GAS SEPARATION TECHNOLOGIES FOR ENERGY PRODUCTION

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INTERNATIONAL CENTRE FOR
SUSTAINABLE CARBON

PRESENTATION OUTLINE

- The importance of air separation units (ASUs)
- ASU technologies and development opportunities
- Patent search results
- Key messages

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Technology Collaboration Programme
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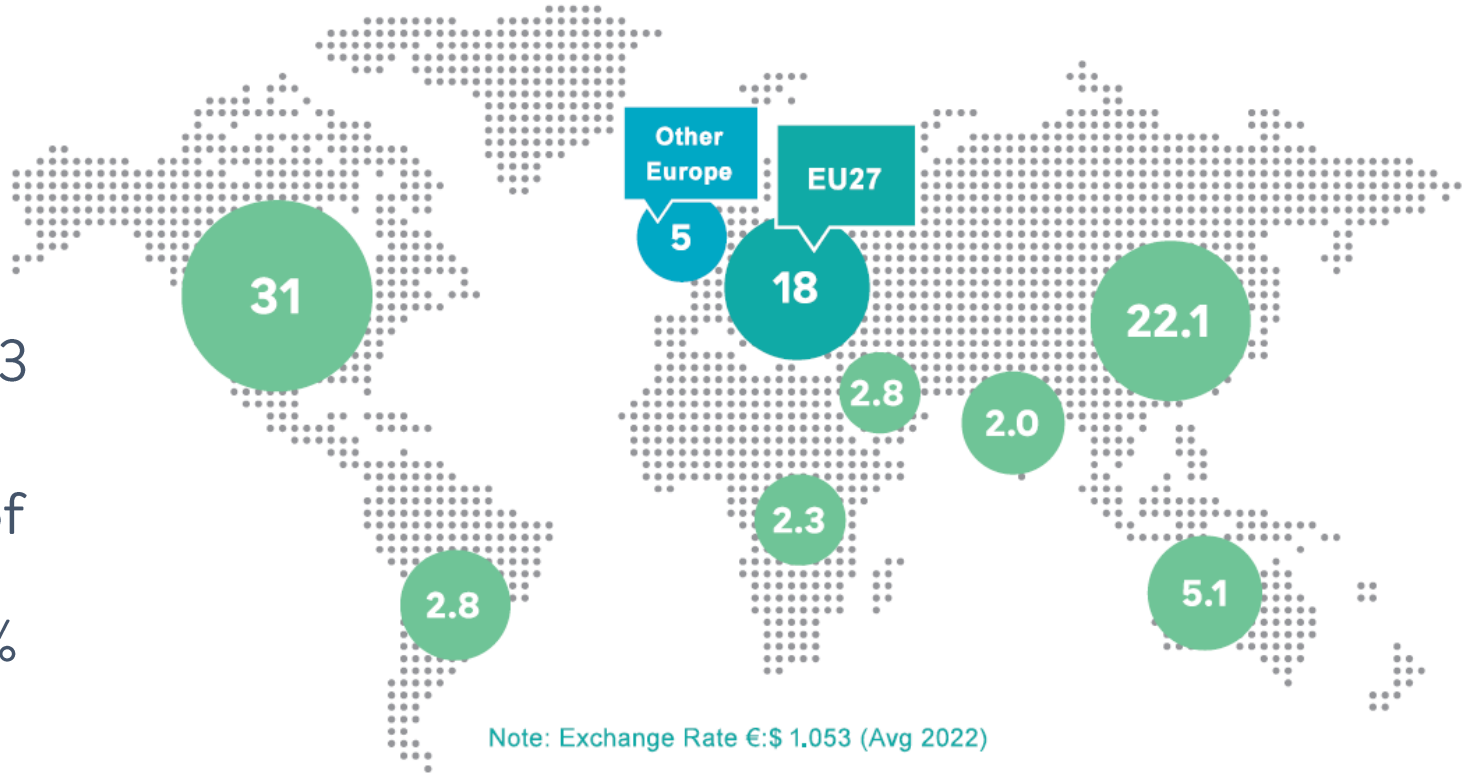
THE IMPORTANCE OF AIR SEPARATION UNITS

OXYGEN MARKET

- Total industrial gases market was ~ $96 billion in 2022
- USA, EU27 and China account for 65%
- Industrial oxygen sales were ~380 Mt in 2018, corresponding to ~$ 48 billion
  - Forecast to be $50-65 billion in 2023 at CAGR of 6.6-7.8%
- ASU energy consumption reached 14% of total electric power in China's iron and steel industry in 2023, accounting for 5% of total national electricity production
- ASU typically located close to point of use
  - Large number of OEMs



Global industrial gas market in 2022, € billions (EIGA, 2023)

INDUSTRIAL OXYGEN APPLICATIONS

- Power generation
  - Oxyfuel and IGCC
- Chemicals, pharmaceuticals and petroleum
  - Raw material
  - Catalytic crackers
  - Oxygen enriched combustion
- Glass and ceramics
  - Oxyfuel and higher efficiency boilers
- Metals
  - Air enrichment in the blast furnace
- Pulp and paper
  - Bleaching chemical

Callide oxyfuel project (Spero and Yamada, 2018)

BOTH OXYFUEL AND IGCC NEED ASU

- Post-combustion capture
- Oxy-combustion
  - Callide project
  - Net Power/Allam cycle
- Pre-combustion
  - GreenGen
  - Sinopec Qilu
  - Great Plains

25MWe Net Power, La Porte, Texas (Martin and others, 2018)

265MWe IGCC-GreenGen, Tianjian (Xia and others, 2020)

CRYOGENIC ASU

CRYOGENIC ASU

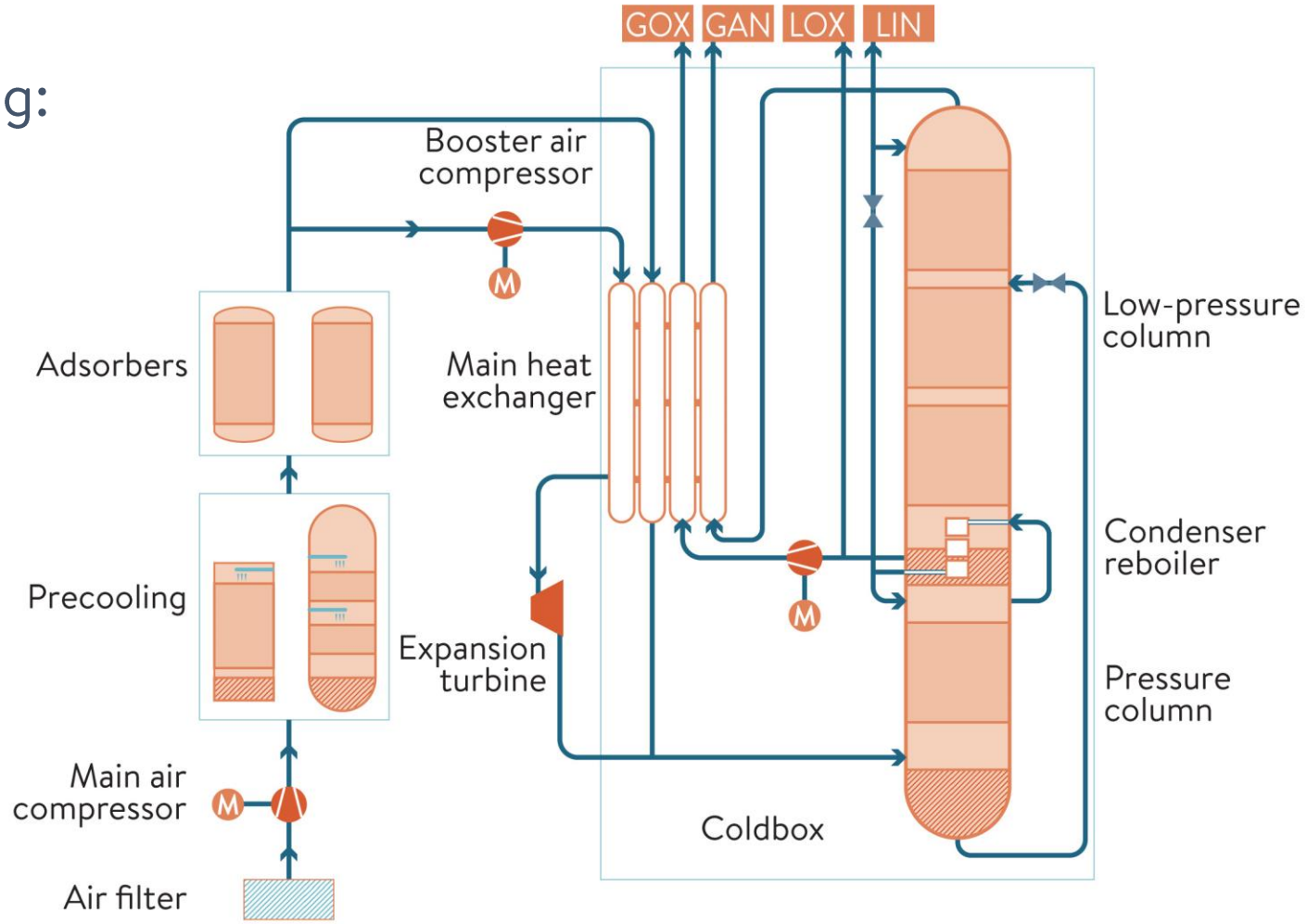
- Established process
- High volumes and purity
  - 5000-6000 tO_2/d
  - >99.99% purity
- Based on different boiling points
  - oxygen boils at -183°C
  - nitrogen boils at -196°C
- Reduce temperature of air to below its triple point of –140.7°C (132.5 K) and 37.7 bar to liquify
  - Usually liquified at about 6 bar, -172°C (101 K)
  - Then separated by rectification/distillation

5800 tO_2/d ASU at Sasol, Secunda, South Africa (Air Liquide)

CRYOGENIC ASU PROCESS

Many different configurations, but typically a 2-tower process comprising:

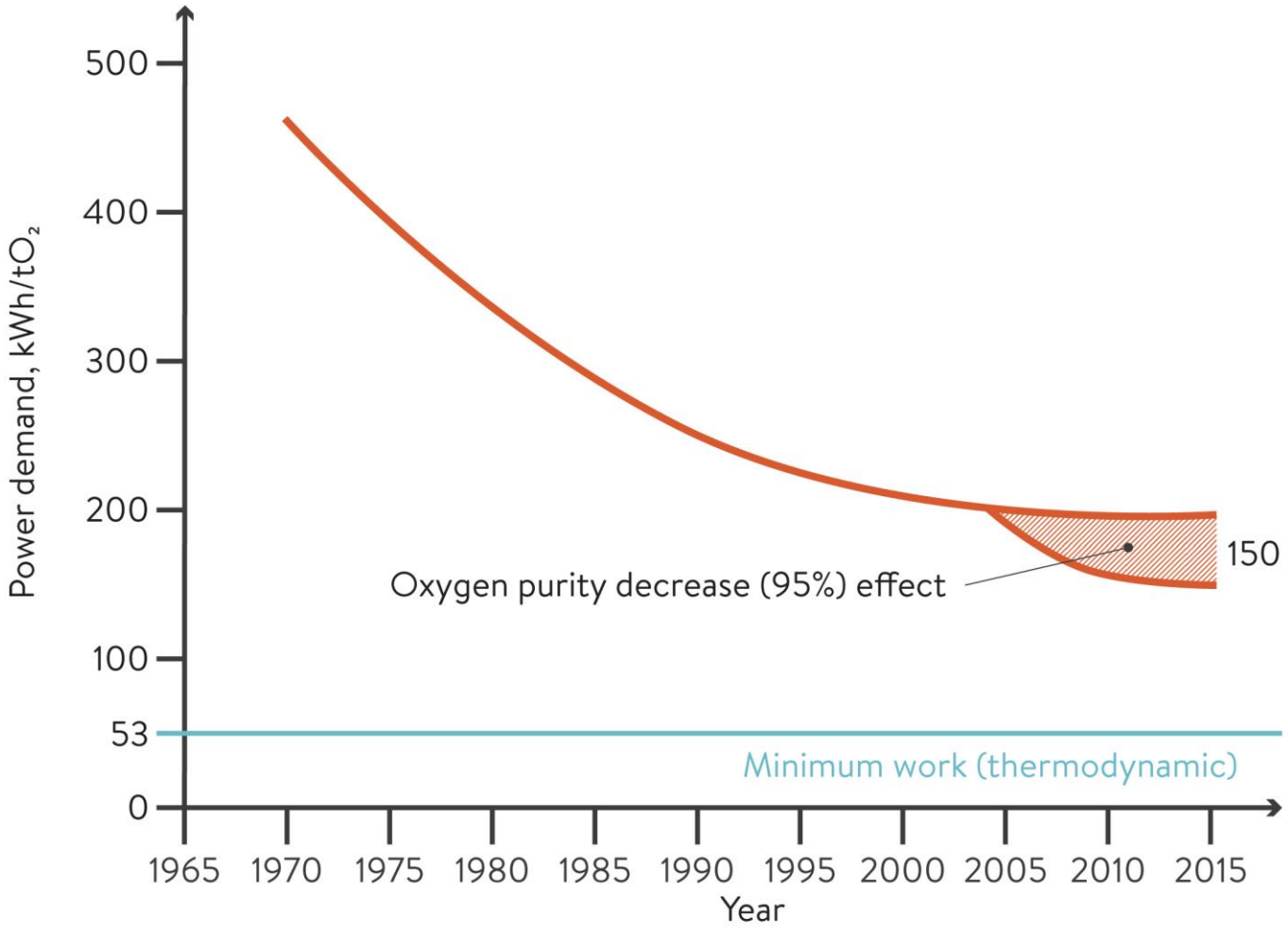
- Filtration
- Compression
- Contaminants removal
- Heat exchange
- Product compression
- Storage



Typical flow diagram for an ASU (Klein and others, 2021)

ASU PROCESS IMPROVEMENT

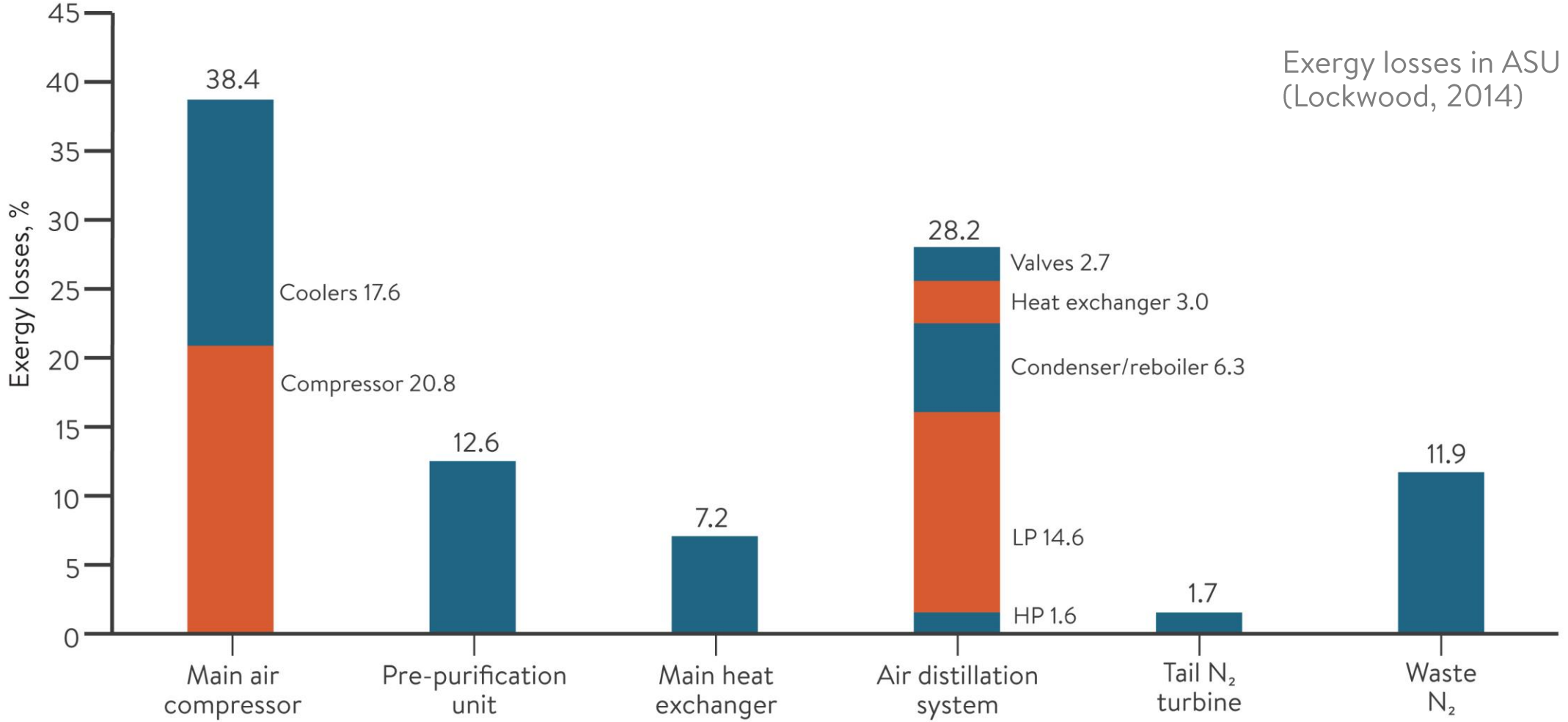
- Energy demand reduced from 500 to 160-225 kWh/tO_2
- Reducing O_2 purity to 95% or below reduces power demand
  - Adequate for most Oxyfuel/IGCC
- Theoretical minimum power demand in 50-53 kWh/tO_2 so scope for further reduction
  - But decrease in last 10 years limited
- Medium term target in oxyfuel application is 120-140 kWh/tO_2



Energy demand for oxygen separation (Banaszkiewicz and others, 2014)

INCREMENTAL IMPROVEMENTS

Advances in ASU optimisation focused on reducing exergy losses, both by technological advantages in equipment and by designing increasingly complex distillation



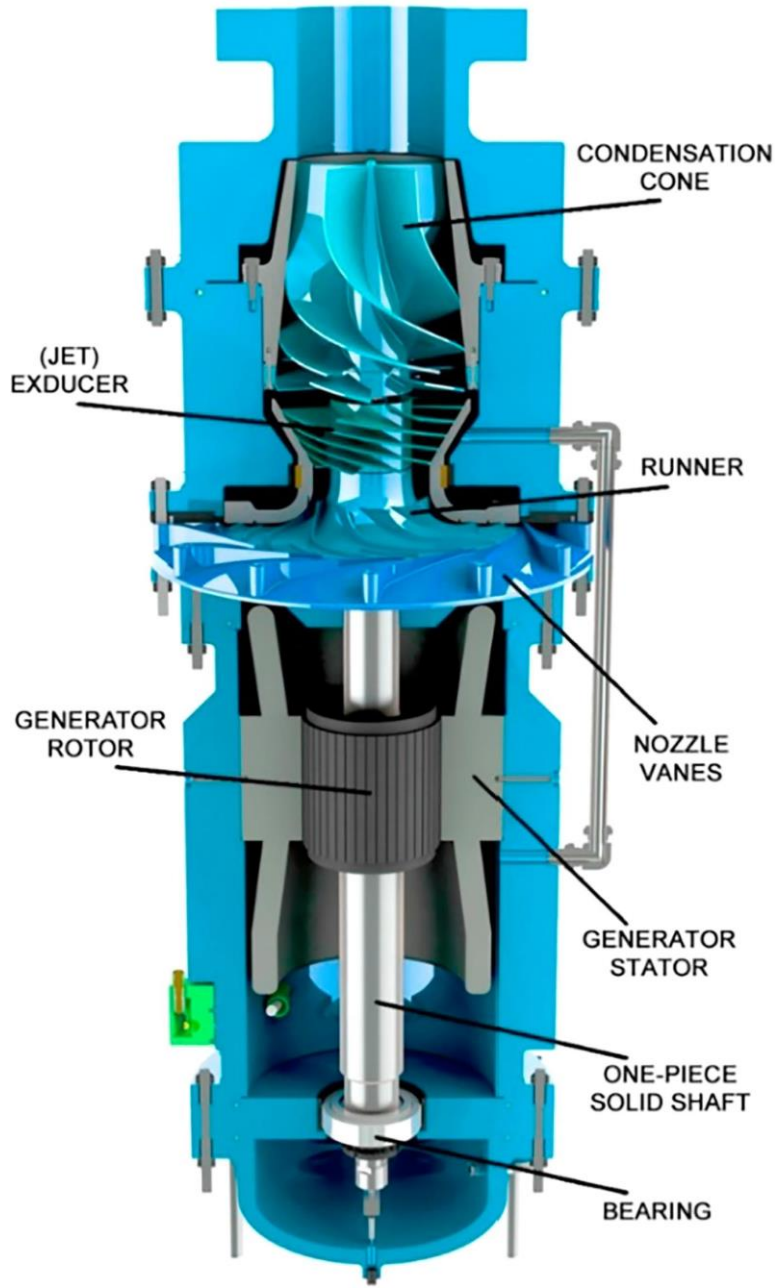
INCREMENTAL IMPROVEMENT - EXAMPLES

Replace Joule-Thompson valve with turbine expander

- liquid or 2-phase expander
- Around 15 kWh/tO_2 reduction possible

Integration with Organic Rankine Cycle (ORC)

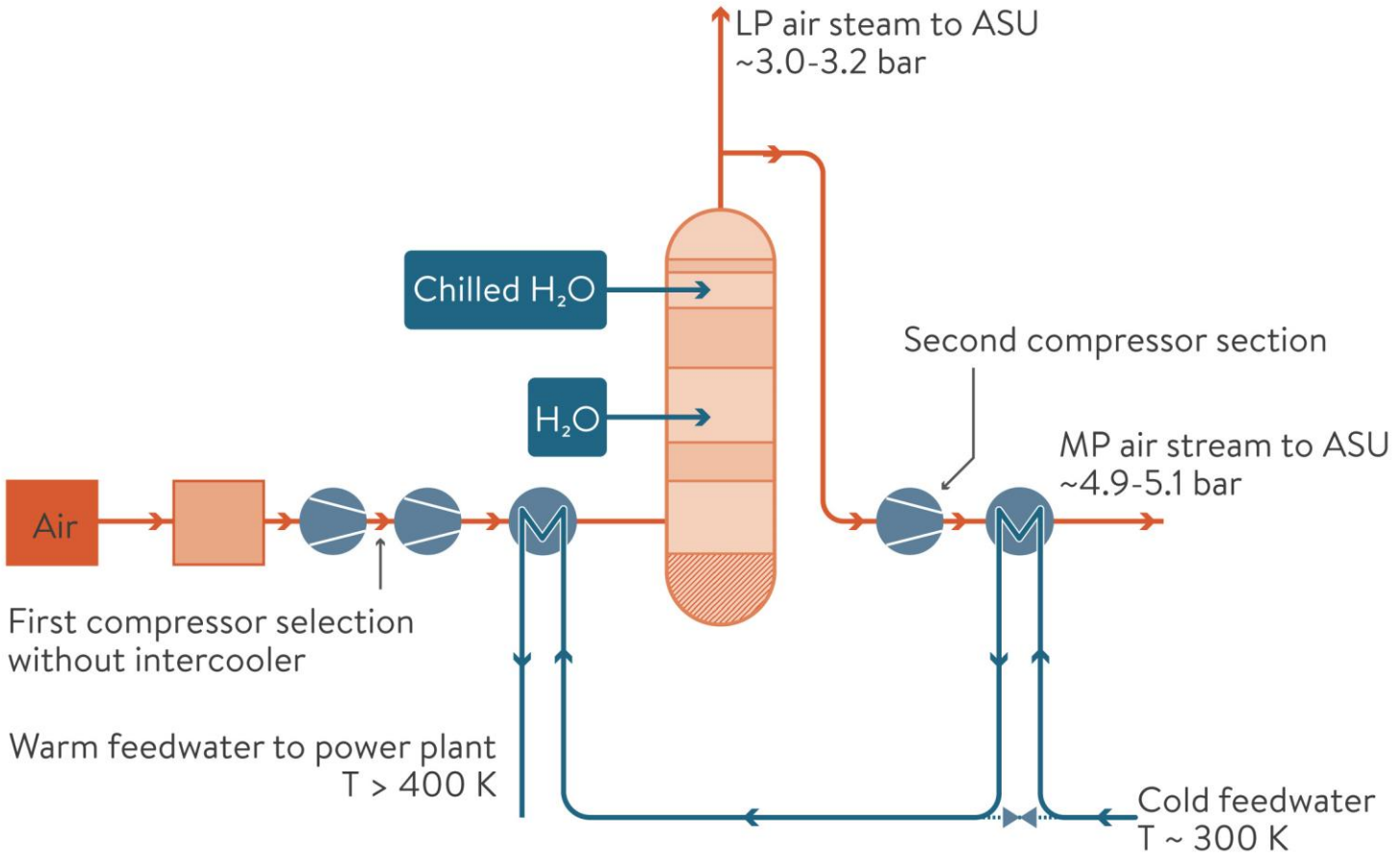
- heat of compression used in ORC, potentially with electrically coupled ORC and vapour compression refrigerator (VCR)
- R134a (tetrafluoroethane) refrigerant



Two phase expander (Klein and others, 2021)

HEAT INTEGRATION OF ASU WITH POWER CYCLE

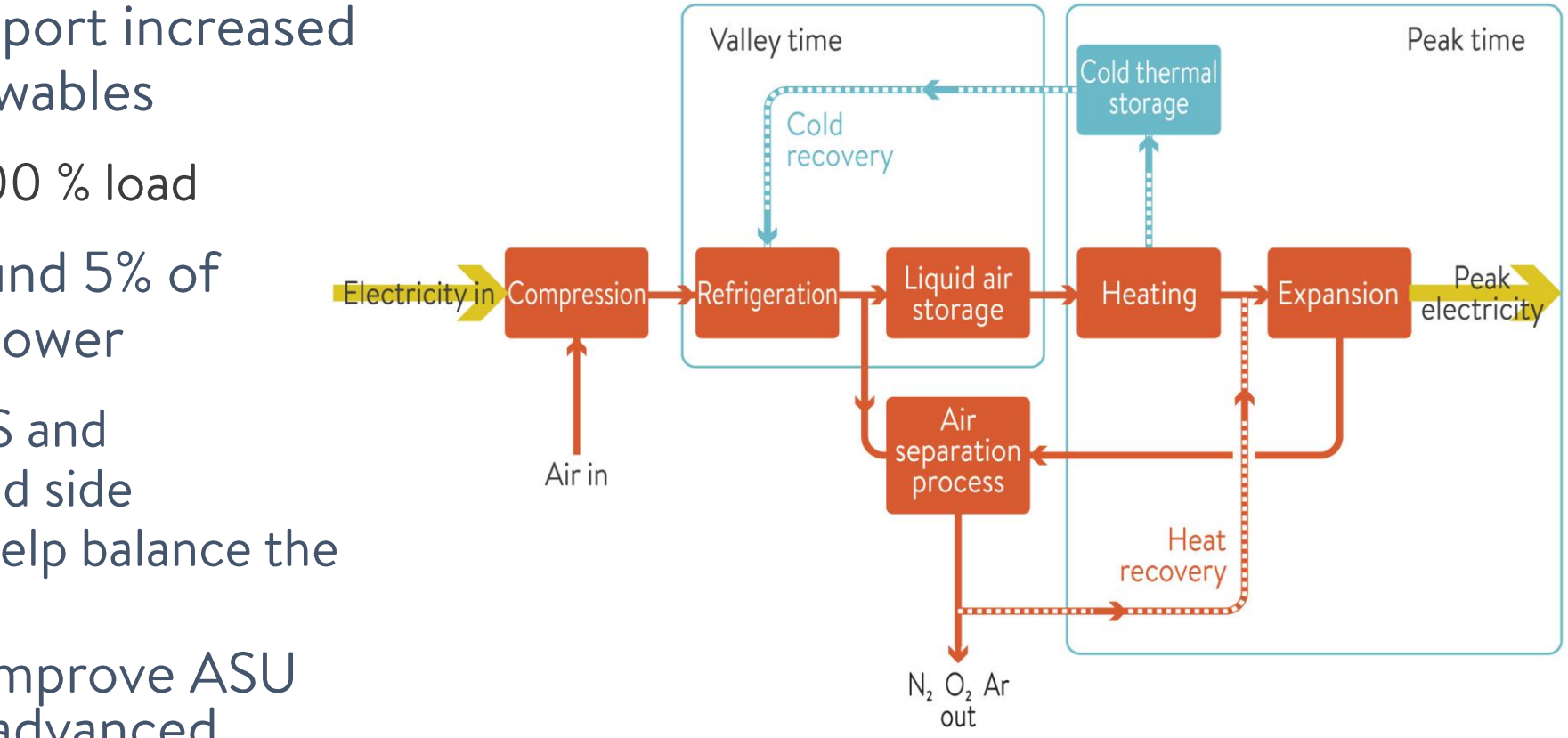
- Highly specific to particular application and site
- Could achieve 150kWh/tO_2 energy demand
- Heat integration based on use of air compressor heat from the ASU
  - boiler feedwater pre-heating in Oxyfuel
  - heating the recycled CO_2 stream and work integration in Allam cycle



Schematic of ASU with feedwater heating (Goloubev and others, 2013)

ASU SYSTEM FLEXIBILITY

- Flexible ASU could support increased non-dispatchable renewables
  - 10 %/min from 40–100 % load
- ASUs, account for around 5% of China's national total power
  - Combining with LAES and implementing demand side management could help balance the grid
- Also opportunities to improve ASU performance through advanced control and product scheduling



Schematic of ASU/LAES approach (Liu and others, 2023)

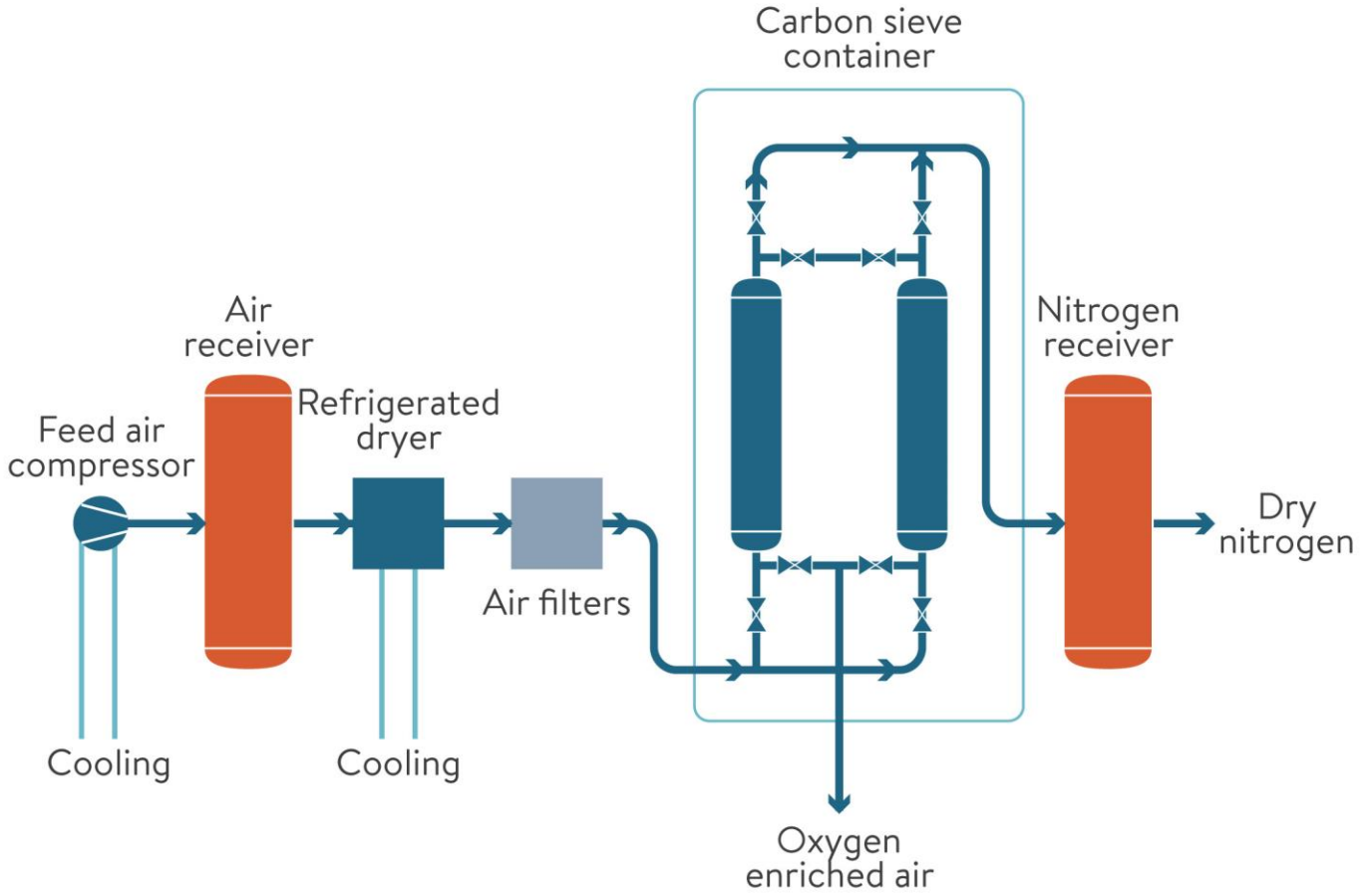
NON-CRYOGENIC ASU

COMPETING TECHNOLOGIES

Comparison of air separation technologies (Adapted from Alivandi and others, 2018; Kiebach and others, 2022)		
Technology type	Specific power consumption, kWh/t	Technology Readiness Level (TRL)
Cryogenic	160-225	9
Pressure swing adsorption	525	9
Vacuum swing adsorption	265	9
Membrane (ITM)	150	6
Electrochemical	1320	4
Chemical looping	30-150	4
Ceramic auto-thermal	115	6
Vortex	-	4
Magnetic	45	3
Chemical MOLTOX	100	6

ADSORPTION

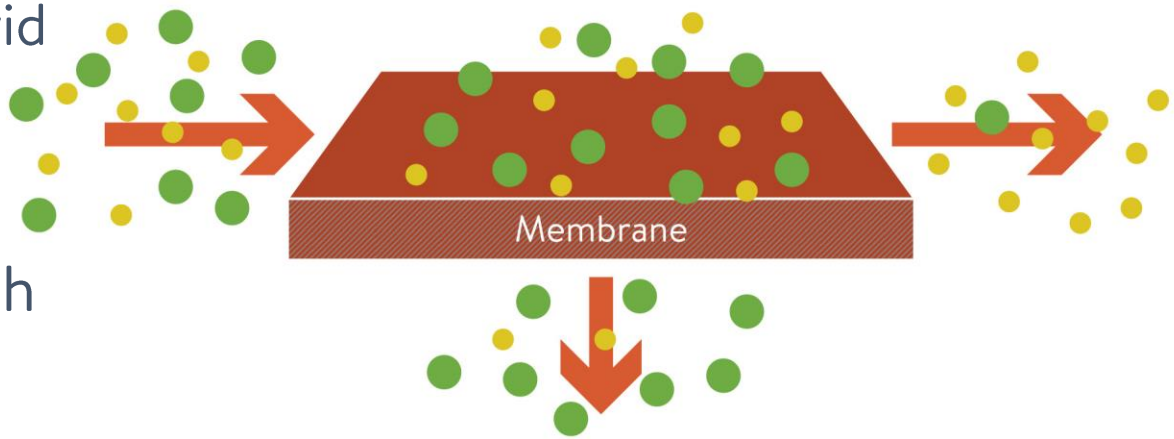
- Adsorption technologies include PSA, VSA, VPSA, TSA
- Typical adsorbents: alumina, active carbon, molecular sieving carbon and zeolite molecular sieves
- Promising, although currently suited for small/medium sized applications
  - 100-300 tO_2/day
- Decreased purity at larger gas flow rates and other factors impede large-scale application



Pressure swing adsorption (PSA) (Darabkhani and others, 2023)

MEMBRANES

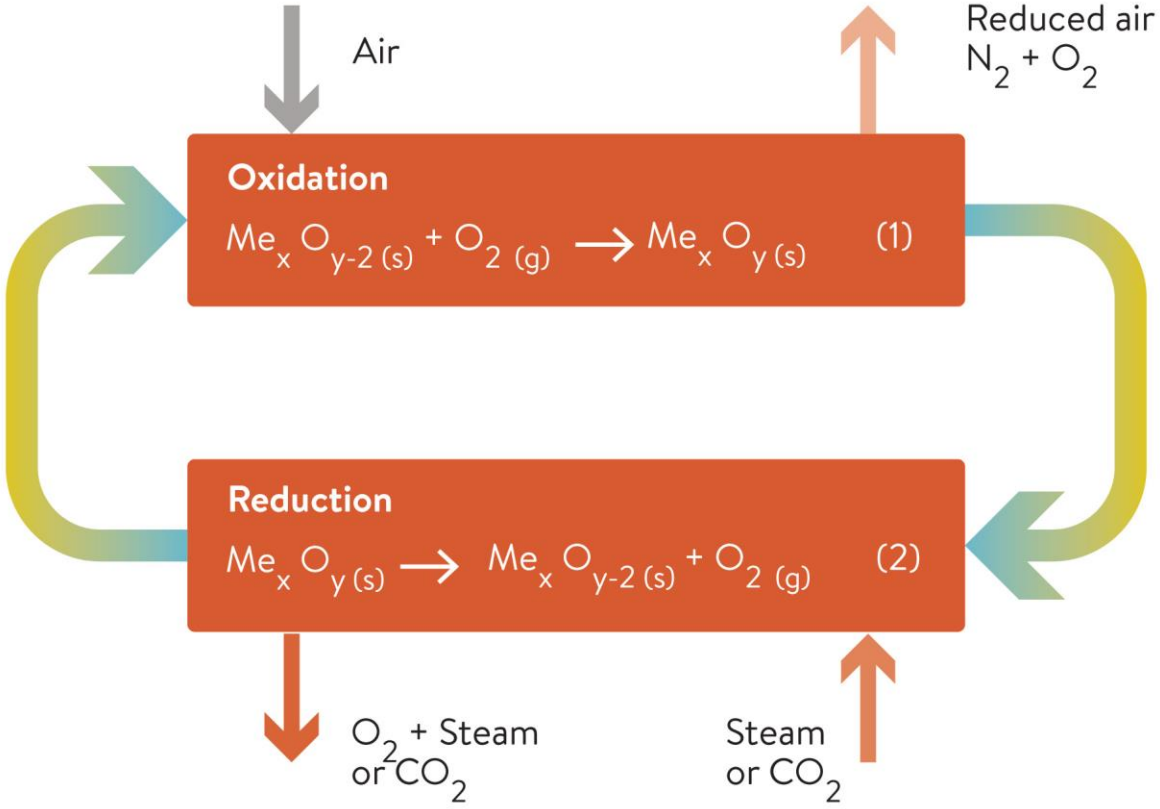
- Polymeric membranes exploit different O_2/N_2 diffusion rates
  - Relatively low O_2 purity
  - Potential for Mixed Matrix Membrane hybrid approach with zeolites/ molecular sieves
- ITMs are solid inorganic oxide ceramic materials that allow O_{2-} ions to pass through
  - High purity O_2 and suitable for thermal integration
  - Potentially economic but materials development and improved system durability required



Gas separation membrane (Wu and others, 2018)

CHEMICAL LOOPING

- Fuel does not have to react directly with the oxygen carrier
  - Typically metal oxides
- Potentially very low specific energy demand
- Materials remain the primary challenge.
- Mechanical stability and oxygen transfer rates are key characteristics for successful systems



Chemical looping air separation (Wu and others, 2018)

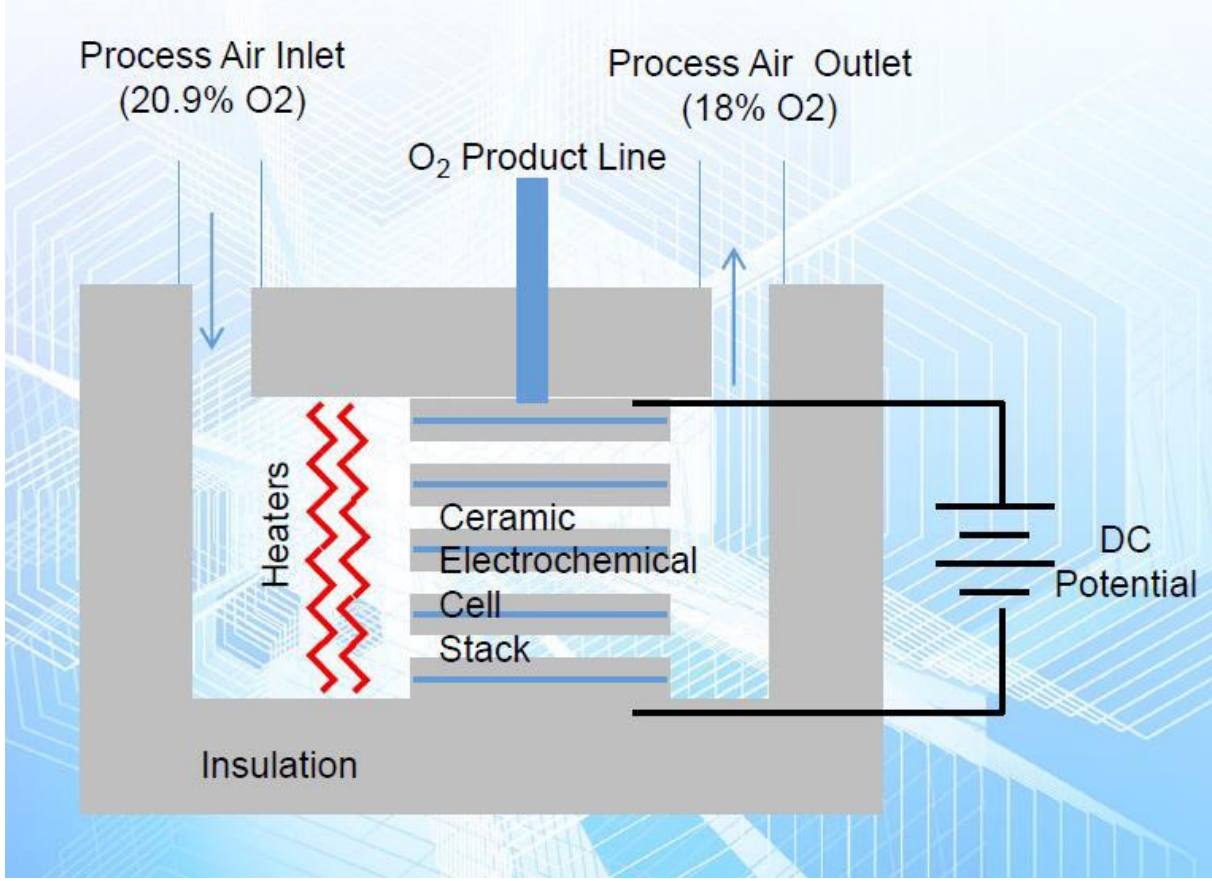
ELECTROCHEMICAL OXYGEN

Electrolyser technologies based on alkaline, proton exchange membrane (PEM) and solid oxide electrolysis cell (SOEC)

- High purity O_2 but relatively low production levels and high specific power consumption

Almost irrespective of costs, targets set for renewable hydrogen production

- 40 GWe of electrolysers in EU by 2030 could produce 80 MtO_2/y, globally by 2050 could be 3500 MtO_2/y
- Oxygen would be a co-valorised stream to the main hydrogen production

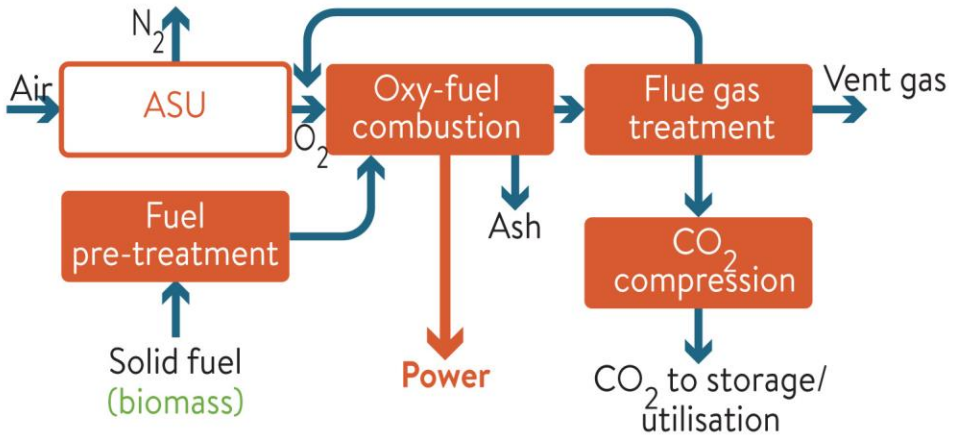


Electrochemical oxygen (Alivandi and others, 2018)

CO-VALORISED ELECTROCHEMICAL OXYGEN

- Electrochemical oxygen seems likely to increase in importance through to 2050

Oxy-fuel combustion

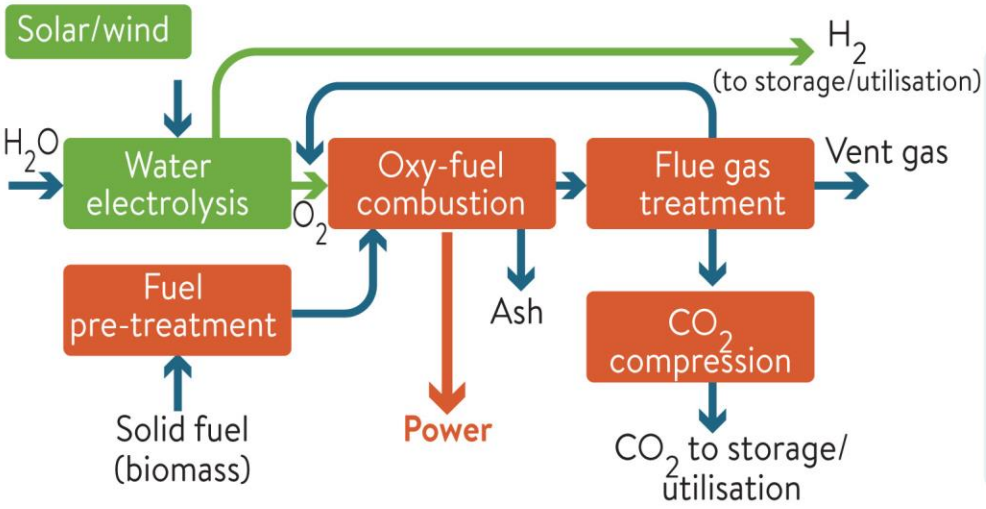


Air separation unit

Highly energy intensive

200 - 225 kWh/t O_2

(commonly supplied by the electricity grid)



O_2 from electrolysis has two benefits:

1 - To provide an extra income for the electrolysis

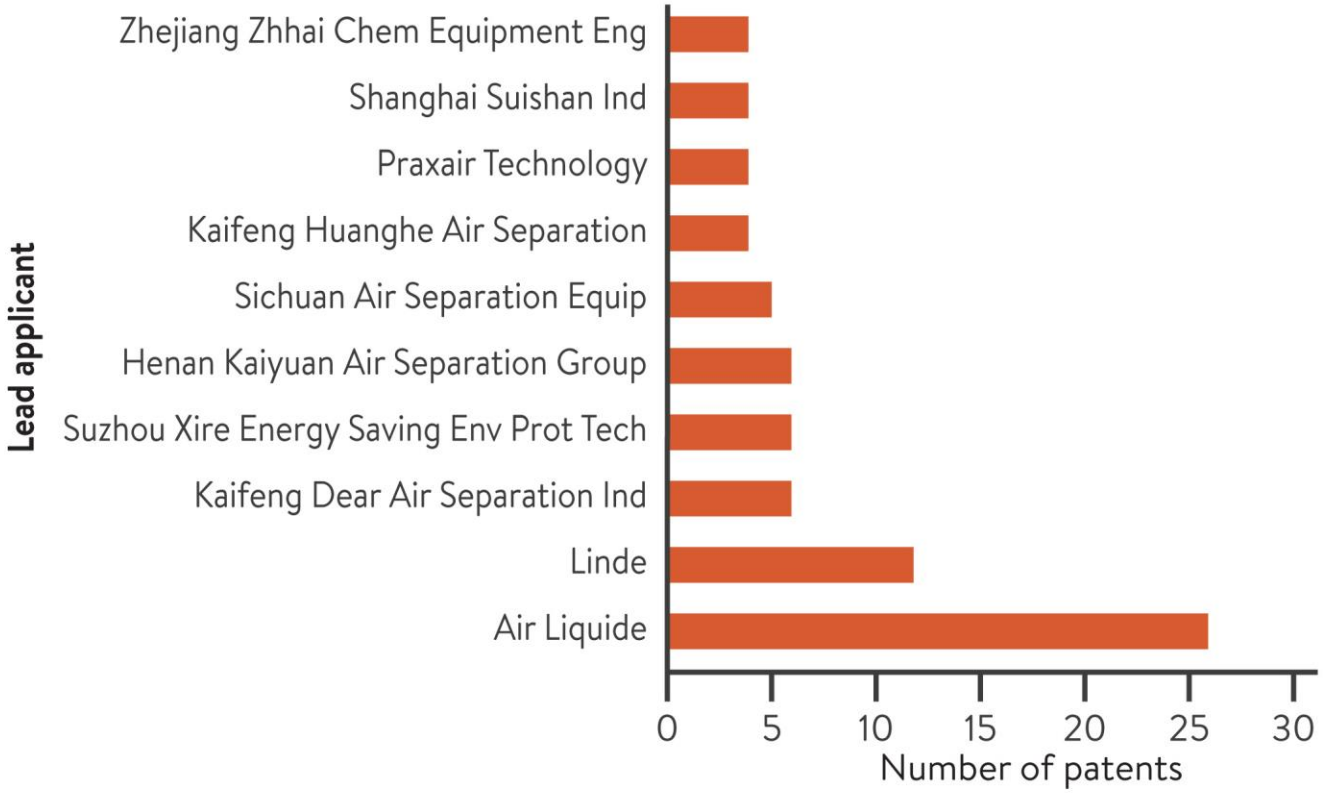
2 - To reduce the costs and the emission intensity from the ASU

ASU PATENT ANALYSIS

ASU PATENTS

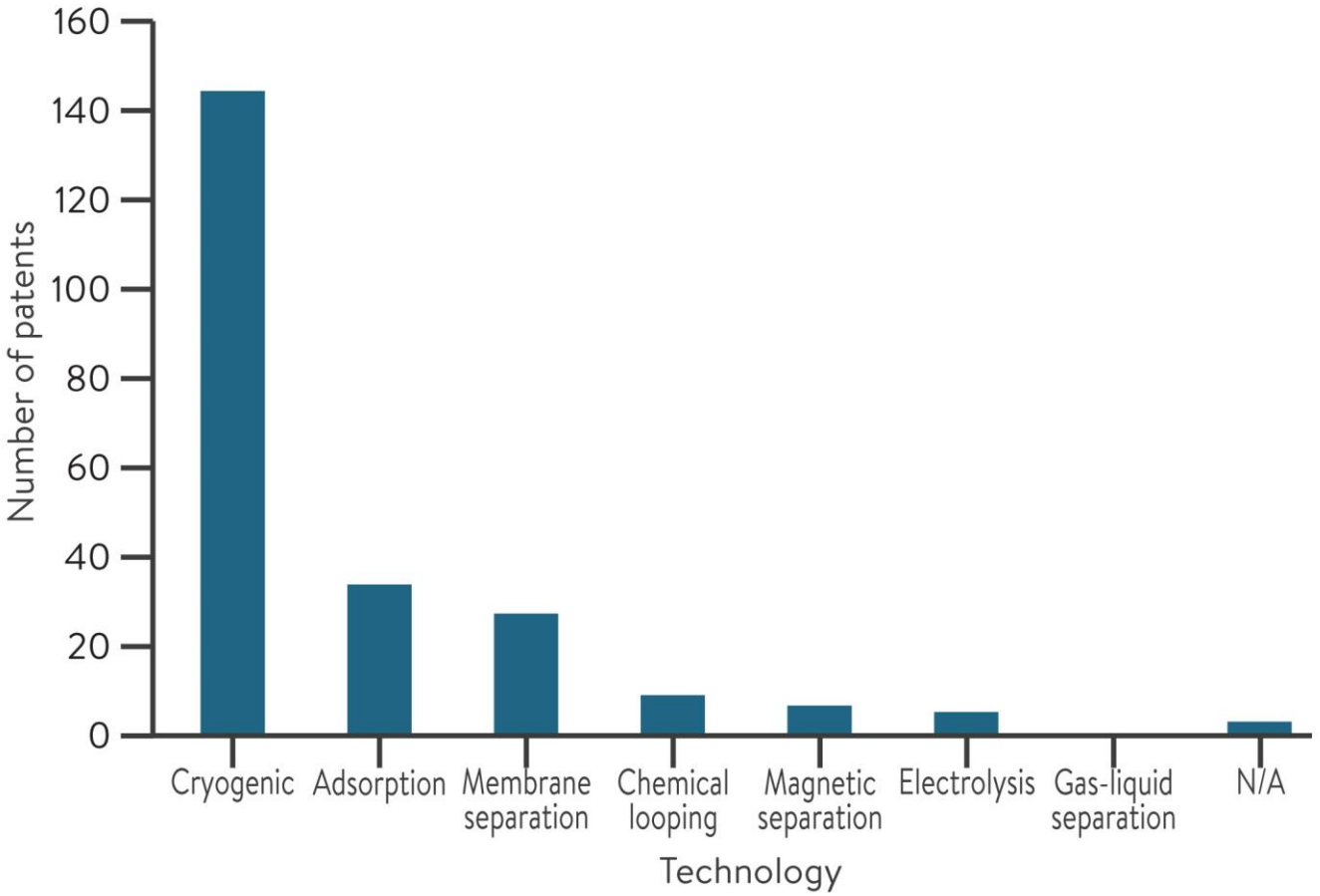
- Search for ‘Air’ *AND* ‘Separation’ *AND* ‘oxygen’ over last 5 years

- 75% of patents assessed are Chinese
- Air Liquide and Linde are largest individual applicants with joint 38 patents
- Cryogenic ASU is primary method
  - 60% of total patents assessed
  - 75% relate to performance or operational improvement



ASU PATENTS - INTEGRATION

- Newer technologies of chemical looping, electrolysis and magnetic separation account for < 10%
- Integration of ASU with power generation/industrial processes features strongly
  - 20% of total patents assessed
  - Features across nearly all technology types
- Can combine aspects of ASU technologies
  - Coupling O_2 production from water electrolysis with cryogenic ASU
  - SOEC downstream of a membrane



KEY MESSAGES

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- Industrial oxygen was ~380 Mt in 2018, corresponding to nearly $48 billion
- Cryogenic ASU remains preferred technology
  - most cost effective for high production rates
  - 5000 tO2/d per single unit achievable
  - specific energy moving down towards medium term target of 120-140 kWh/tO_2 for oxyfuel application
  - heat integration and oxygen purity are key drivers
- Chemical looping offers potential advantage of reduced energy demand
  - durability and materials issues to be overcome
- Electrochemical O_2 as co-product of renewable hydrogen seems set to increase significantly to 2050
- Opportunities to combine air separation technologies

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THANK YOU FOR LISTENING

ANY QUESTIONS?

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