<sub>2</sub>O<sub>4</sub> (2) Fast
  - 2 NO<sub>2</sub> + H<sub>2</sub>O = HNO<sub>2</sub> + HNO<sub>3</sub> (3) Slow
  - 3 HNO<sub>2</sub> = HNO<sub>3</sub> + 2 NO + H<sub>2</sub>O (4) Fast
  - NO<sub>2</sub> + SO<sub>2</sub> = NO + SO<sub>3</sub> (5) Fast
  - SO<sub>3</sub> + H<sub>2</sub>O = H<sub>2</sub>SO<sub>4</sub> (6) Fast
- Rate of Reaction 1 increases with Pressure to the 3<sup>rd</sup> power
  - only feasible at elevated pressure
- No Nitric Acid is formed until all the SO<sub>2</sub> is converted
- Pressure, reactor design and residence times, and NO concentration are important

# CO<sub>2</sub> Compression and Purification System – Removal of SO<sub>2</sub>, NO<sub>x</sub> and Hg

- **SO<sub>2</sub> removal: 100%**      **NO<sub>x</sub> removal: 90-99%**



# SO<sub>x</sub>/NO<sub>x</sub> Removal – Key Features

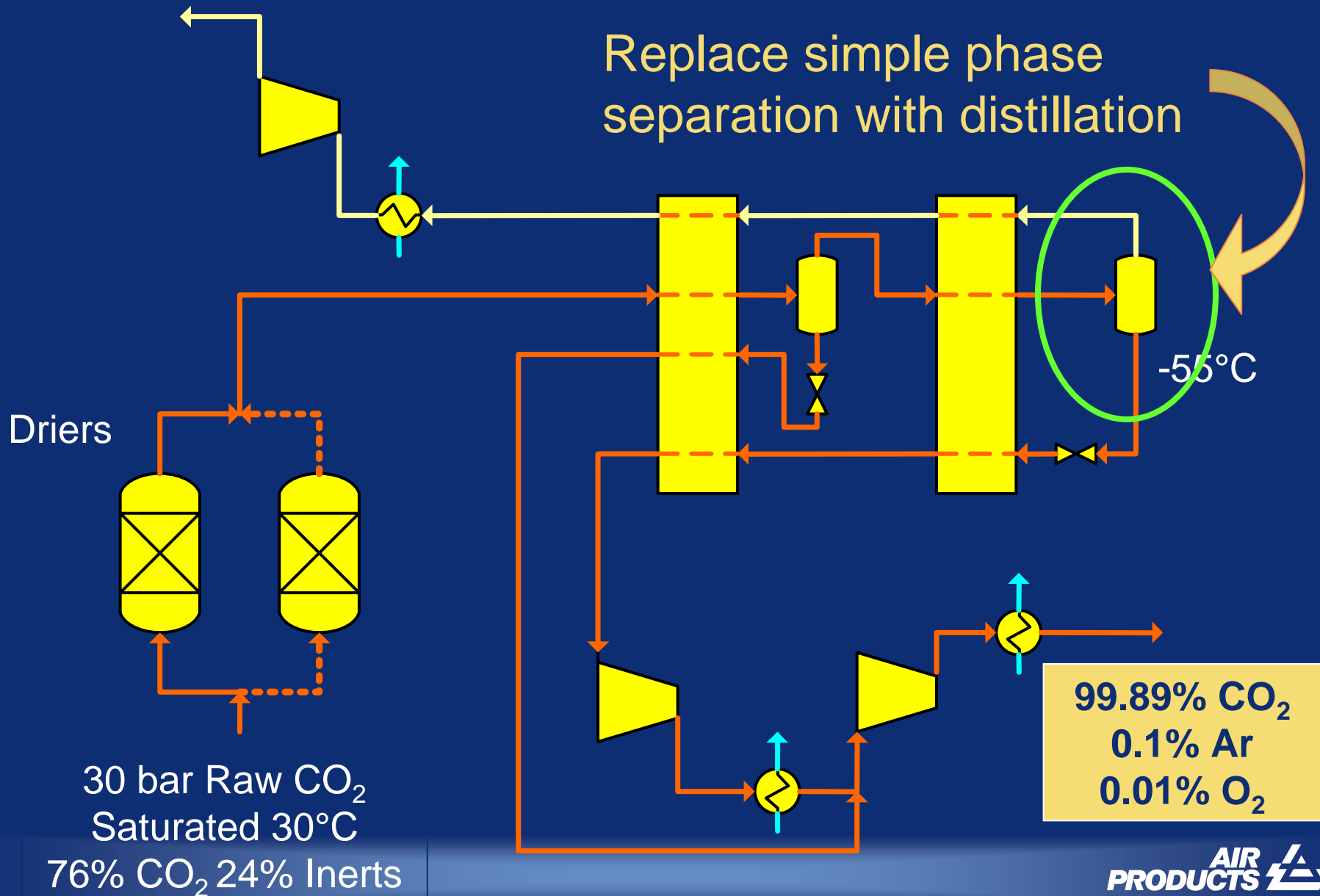
- **Adiabatic compression to 15 bar:**
  - No interstage water removal
  - All Water and SO<sub>x</sub> removed at one place
- **NO acts as a catalyst**
  - NO is oxidised to NO<sub>2</sub> and then NO<sub>2</sub> oxidises SO<sub>2</sub> to SO<sub>3</sub>: The Lead Chamber Process
- **Hg will also be removed, reacting with the nitric acid that is formed**

# Corrected CO<sub>2</sub> Purity

	Raw Flue Gas @ 35°C, 1.02 bara mol%	CO <sub>2</sub> Product @ 35°C, 110 bar mol% Prior Art	Vent @ 11°C, 1.1 bar mol% Prior Art	CO <sub>2</sub> Product @ 35°C, 110 bar mol% Corrected	Vent @ 11°C, 1.1 bar mol% Corrected
CO <sub>2</sub>	71.5	95.8	24.6	96.3	24.6
N <sub>2</sub>	14.3	2.0	48.7	2.0	48.7
O <sub>2</sub>	5.9	1.1	19.4	1.1	19.4
Ar	2.3	0.6	7.1	0.6	7.1
SO <sub>2</sub>	0.4	0.5	0	0	0
NO	400 ppm	13 ppm	1180 ppm	< 10 ppm	< 100 ppm
NO <sub>2</sub>	10 ppm	0	0	< 10 ppm	0
H <sub>2</sub> O	5.6	0	0	0	0

# And Oxygen removal from the CO<sub>2</sub>?

Replace simple phase separation with distillation



Driers

30 bar Raw CO<sub>2</sub>  
Saturated 30°C

76% CO<sub>2</sub> 24% Inerts

-55°C

99.89% CO<sub>2</sub>  
0.1% Ar  
0.01% O<sub>2</sub>

# The Cost of Higher Purity CO<sub>2</sub>

- 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

	CO <sub>2</sub> Purity	Oxygen Content	CO <sub>2</sub> Recovery	Power kWhr/tonne
Case 1	95.9 mol%	0.9 mol%	89.0%	168.5
Case 2	98 mol%	0.4 mol%	87.0%	166.5
Case 3	99.97 mol%	10 ppmv	87.4%	177.1

# Summary of CO<sub>2</sub> Purification

- FGD and DeNOx systems are not required to meet tight CO<sub>2</sub> purity specifications
- Co-disposal of SO<sub>2</sub> with CO<sub>2</sub> is not possible
  - Compressing CO<sub>2</sub> with NO + SO<sub>2</sub> + O<sub>2</sub> + Water will result in H<sub>2</sub>SO<sub>4</sub> production
- Low NOx burners are not required for oxyfuel combustion
- Oxygen can be removed for EOR-grade CO<sub>2</sub>
- Large-scale demonstration is required
  - Further development is planned

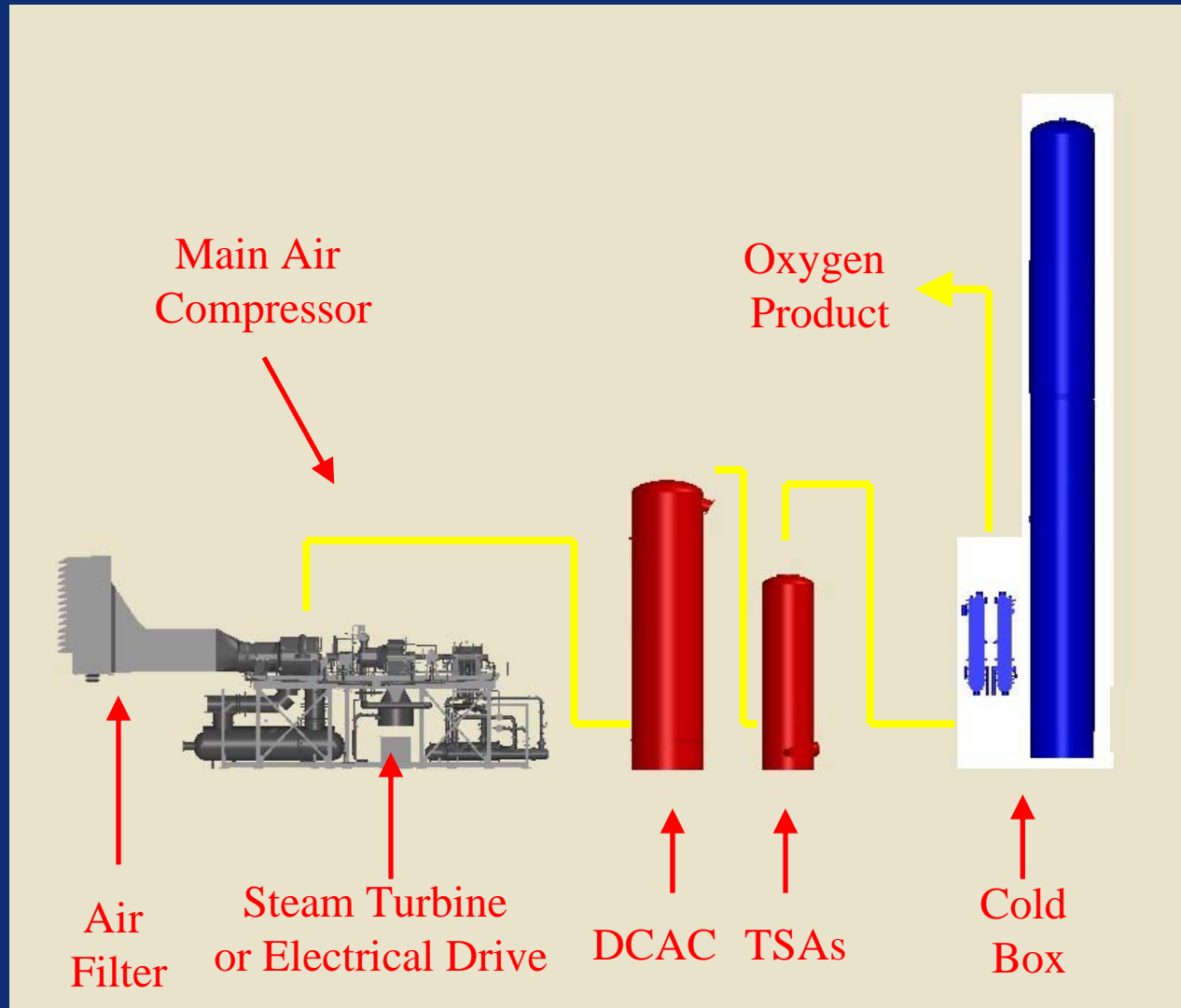
# FUTURE DEVELOPMENT OF OXYFUEL ASC BOILER SYSTEM

- Studies on retrofit to existing power stations
- Efficiency increase to 36.4% by improved coal drying using warm N<sub>2</sub>, more O<sub>2</sub> 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



# Large size single train plants – 3500 tonne/day for Qatar



# Prefabricated modularised design

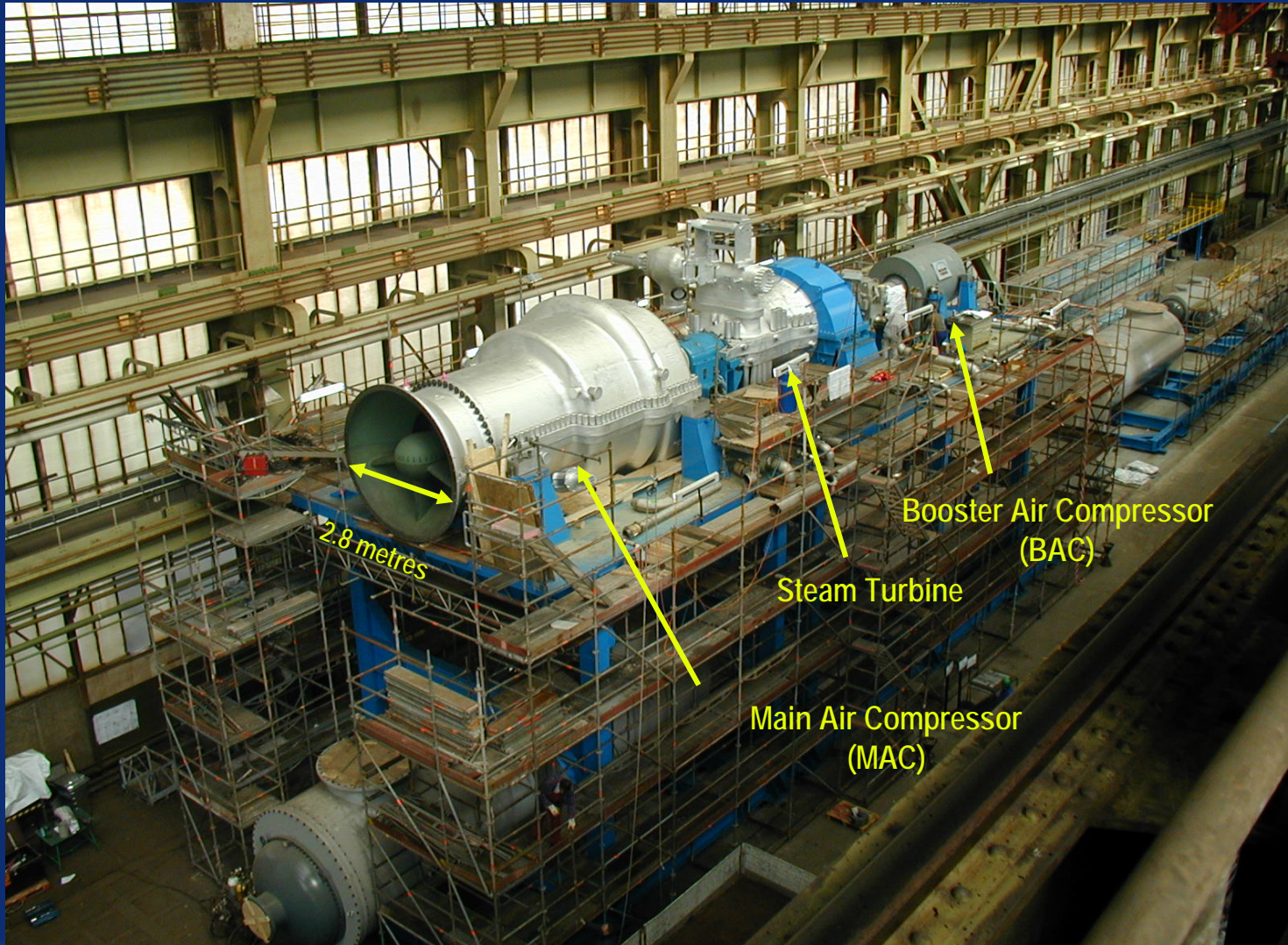








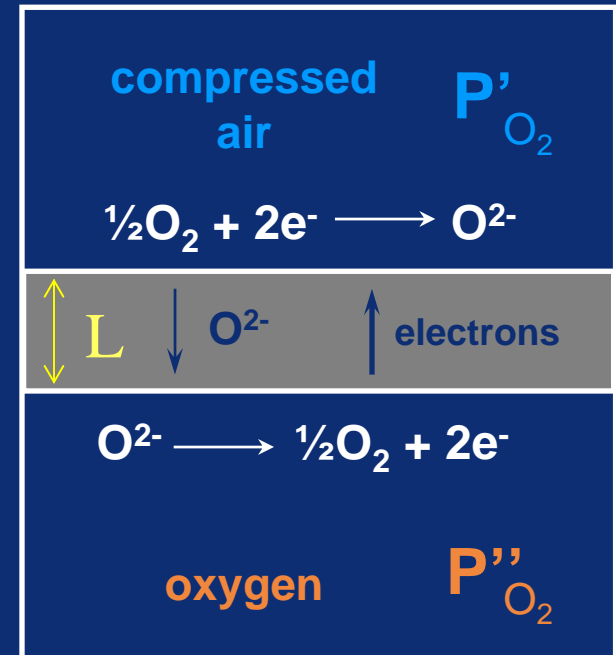
# Proven Machinery Systems – Double-ended Steam Turbine



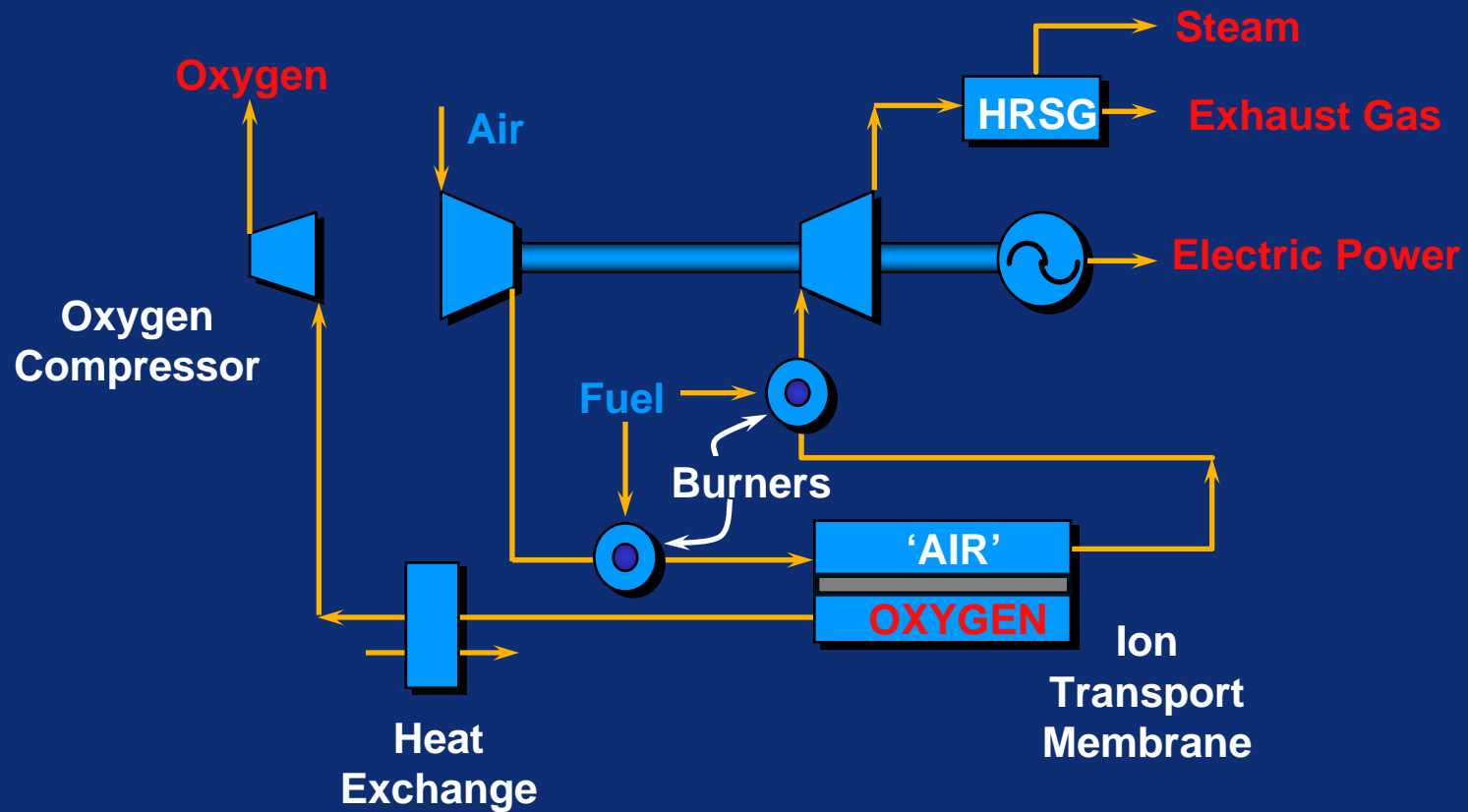
# Ion Transport Membranes (ITM): High-flux, High-purity Oxygen

- 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<sub>2</sub>

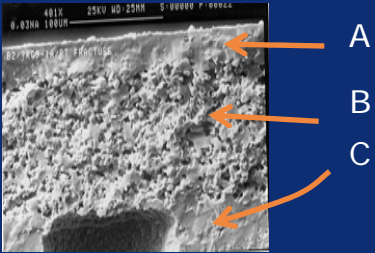
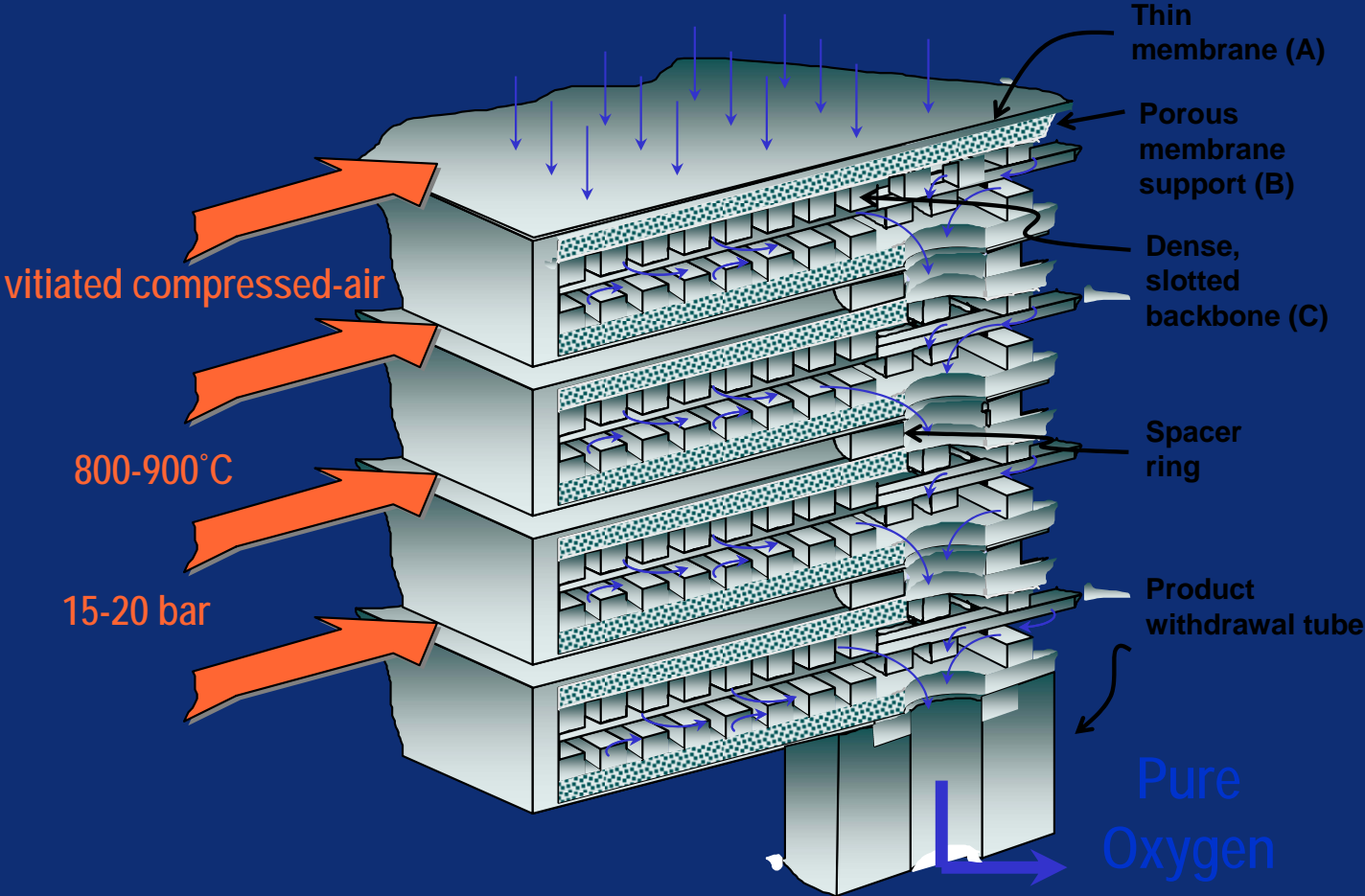
- $$O_2 Flux \propto \frac{1}{L} \ln \left( \frac{P'_{O_2}}{P''_{O_2}} \right)$$



# Gas Turbine ITM Integration



# Ion Transport Membrane For Low Cost Oxygen Production



Thank you

tell me more

[www.airproducts.com](http://www.airproducts.com)