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Overview of CO₂ Capture Methods in the Petrochemical and Refining Industry

TIEEP Energy Forum

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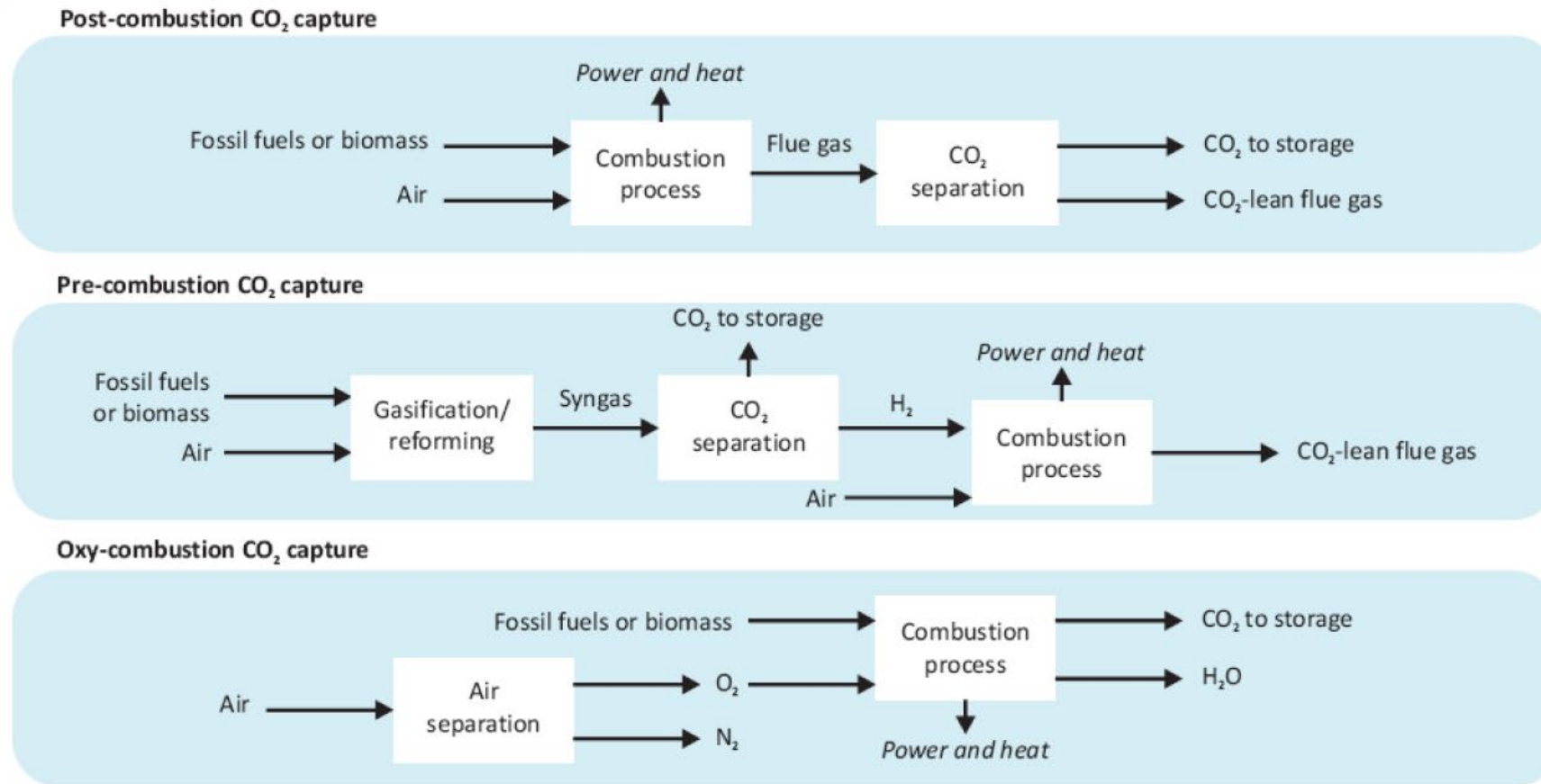
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Introduction

Introduction

- Crackers are large emitters of CO₂ when internally generated fuel gas (and natural gas) is consumed
- 90-95% of CO₂ from the furnaces
- To reduce CO₂, the following options currently exist:
 - Reduce firing demand by raising less steam / electrification of main compressors
 - Post combustion carbon capture from furnace flue gas
 - Increase the hydrogen content of the furnace fuel gas
- Hydrogen from:
 - Electrolysis
 - Conversion of cracker tail-gas to hydrogen rich fuel (with CCS)
 - Steam Methane Reforming (SMR)
 - Autothermal Reforming (ATR)
 - Partial Oxidation (POX)

Introduction



Source: IEA (2012a), *Energy Technology Perspectives 2012*.



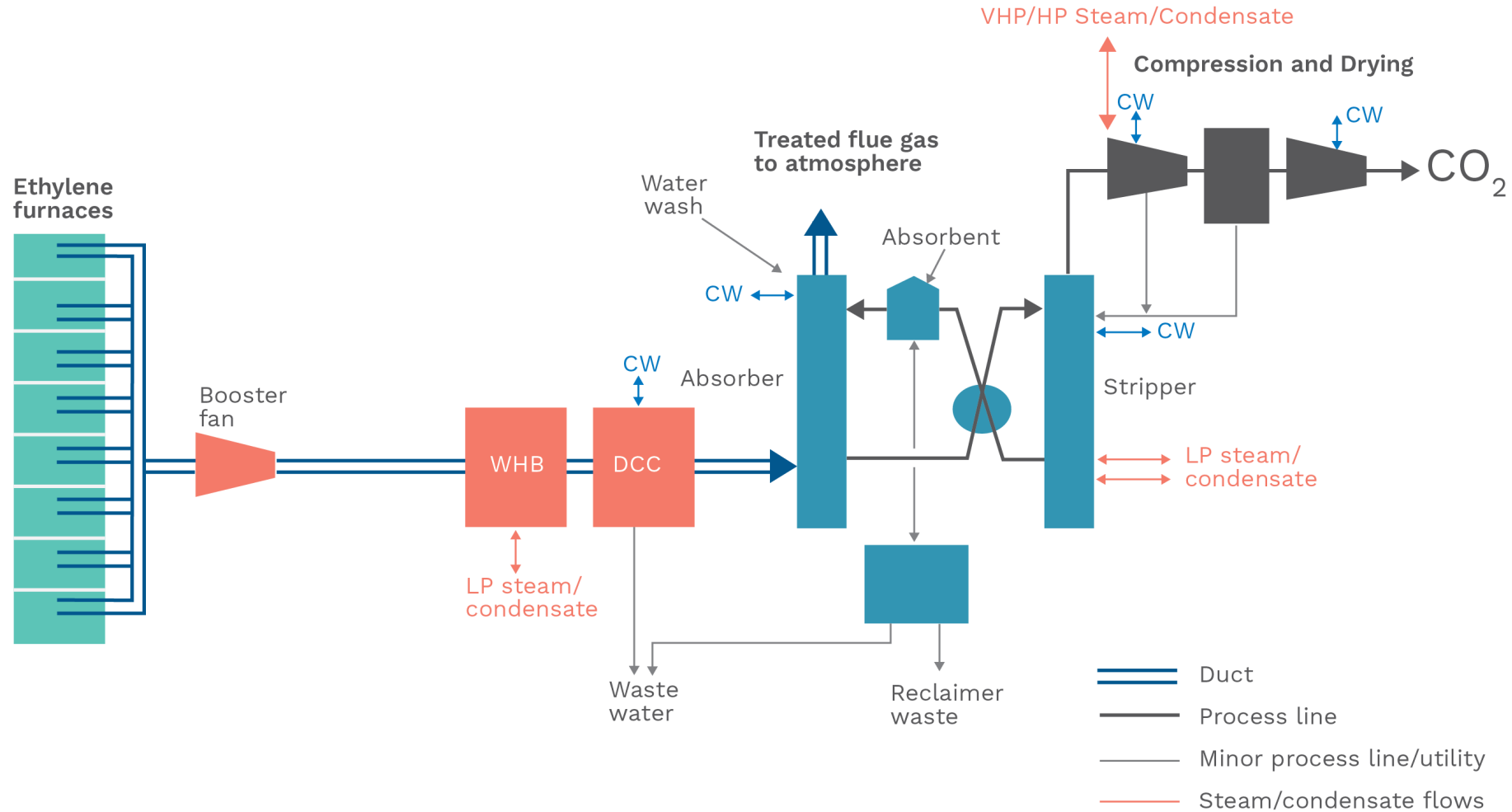
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Post Combustion

Post-combustion carbon capture

- Low pressure gas scrubbing process using hindered amine solvents, paralleled from natural gas scrubbing processes (MEA used since 1930s)
- Amine scrubbing is the single source process for proven capacities greater than 1 MTPA on flue gas
- Alternative processes still under development: cryogenic separation, adsorption on solid beds, new solvents. Target lower energy penalty, < 2.1 GJ/ton of capture CO_2 (benchmark for coal fired power plant)

Post-combustion carbon capture



Post Combustion Closing remarks

- Global demand, industrialization at large scale
- The addition of the post-combustion carbon capture plant will not interfere with the performance of the ethylene plant. In addition, the capture will be started after the ethylene plant is started and it's easy to retrofit
- Capturing the CO₂ from furnaces and auxiliary boilers will reduce the CO₂ emissions by 90-95%
- Operating margins can increase if the CO₂ is utilised, specially if green ethylene can be produced – there is likely to be a market premium for green polyethylene!



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Pre-Combustion

Typical CO₂ emissions for hydrogen plants

Sources

Reforming



Partial Oxidation



Water-Gas Shift



Hydrocarbon Combustion



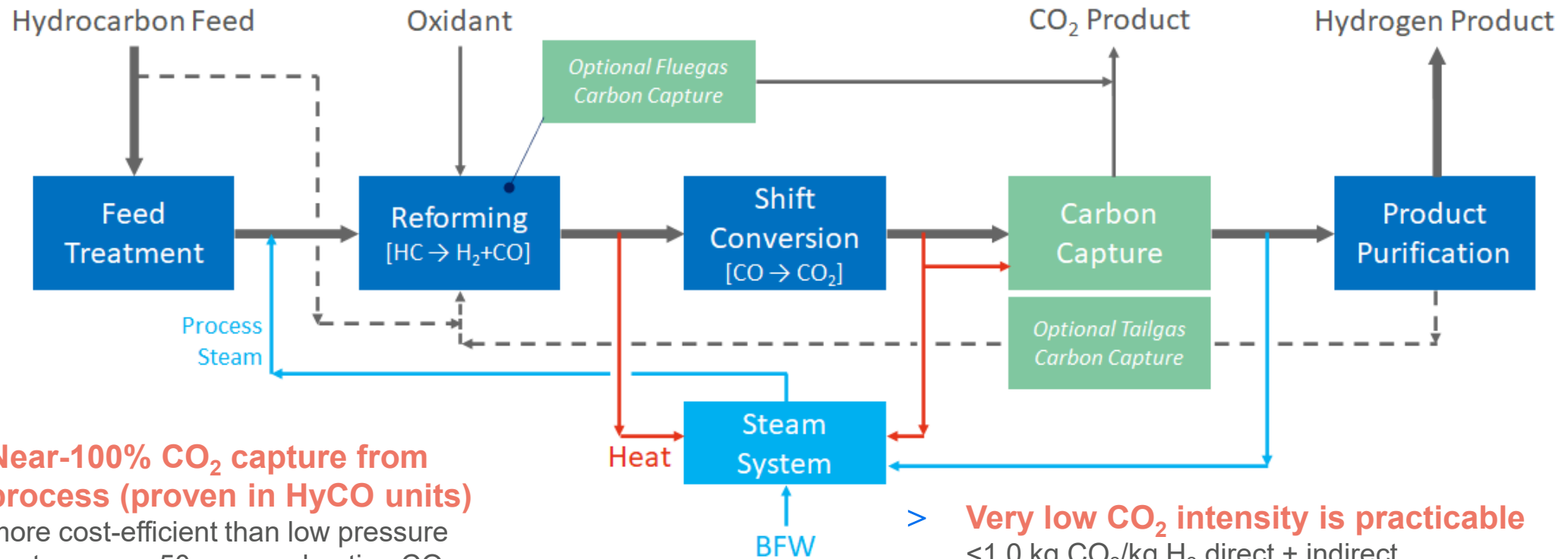
For GREY hydrogen:

- 1 kg of H₂ production typically emits 9-12 kg CO₂
 - To be fair, H₂ doesn't weigh very much...
~22 times less than CO₂
 - Two H₂ molecules net about one CO₂ molecule

Baseline depends on:

- Feedstock quality (H/C ratio, fossil C content)
 - Process scheme
 - quantity of export steam/power etc.
 - quantity/dependency on imported resources, and their carbon footprints
- > CO₂ present in process gas and flue gas (where carbon emitting fuel is fired)

Hydrogen with carbon capture



> **Near-100% CO₂ capture from process (proven in HyCO units)**
more cost-efficient than low pressure capture; over 50 pre-combustion CO₂ capture references deployed

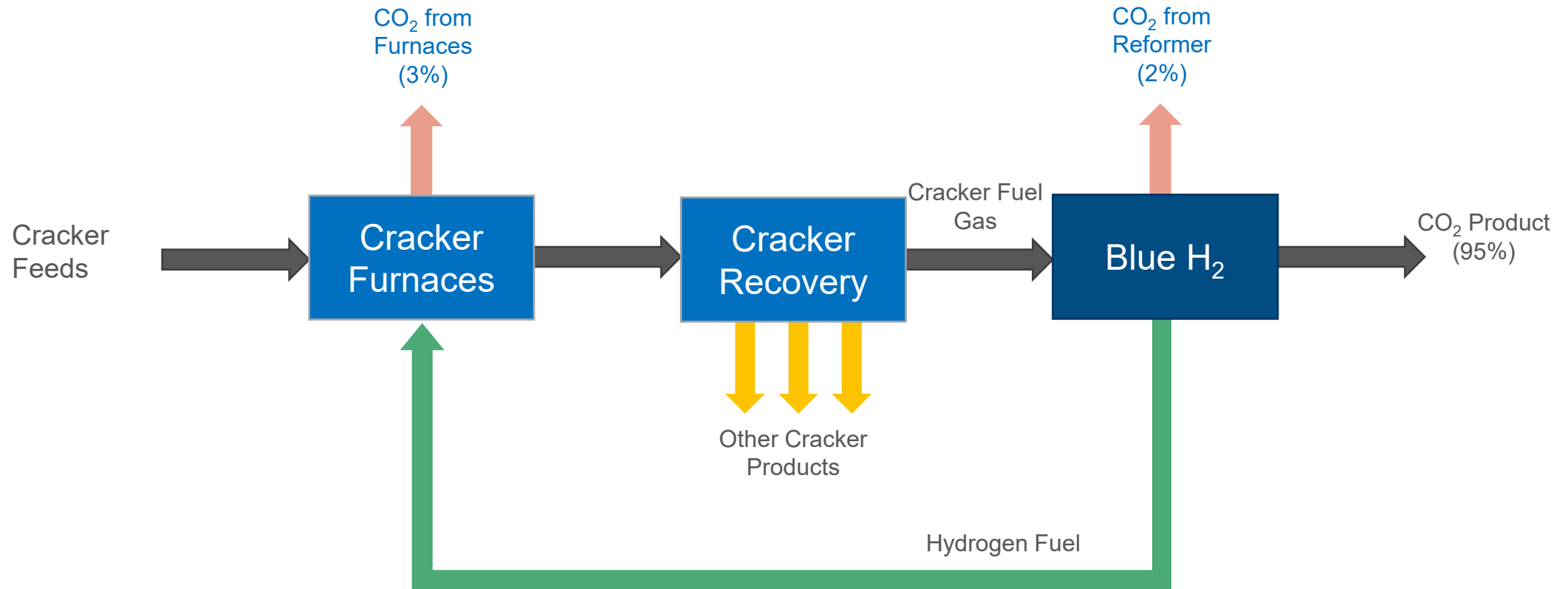
> **Very low CO₂ intensity is practicable**
<1.0 kg CO₂/kg H₂ direct + indirect

Overall concept

- Liquids crackers
 - Typical liquids cracker has a small excess of fuel gas
 - Excess increases with electrification
 - Biggest CO₂ savings will come from maximizing hydrogen production, so send all fuel gas to a Hydrogen Plant
 - Cheaper to recover CO₂ from syngas than from cracker furnace flue gas
- Gas crackers
 - Typical gas cracker is short in fuel gas
 - Fuel is already high in hydrogen
 - How to ensure sufficient fuel hydrogen is always available?

Decarbonized cracker concept

Base arrangement



Comparison with hydrogen from electrolysis

Parameter	Unit	Source of Hydrogen	
		Alkaline Electrolysis	SMR (Blue H ₂)
Quantity of Hydrogen	t/h (Nm ³ /h)	29.9 (332,500)	29.9 (332,500)
Levelized Cost of Hydrogen	\$/kg	3.5	0.33
Electrical Power	GWh	1.5	0.02
CAPEX	\$BN	1.6	0.5
CO ₂ from Electricity @ 376 tCO ₂ e/GWh	MMt/year	4.9	0.11
CO ₂ from Electricity @ 26 tCO ₂ e/GWh	MMt/year	0.38	0.04

As an alternative to using a reformer to generate hydrogen as fuel, the hydrogen could be generated from water using electrolysis:

- Based on Alkaline Electrolysis (AE) – the most mature electrolysis technology
- Basis is to supply 100% pure hydrogen from electrolysis to provide the same heat duty as the hydrogen from the reformer in the previous example

Data in DNV Technology Progress Report 2021 used as the basis of calculations for electrolysis – levelized cost based on 20 years, 8000 hours/year and electricity price of 40€/MWh, based on 1500 KTA liquids cracker.

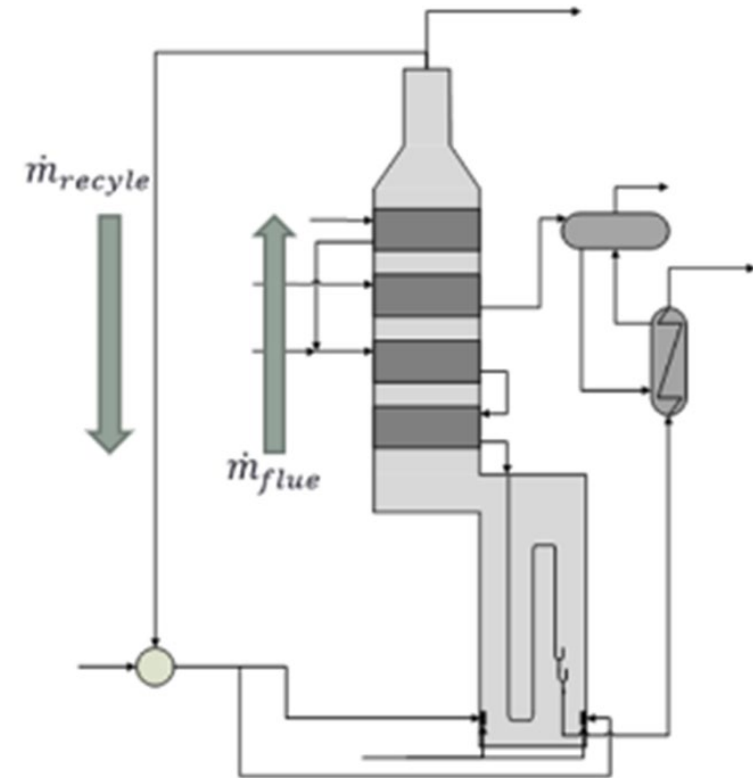


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Oxy-fuel Combustion

Oxy-fuel combustion

- Use of purified O₂ results in Flue gas with higher concentration of CO₂ with minimal N₂
- No recycle – grass roots
 - Reduced Flue Gas flowrate
 - High adiabatic flame temperature
 - New burner technology
 - Upgraded materials required
- With recycle – revamp
 - Similar adiabatic flame temperature to traditional
 - New burner technology
 - No change to convection section
 - Same materials required



Recycle ratio= 0.74

Oxy-fuel combustion

- The furnace is integrated with an ASU and carbon capture system increasing thermal efficiency (oxygen and flue gas are recycled as oxidizer)
 - The ASU provides oxygen to burn in the furnace
 - The carbon capture is simple as high purity CO₂ is recovered from the process
- Possibly difficult retrofit without recycle



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Direct Air Capture

Direct Air Capture

- **Various technologies to capture CO from atmosphere:**
 - Liquid Based
 - Solid Based
- **Many different routes being explored**
- **Generally, Technologies are early in development**
- **Not a near term solution, but will part of final Net-Zero configurations**



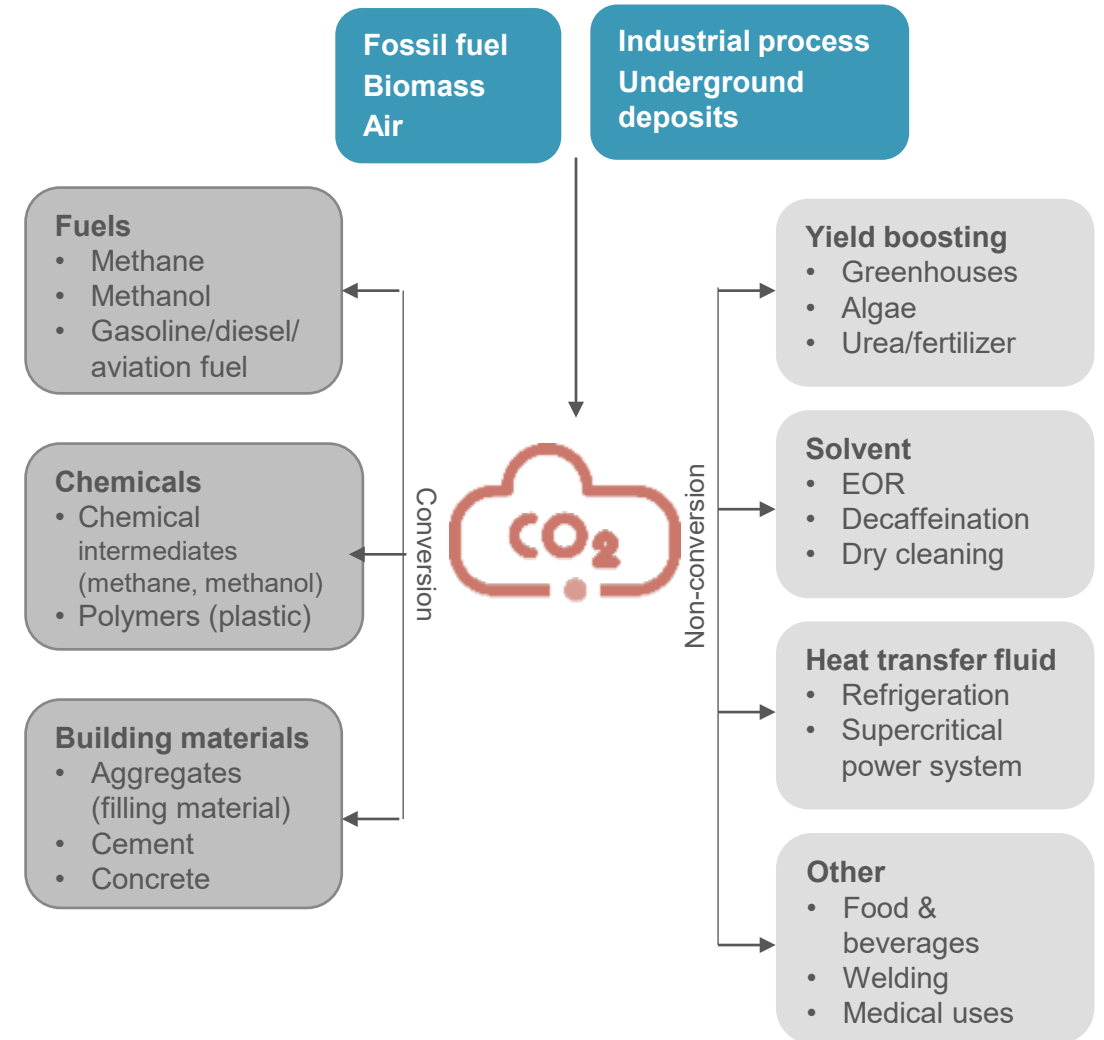
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CO₂ Utilization

CO₂ utilization routes

Our selection for this presentation:

- Option 1: CO₂ can be directly used for enhanced oil recovery (EOR) or storage/sequestration
- Option 2: CO₂ to derived fuels: methane, methanol, gasoline and aviation fuels
- Option 3: CO₂ to derived chemicals:
 - Plastics, fibers, synthetic rubber (through methanol)
 - Specialty chemicals: polymers
 - Green polyethylene



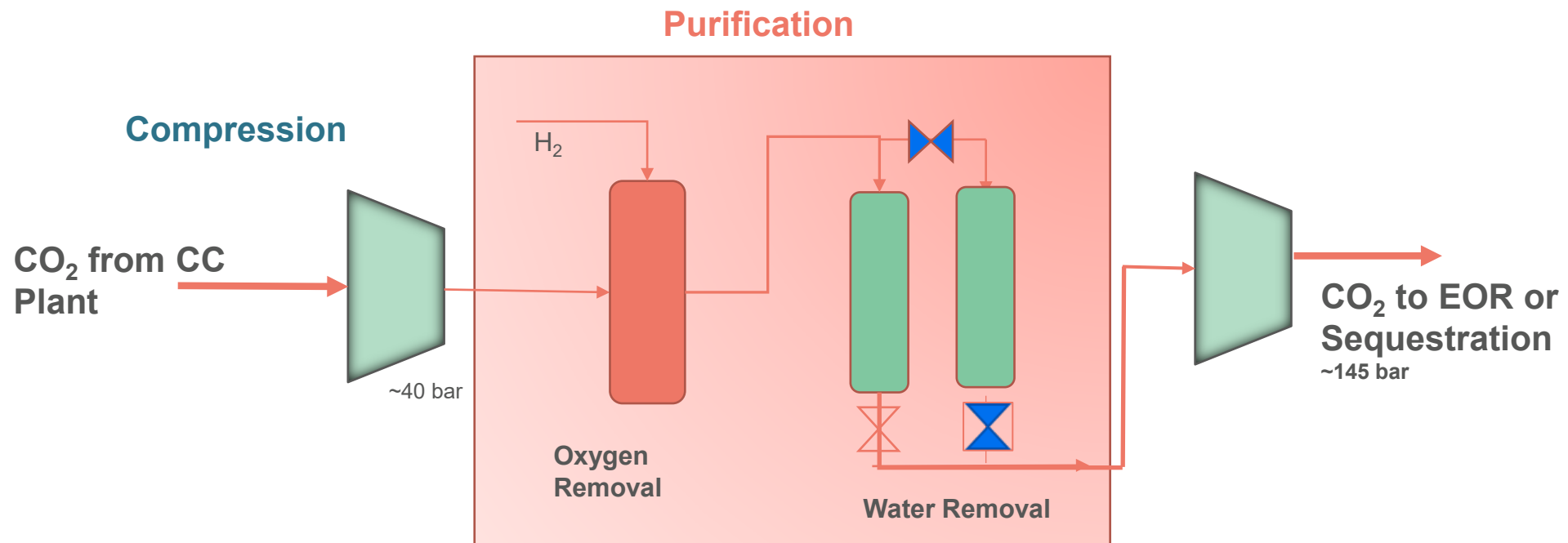
CO₂ utilization routes – front line options

- Option 1 – CO₂ to Storage/Enhanced Oil Recovery (EOR)
 - Storage of CO₂ in underground reservoir/aquifers is one the proven routes for the CO₂ captured (due to magnitude).
 - EOR: the main aim of utilizing CO₂ for EOR is to maximize oil recovery, not to store CO₂. However, by injecting CO₂ into a reservoir it is “permanently” stored as it becomes trapped in the pore space that previously held hydrocarbons.
- Option 2 – CO₂ to Bio-Methane
 - BioCH₄ : Methanation of CO₂ with green hydrogen (through electrolysis of water).
 - Catalytic conversion
 - Biological conversion (solid and liquid)
- Option 3 – CO₂ to Green Ethylene (then to polyethylene):
 - Green polyethylene through ethanol and green ethylene

CO₂ utilization routes

Option 1 – CO₂ to Storage/Enhanced Oil Recovery (EOR)

- **Process** line-up & requirements
 - The CO₂ captured in the CC plant, requires compression to ~145 bar and purification (dense phase/liquid CO₂) to be sequestered or used for EOR.

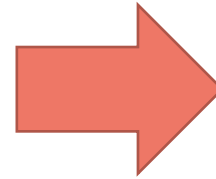


CO₂ condition for export to offshore storage

Option 1 – CO₂ to Storage/Enhanced Oil Recovery (EOR)

- Pipeline Northern Europe CO₂ Specification Contaminants list:

- SOX ≤ 10 ppmv
- NOX ≤ 10 ppmv
- CO ≤ 100 ppmv
- Amine ≤ 10 ppmv
- NH₃ ≤ 10 ppmv
- H₂ ≤ 50 ppmv
- Formaldehyde ≤ 20 ppmv
- Acetaldehyde ≤ 20 ppmv
- H₂O ≤ 30 ppmv
- O₂ ≤ 10 ppmv
- H₂S ≤ 9 ppmv
- Hg ≤ 0.03 ppmv
- Cd+Tl ≤ 0.03 ppmv



- CO₂ conditioning highlights:

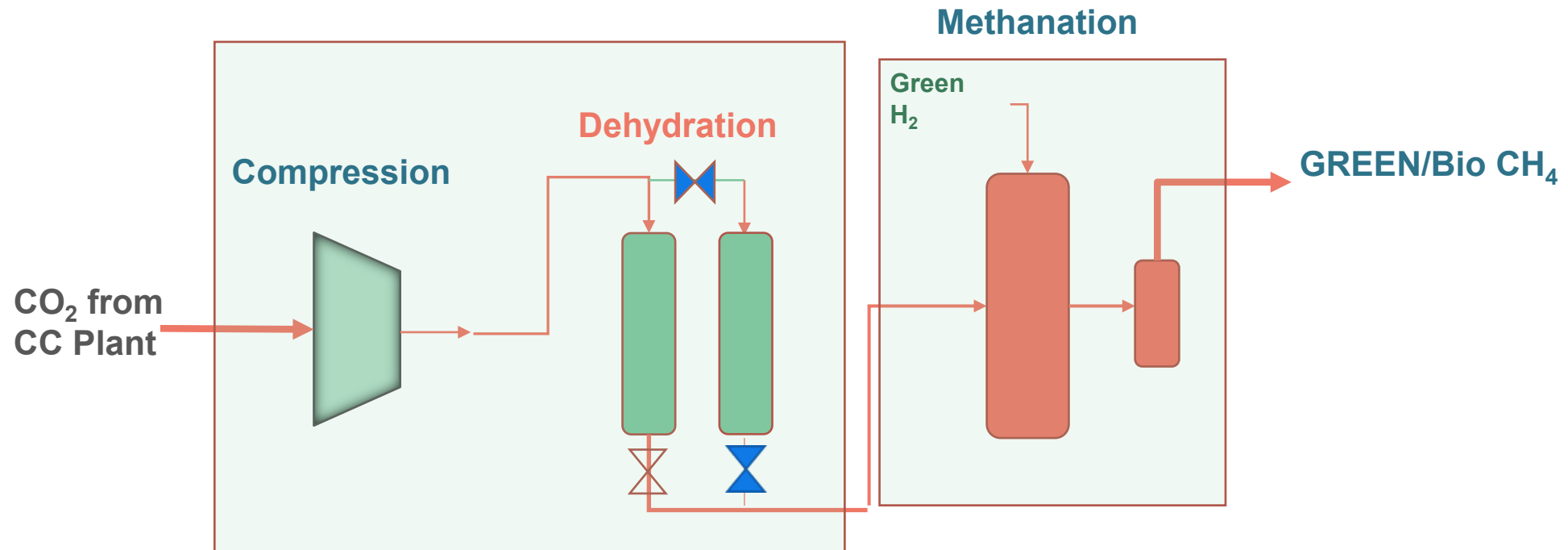
- Liquid transportation at 15 barg at -30°C to -26°C
- High pressure dense phase export up to 150 barg
- Oxygen removal with solid bed catalyst
- DeSO_x with solid bed
- CO₂ drying with molecular sieves, glycol possible for some applications
- Compression using centrifugal compressors (integrally geared compressor are generally selected)
- Non-condensables are removed in liquefaction process.
- Liquefaction: with NH₃ refrigeration cycle, alternate with cooling duty integration from cooling duty available in the complex
- Many liquefaction, compression and conditioning processes and technologies already available (use of food grade CO₂, or for fire protection systems).

CO₂ utilization routes

Option 2 – CO₂ to BioMethane (one selected case)

- **Conversion** to Bio-methane:

- The CO₂ captured in the CC plant, requires compression to 10-40 bar and dehydration* before being fed to a methanation process to obtain bio-CH₄

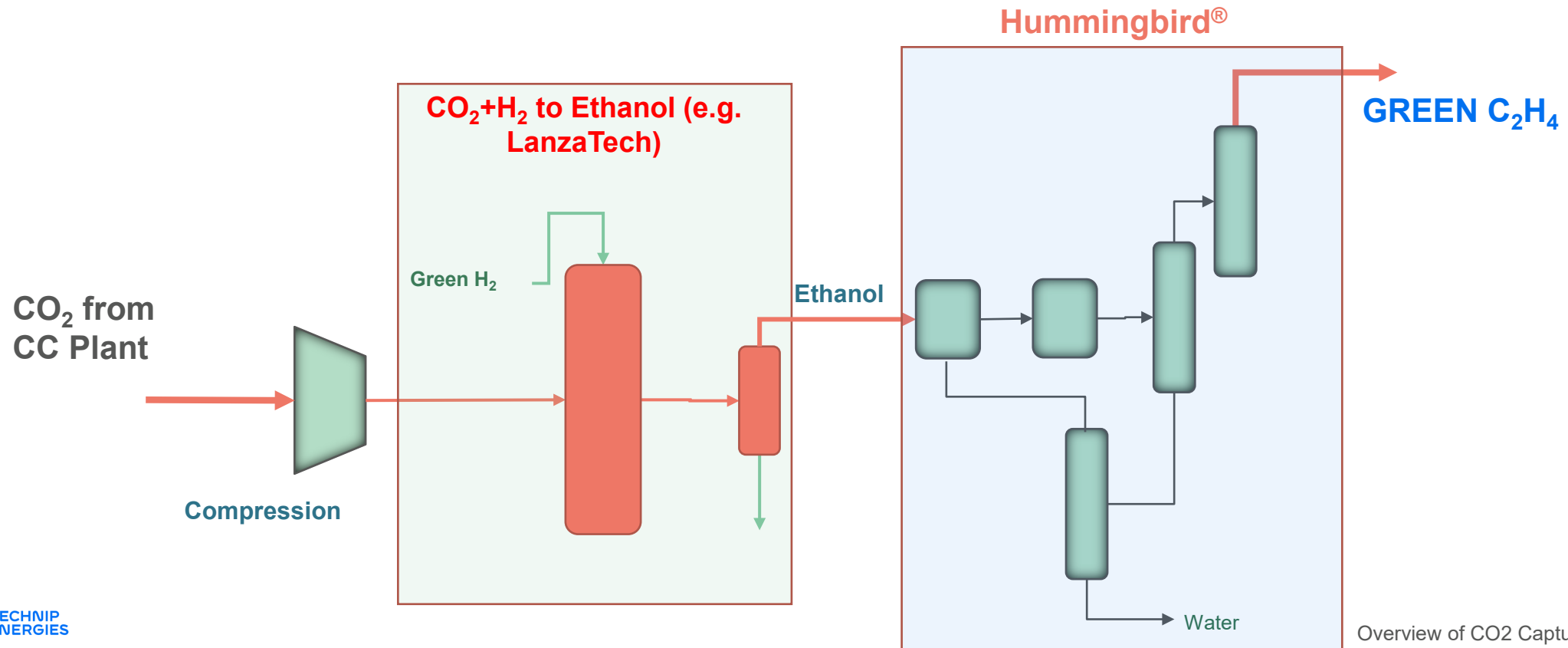


* Dehydration might be required, depends on methanation technology selection

CO₂ utilization routes

Option 3 – CO₂ to green ethylene (one selected case)

- **Conversion** to green ethylene:
 - The CO₂ captured in the CC plant is compressed to about 10 bar convert into ethanol (e.g., utilizing LanzaTech technology). This ethanol is the feed to Technip Energies' Hummingbird[®] technology to produce Green Ethylene



CO₂ utilization routes

Conversion products and utilities

Existing C ₂ H ₄ – Gas cracker plant	CO ₂ captured	
1,300 kTA Ethylene Plant 700 kTA Ethylene Plant	1 - 102.5 te/h – 0.8 MTPA (800 kTA) 2 - 47.5 te/h – 0.38 MTPA (380 kTA)	
Product		Main Utilities
Option 1: CO ₂ to Storage/Enhanced Oil Recovery (EOR)	<p style="text-align: center;">CO₂</p> 1 - 102.5 te/h – 0.8MTPA (800kTA) 2 - 47.5 te/h – 0.38MTPA (380kTA)	1 – Power: 8 MWh, Cooling Water:10,000 ton/h 2 – Power: 3.5MWh, Cooling Water: 5,000 ton/h
Option 2: CO ₂ to Bio-Methane	<p style="text-align: center;">Methane</p> 1 – 37.6 te/h - 0.3 MTPA (300 kTA) 2 – 17.4 te/h – 0.14 MTPA (139 kTA)	1 - Hydrogen: 20 ton/h 2 - Hydrogen: 10 ton/h
Option 3: CO ₂ to Green Ethylene	<p style="text-align: center;">Ethylene</p> 1 - 13.5 te/h – 0.12MTPA (120kTA)	1 – Hydrogen: 6 ton/h; Steam: 47 ton/h Power: 1.5 MWh Cooling Water: 2,000 ton/h

CO₂ utilization economics

<p>Existing C₂H₄ – Gas cracker plant</p> <p>1,300 kTA Ethylene Plant 700 kTA Ethylene Plant</p>	<p>CO₂ – Technical cost Product: CO₂</p> <p>1 – 31 \$/tonCO₂ 2 – 61 \$/tonCO₂</p>
<p>Option 1: CO₂ to Storage/Enhanced Oil Recovery (EOR)</p>	<p>Product: CO₂</p> <p>1 – 38 \$/tonCO₂ 2 – 72 \$/tonCO₂</p>
<p>Option 2: CO₂ to BioMethane</p>	<p>Product: Methane</p> <p>1 – 23 \$/tonCO₂ 2 – 82 \$/tonCO₂</p>
<p>Option 3: CO₂ to Green Ethylene (extended to 1,300kTA - capturing CO₂ will no longer cost and instead will offer a benefit of approximately \$22/tonCO₂)</p>	<p>Product: Ethylene</p> <p>2 – 32 \$/tonCO₂</p>



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Summary

Summary of CO₂ reduction techniques

Technology	CO ₂ Reduction Achievable	Surplus Fuel Gas ⁽⁴⁾	Levelized Cost of CO ₂ Removal	Estimated Date of Commercialization	Remarks
Firing Hydrogen from SMR Reforming	65-85%	No	\$50-80/tCO ₂ (Liquid Cracker), \$70-160/tCO ₂ (Gas Cracker) ⁽¹⁾⁽²⁾	Now	Requires a route to use CO ₂ , CO ₂ reduction depends on CO ₂ footprint of electricity
Firing Hydrogen from Electrolysis	0-70%	Yes	\$500/tCO ₂ (Liquid Cracker) \$1300/tCO ₂ (Gas Cracker) ⁽¹⁾⁽³⁾	Depends on progress in cost reduction and increase in size of electrolyzers	CO ₂ reduction depends on CO ₂ footprint of electricity
Oxy-Fuel Combustion	0-40% 90-95%	Maybe	CC \$20-25/tCO ₂ O ₂ breakeven @ 55% of CO ₂	Depends on application	Requires a route to use CO ₂ and O ₂ supply, CO ₂ reduction depends on CO ₂ footprint of electricity
Direct Air Capture		N/A	\$100-1000/tCO ₂ ⁽⁵⁾	Depends on progress in the development and scaling of these Technologies.	Requires a route to use CO ₂ , CO ₂ reduction depends on CO ₂ footprint of electricity
Carbon Capture and Storage / Utilization	90-95%	No	\$40-60/tCO ₂ (Liquid Cracker), \$50-80/tCO ₂ (Gas Cracker) ⁽¹⁾⁽²⁾	Now	Requires a route to use or store CO ₂ ,

Notes:

1. Compound interest (annuity method) is used to account for capital costs- 8% discount rate over 25 years of investment.
2. For options which export CO₂, any capital cost and CO₂ associated with processing or storage of the CO₂ are not included
3. Data for CAPEX and OPEX of AE electrolyzers: *DNV Technology Progress Report 2021*
4. For all cases which produce surplus fuel gas, it is assumed the fuel gas exported does not generate additional CO₂
5. IEA (2021), Direct Air Capture, IEA, Paris

Final Thoughts

- Reduction of CO₂ emissions from crackers will be a large part of the considerations for both new and existing crackers from now to 2050 and beyond
- The cost in CAPEX and OPEX of existing commercialised solutions mean that a market price (or tax credit) for CO₂ of \$40-100/tonne is required to make these solutions break even
- New solutions (such as electric cracking furnaces and the use of hydrogen from electrolysis) are not yet fully commercialised and their CO₂ reduction potential is heavily dependent on the CO₂ footprint of the electrical supply
- Some solutions mean that the fuel gas generated from the process is surplus, and needs to be processed in a way that does not add to the overall CO₂ footprint
- Developing technologies which enable CO₂ to be converted to product will provide better economics, in most cases, than storage or sequestration of the CO₂



Thank you