Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Flowsheet basics

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Contents

Flowsheet overview

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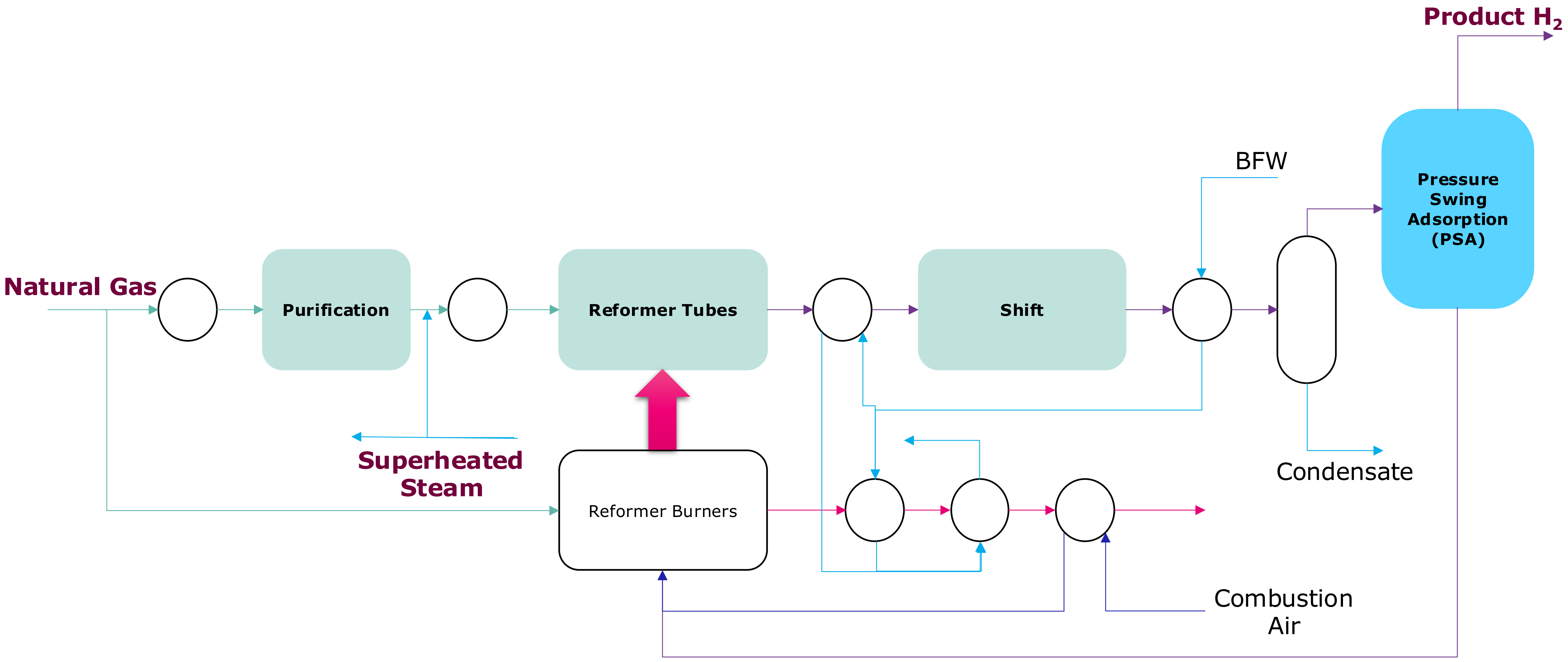
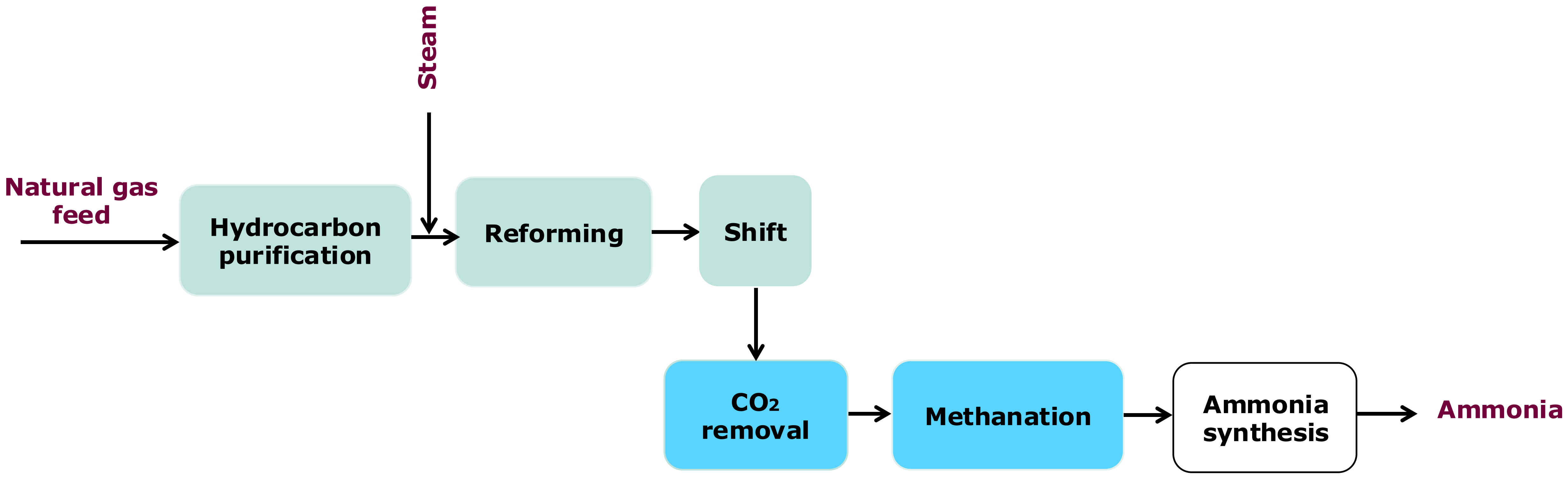
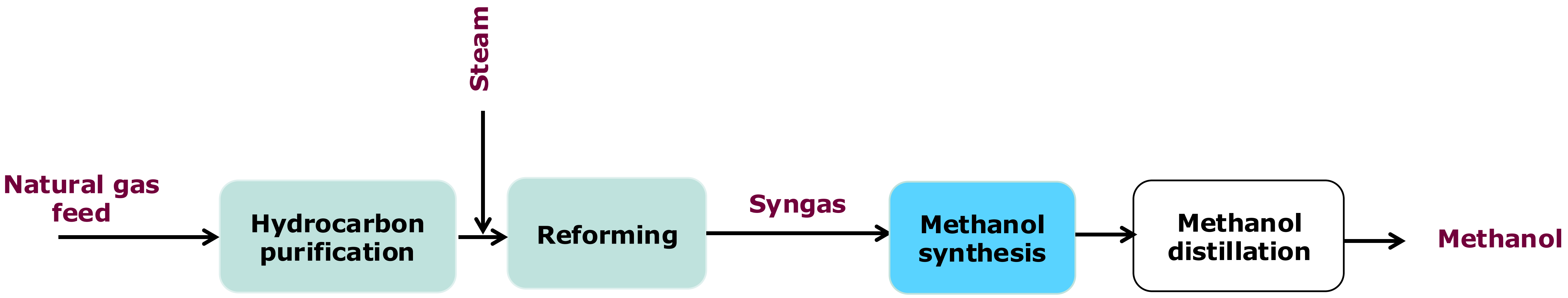
Hydrogen flowsheet



Ammonia flowsheet



Methanol flowsheet

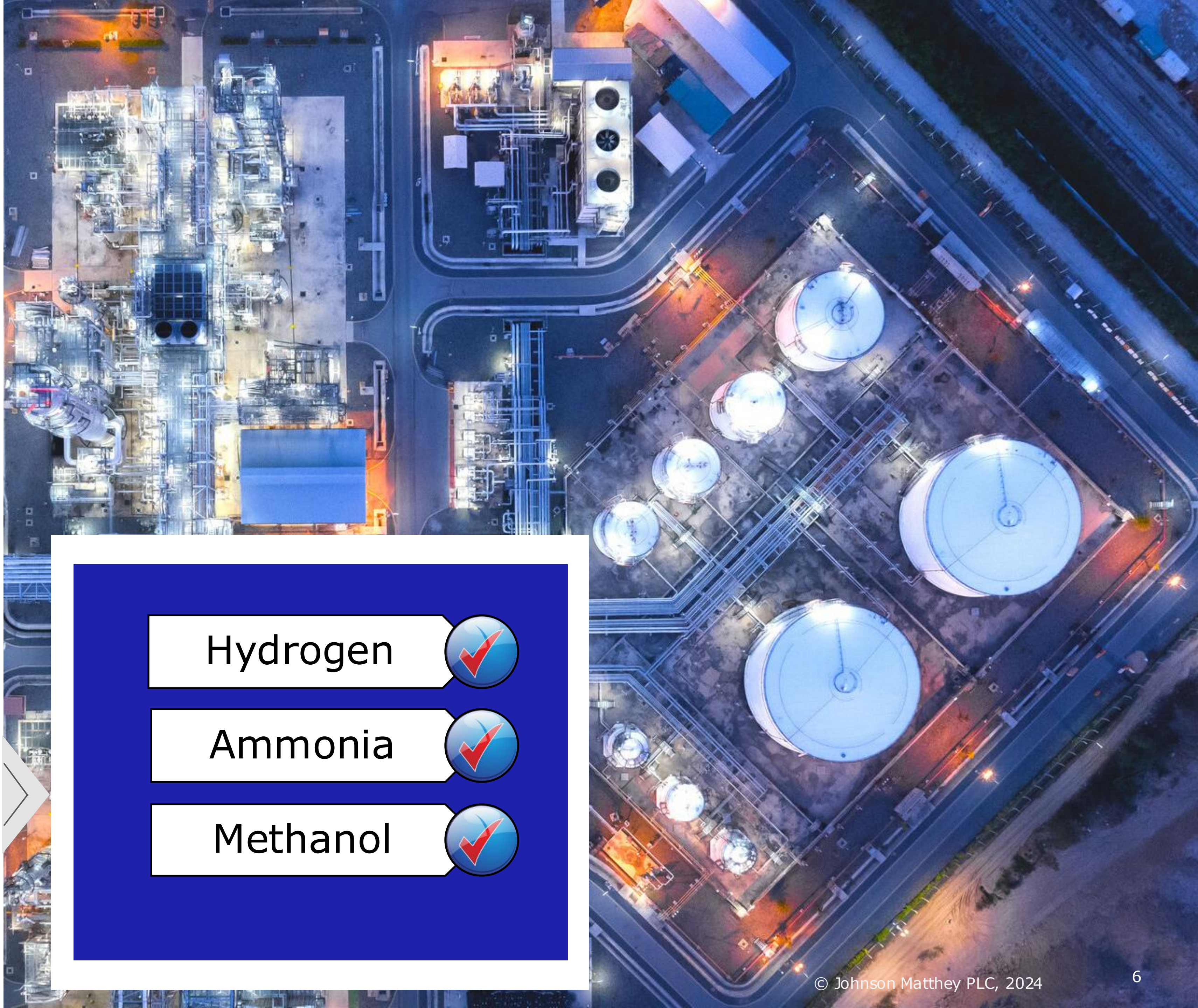


Purification

Function:

1. Converts organics
2. Absorbs impurities
3. Protects downstream catalysts

Technology used



- Hydrogen ✓
- Ammonia ✓
- Methanol ✓

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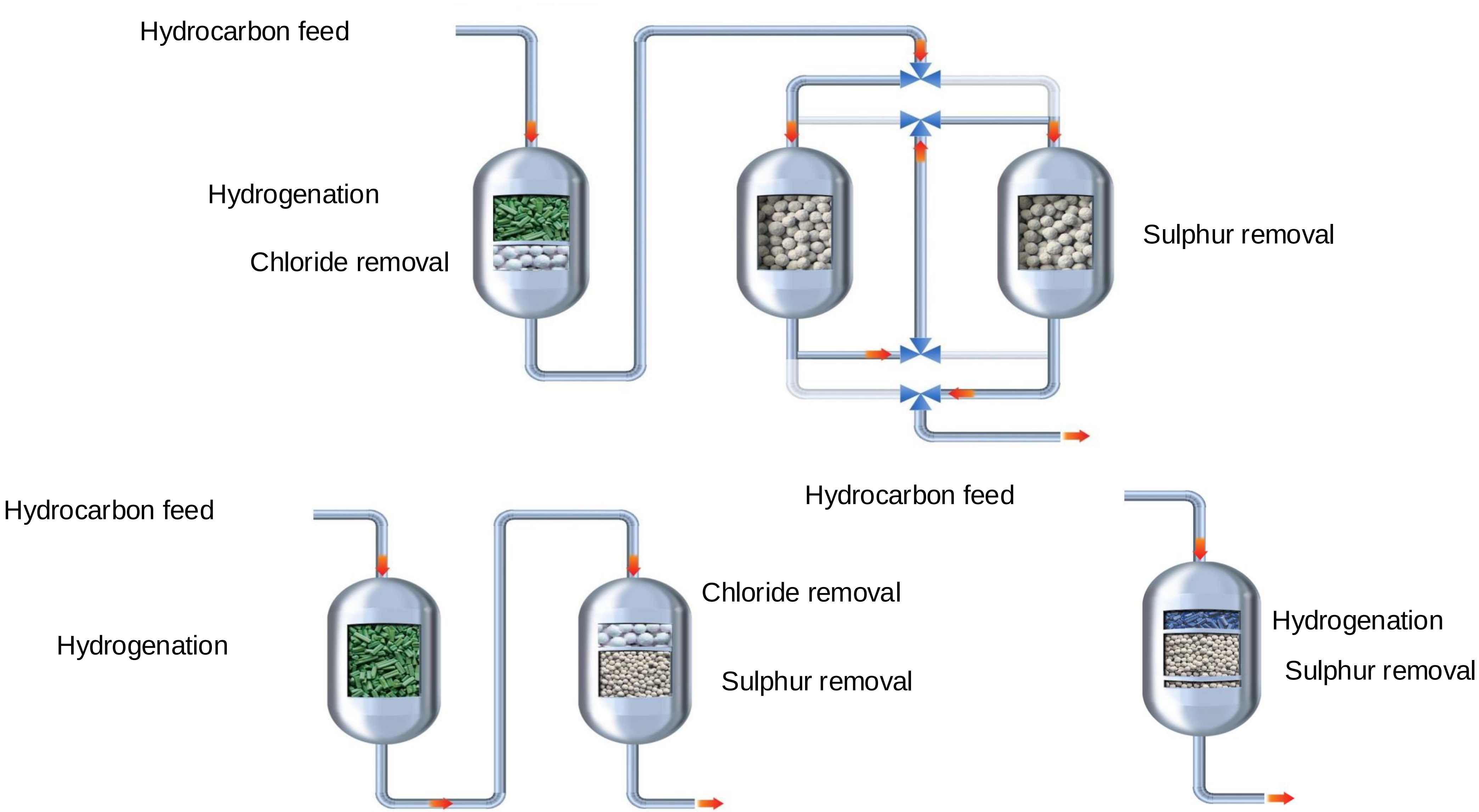
Purification – Possible layouts



Purification - Differences

Hydrogen

- Variety of feeds
- Removal of impurities including olefins for ROG or light naphtha feed

Ammonia

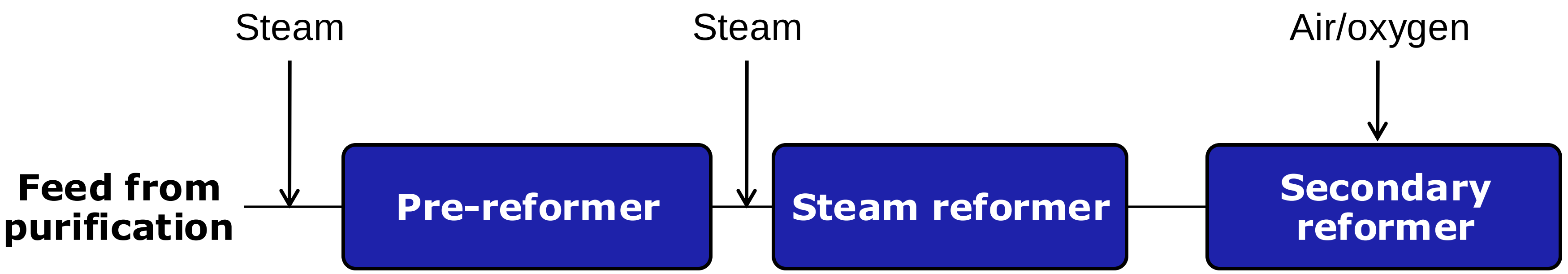
- Typically NG feed
- Recycle from syn loop
- Pressure drop importance
- Downstream CuZn protection

Methanol

- Typically NG feed
- Downstream CuZn protection

Operating conditions generally the same

Steam reforming



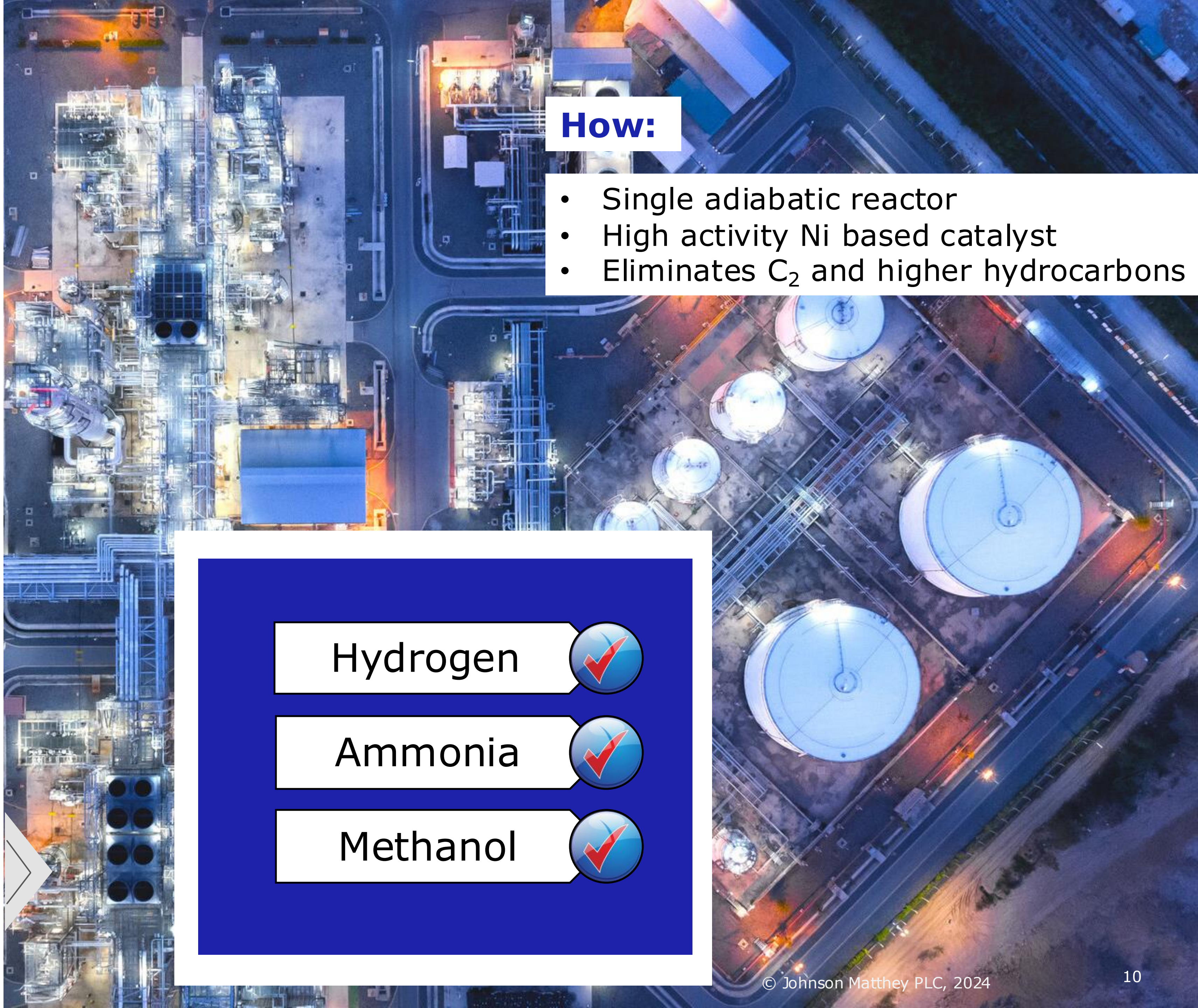
Hydrogen	Optional	✔	Rare
Ammonia	Optional	✔	✔
Methanol	Optional	✔	Sometimes

Pre-reformer

Function:

1. Convert hydrocarbons to CH_4, CO, CO_2 and H_2
2. Feedstock flexibility
3. Reduction of SMR size and fuel and emissions
4. Revamp to increase hydrogen production

Technology used

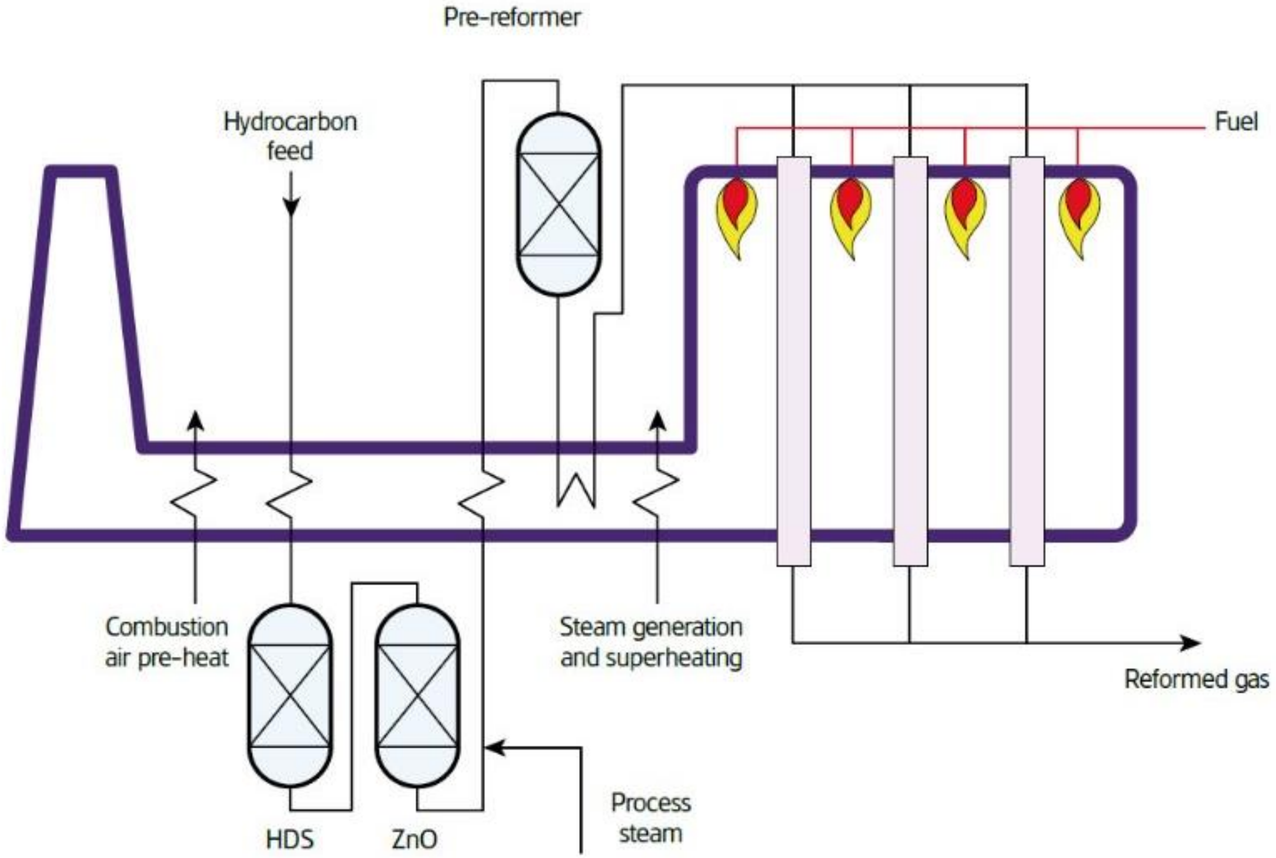


How:

- Single adiabatic reactor
- High activity Ni based catalyst
- Eliminates C_2 and higher hydrocarbons

- Hydrogen ✓
- Ammonia ✓
- Methanol ✓

Pre-reformer



Pre-reformer - Differences

Hydrogen

- Feed stock flexibility including naphtha feeds
- Increased hydrogen production
- Prolonged reformer life

Ammonia

- Feed stock flexibility
- Increased plant rate
- Prolonged reformer life
- Use of larger primary reformer catalyst for reduction in pressure drop

Methanol

- Feed stock flexibility
- Increased plant rate
- Prolonged reformer life
- Use of larger primary reformer catalyst for reduction in pressure drop

Heat is integrated with primary reformer

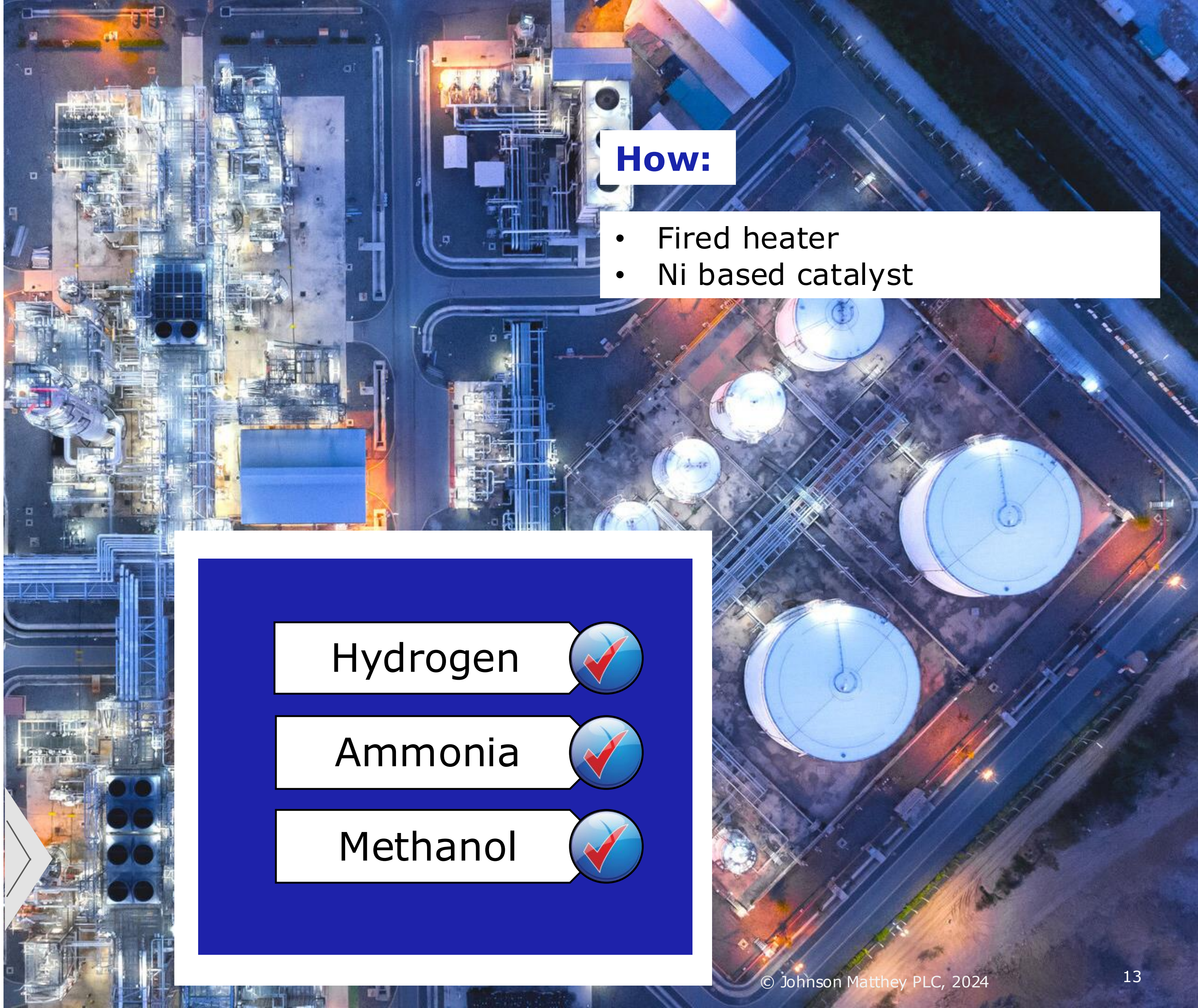
Primary reformer

Function:

1 Convert hydrocarbons to CH_4, CO, CO_2 and H_2

2 Generate hydrogen

Technology used



How:

- Fired heater
- Ni based catalyst

Hydrogen ✓

Ammonia ✓

Methanol ✓

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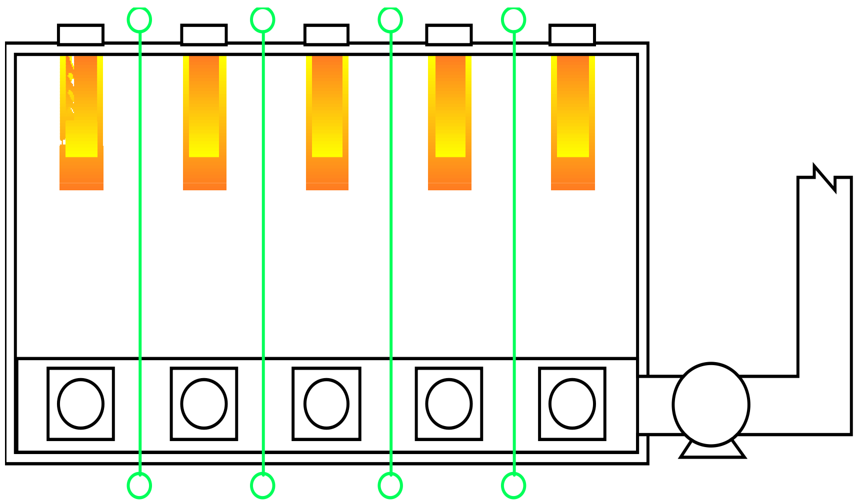
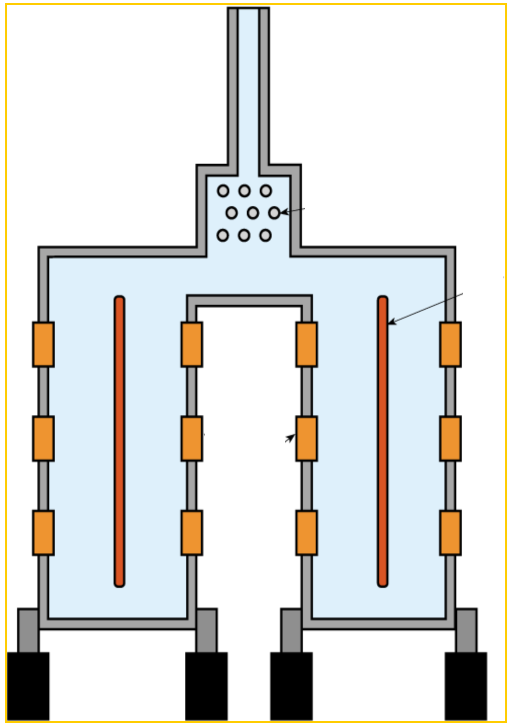
Primary reforming – Various technologies

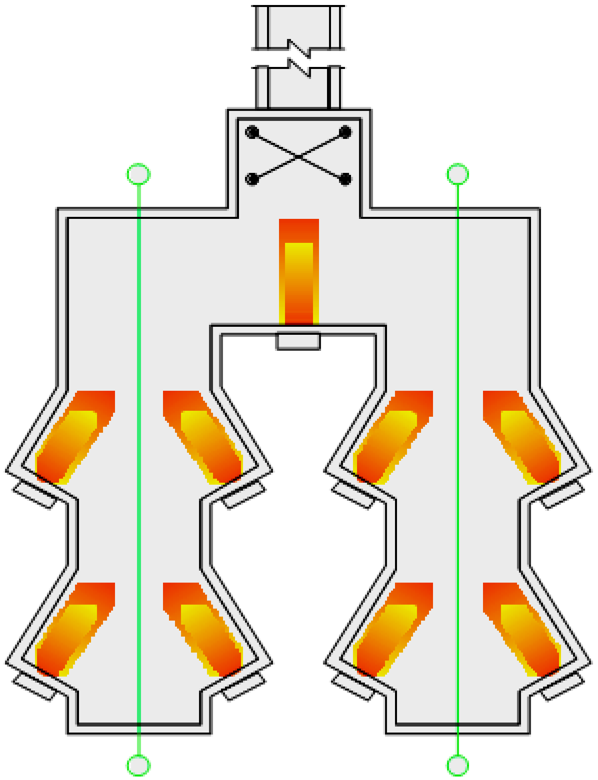
Top fired

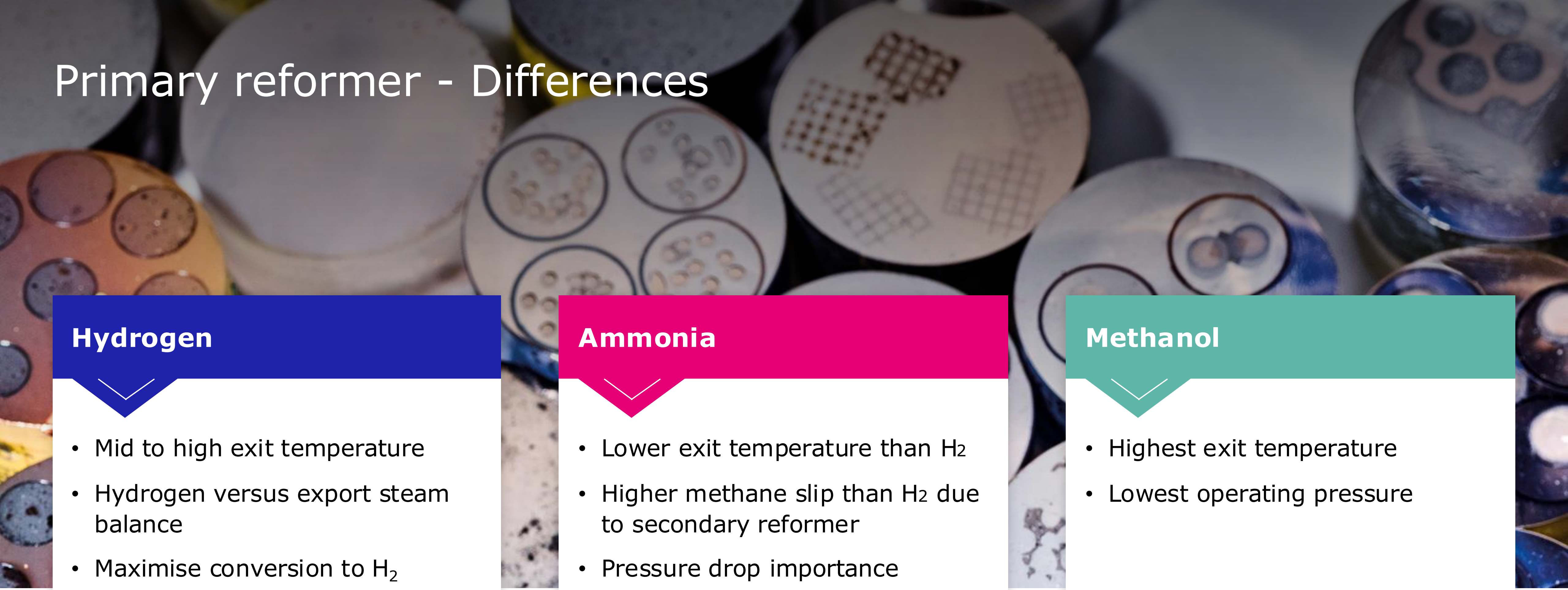


Side fired



Terrace wall





Primary reformer - Differences

Hydrogen

- Mid to high exit temperature
- Hydrogen versus export steam balance
- Maximise conversion to H_2

Ammonia

- Lower exit temperature than H_2
- Higher methane slip than H_2 due to secondary reformer
- Pressure drop importance
- Above design production

Methanol

- Highest exit temperature
- Lowest operating pressure

S:C set by feed carbon number or downstream units for hydrogen and ammonia: HTS / CO_2 removal

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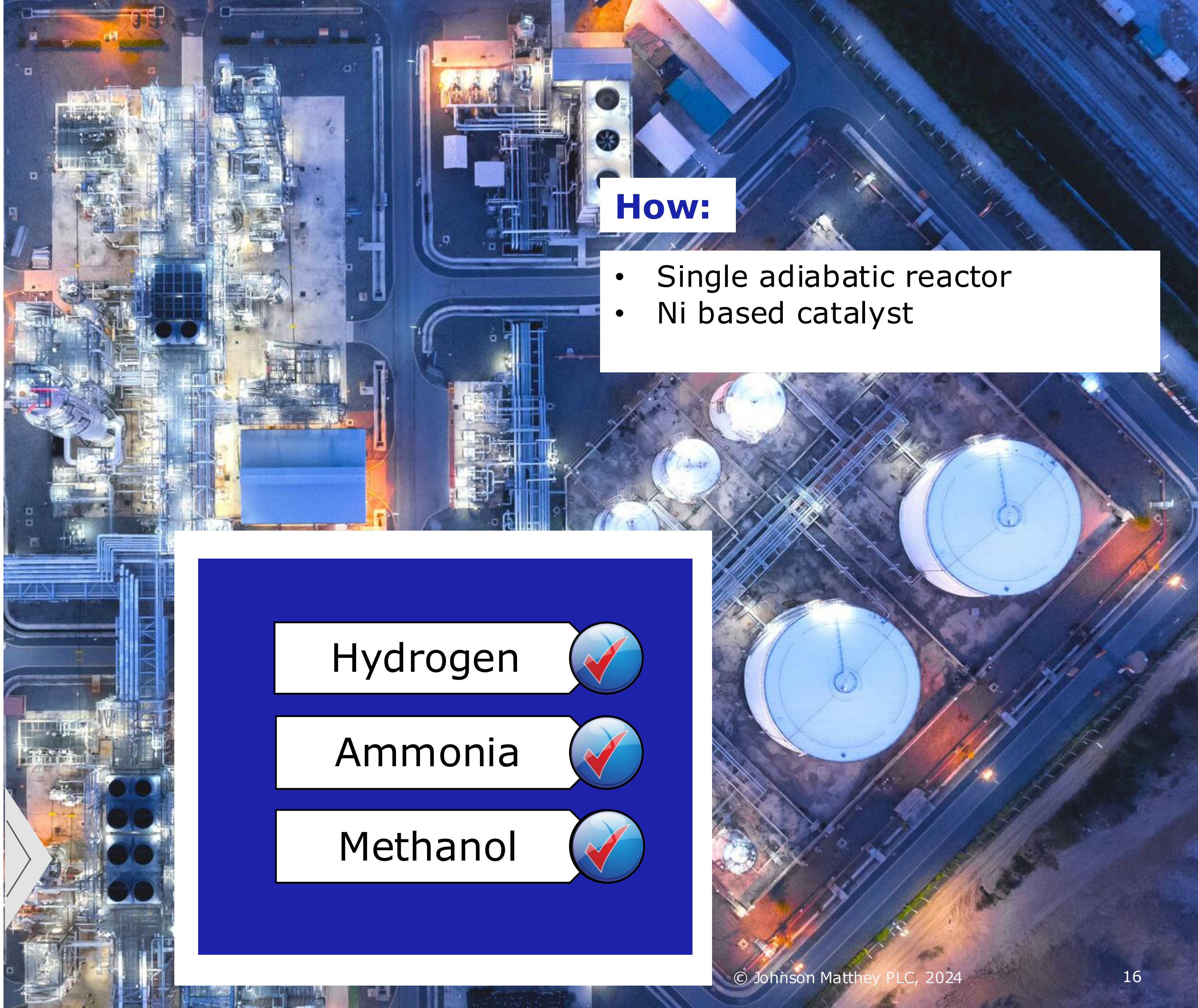
Secondary reformer

Function:

1. Convert hydrocarbons to CH_4, CO, CO_2 and H_2
2. Heat of reaction supplied by combustion

Technology used



How:

- Single adiabatic reactor
- Ni based catalyst

- Hydrogen ✓
- Ammonia ✓
- Methanol ✓

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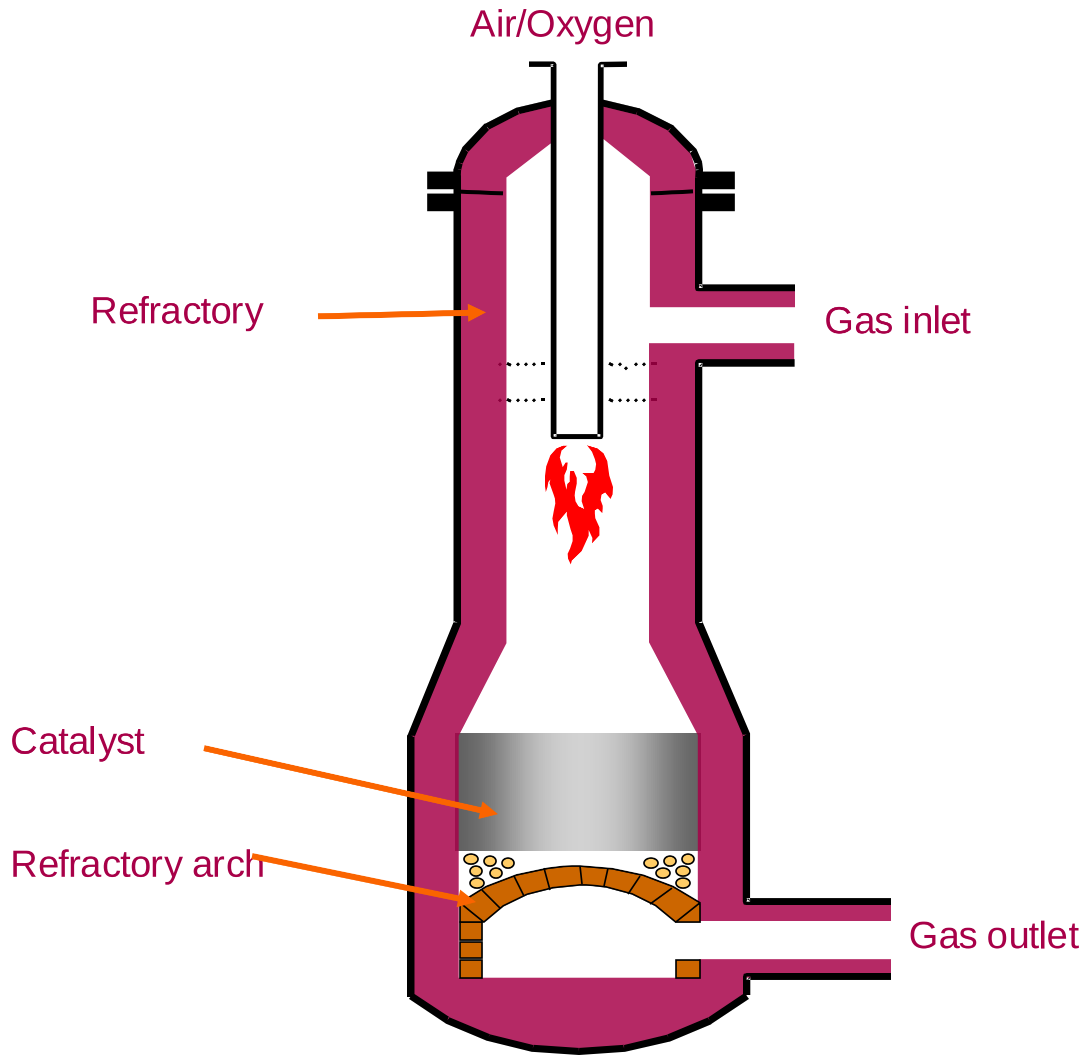
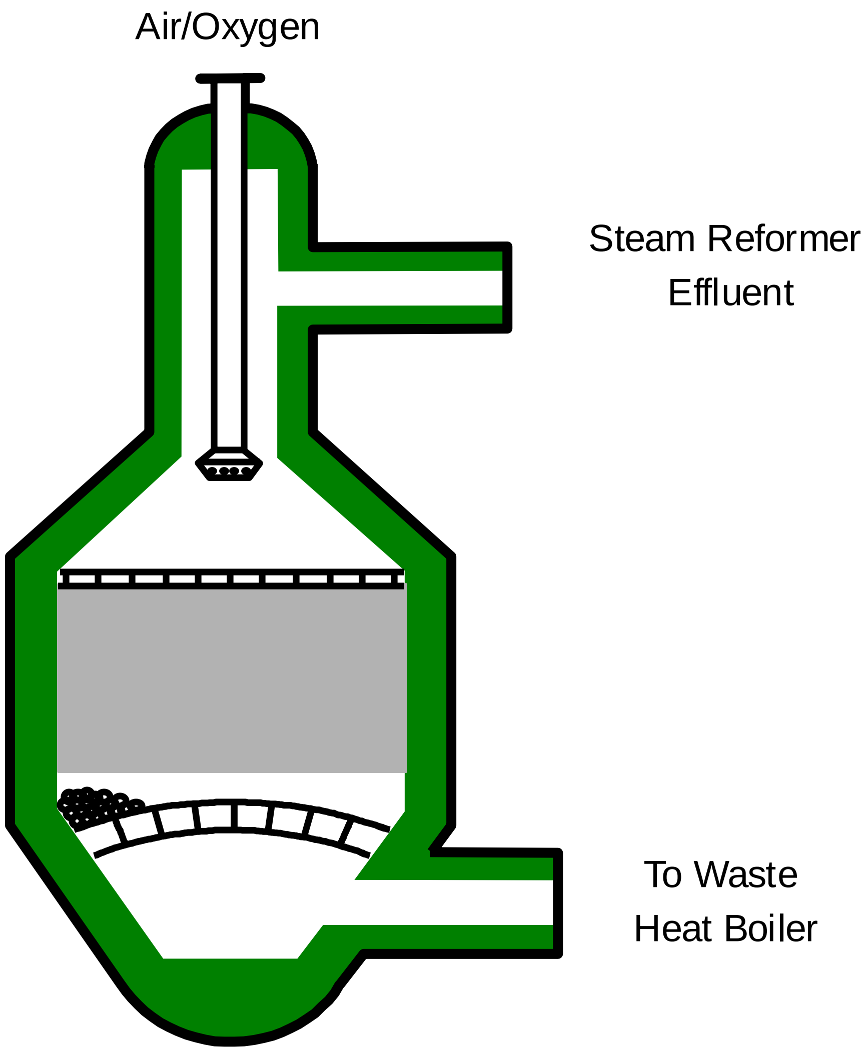
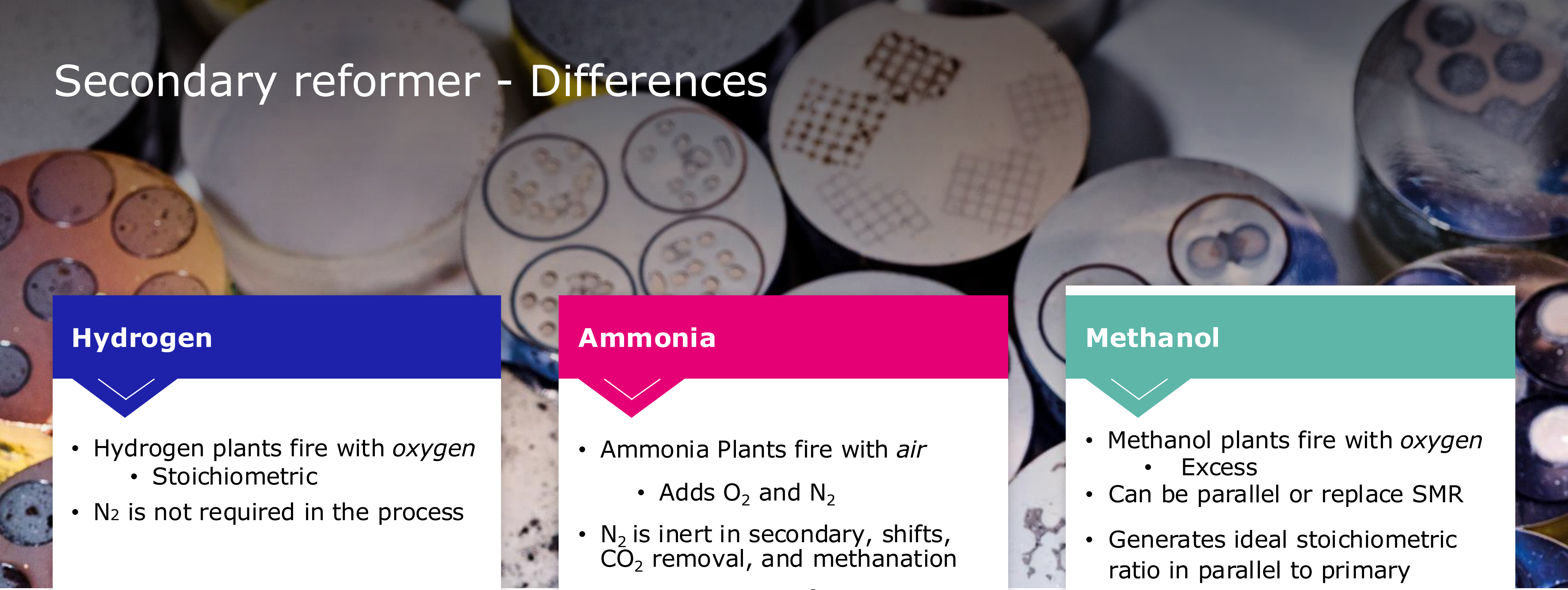
Secondary reformers







Secondary reformer - Differences

Hydrogen

- Hydrogen plants fire with *oxygen*
    - Stoichiometric
- N_2 is not required in the process

Ammonia

- Ammonia Plants fire with *air*
    - Adds O_2 and N_2
- N_2 is inert in secondary, shifts, CO_2 removal, and methanation
- N_2 injection point for NH_3 synthesis

Methanol

- Methanol plants fire with *oxygen*
    - Excess
- Can be parallel or replace SMR
- Generates ideal stoichiometric ratio in parallel to primary
- Lower carbon intensity than SMR

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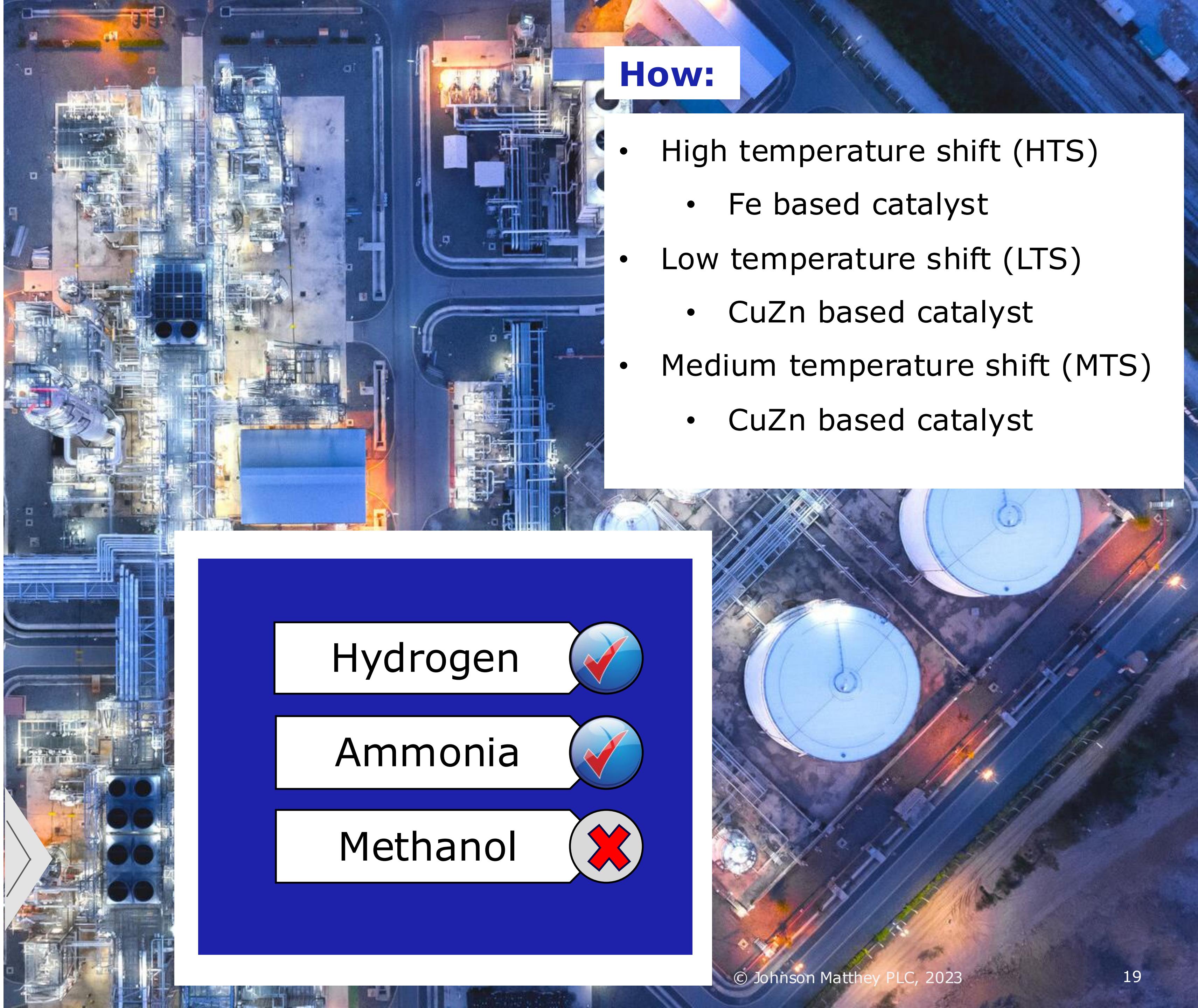
Shift

Function:

1. Convert CO to CO_2
2. Increase H_2 make

Technology used



How:

- High temperature shift (HTS)
  - Fe based catalyst
- Low temperature shift (LTS)
  - CuZn based catalyst
- Medium temperature shift (MTS)
  - CuZn based catalyst

Hydrogen ✓

Ammonia ✓

Methanol ✗

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Shift

High temperature shift (HTS)

Low temperature shift (LTS)

Medium temperature shift MTS)

Each technology has different:

- Operating temperatures
- Resistance to poisoning
- Expected life
- Catalyst reduction and start-up procedures

High temperature shift - Differences

Hydrogen

- Mid to high exit temperature
- Hydrogen versus export steam balance
- Convert CO to CO_2 for easier removal
- CO slip dictated by PSA

Ammonia

- Higher inlet and exit temperature
- DP growth rate importance
- Above design rate operations
- Improved efficiency of downstream reactions
- Steam start up typical

Methanol

- N/A

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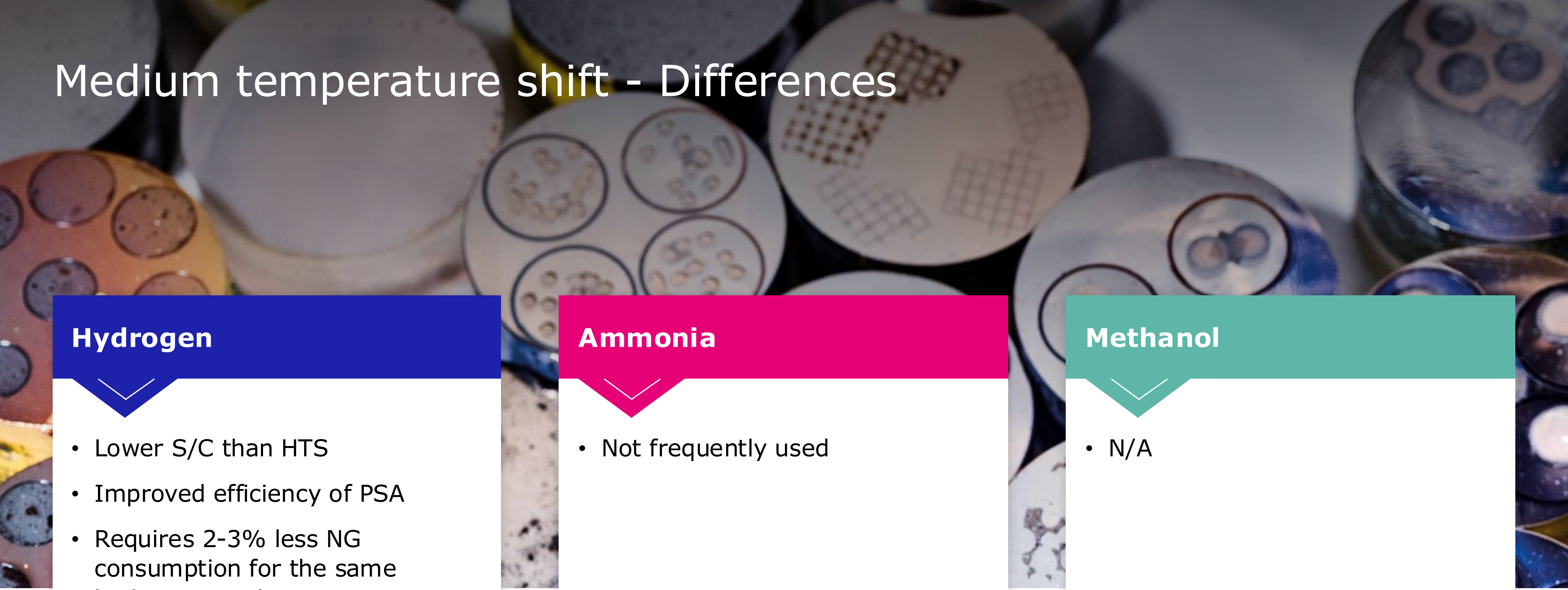

Medium temperature shift - Differences

Hydrogen

- Lower S/C than HTS
- Improved efficiency of PSA
- Requires 2-3% less NG consumption for the same hydrogen production

Ammonia

- Not frequently used

Methanol

- N/A

Preferred for low S/C flowsheets

Low temperature shift - Differences

Hydrogen

- Generation of more H_2
- Polishing step for CO conversion to CO_2

Ammonia

- Polishing step for CO conversion to CO_2
- Generation of more H_2

Methanol

- N/A

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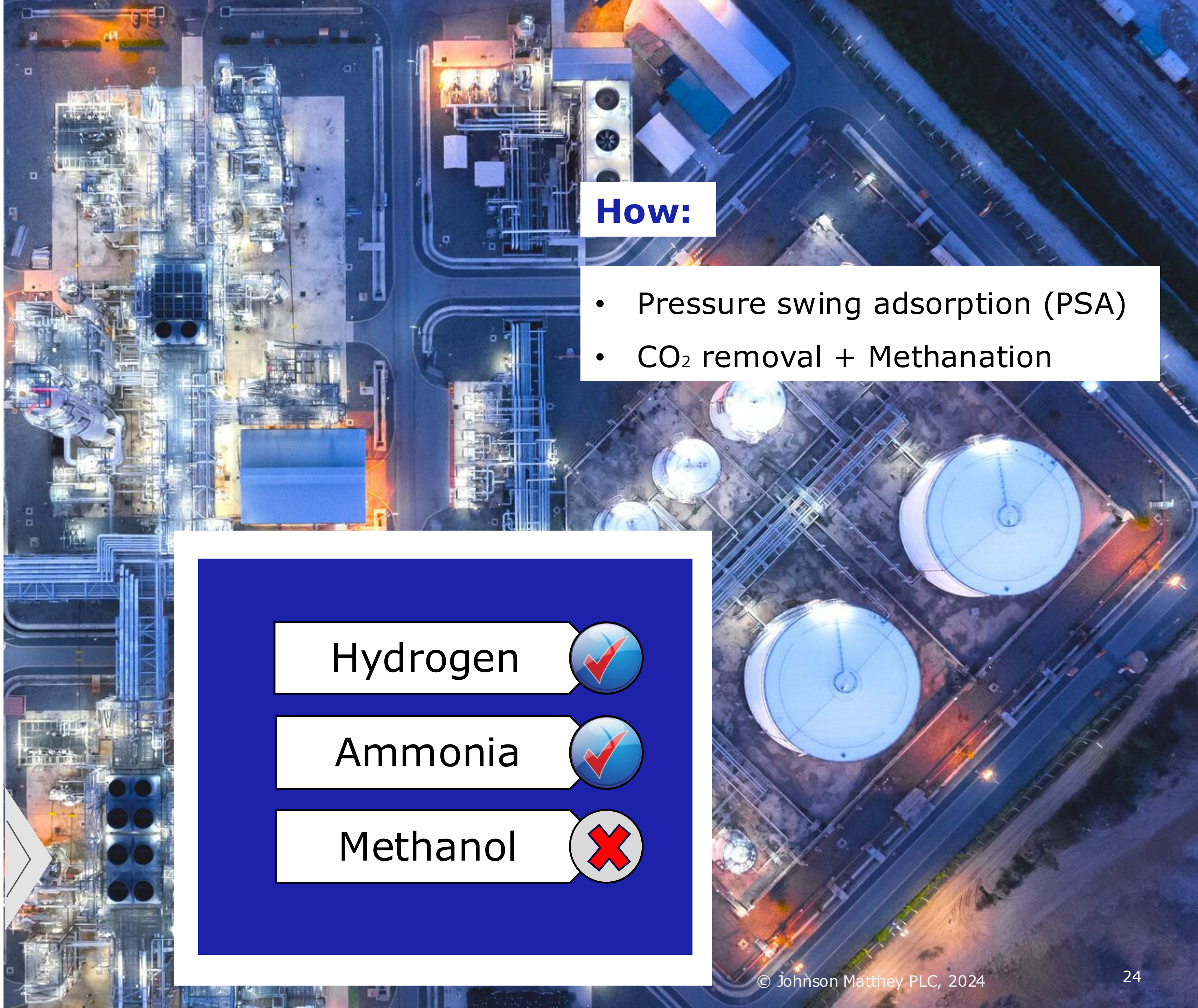
Hydrogen purification

Function:

1. Produce high purity hydrogen
2. Increase H_2 make
3. Convert CO to CO_2

Technology used

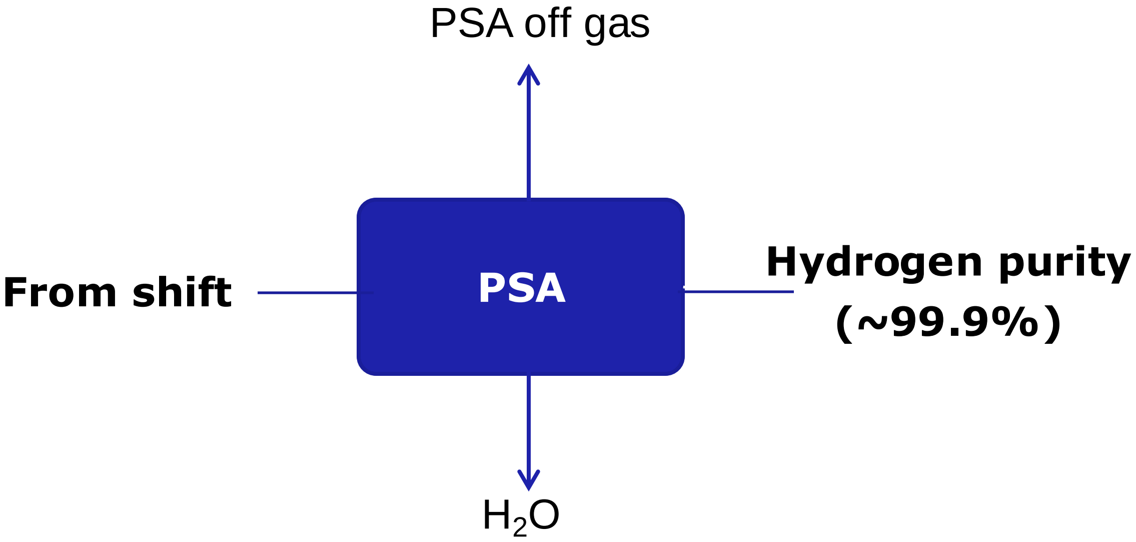


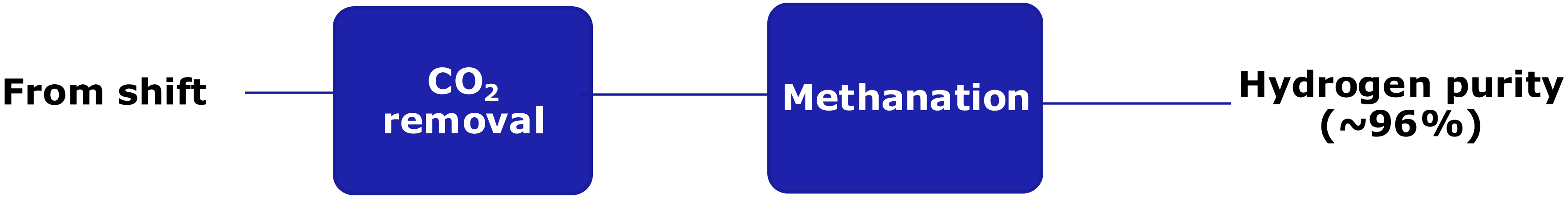
How:

- Pressure swing adsorption (PSA)
- CO_2 removal + Methanation

- Hydrogen ✓
- Ammonia ✓
- Methanol ✗

Hydrogen purification





Hydrogen purification- Differences

Hydrogen

- PSA generally used
- Production high purity hydrogen product

Ammonia

- Methanation generally used
- Protection of NH_3 syn catalyst by converting CO and CO_2 (poisons) to CH_4

Methanol

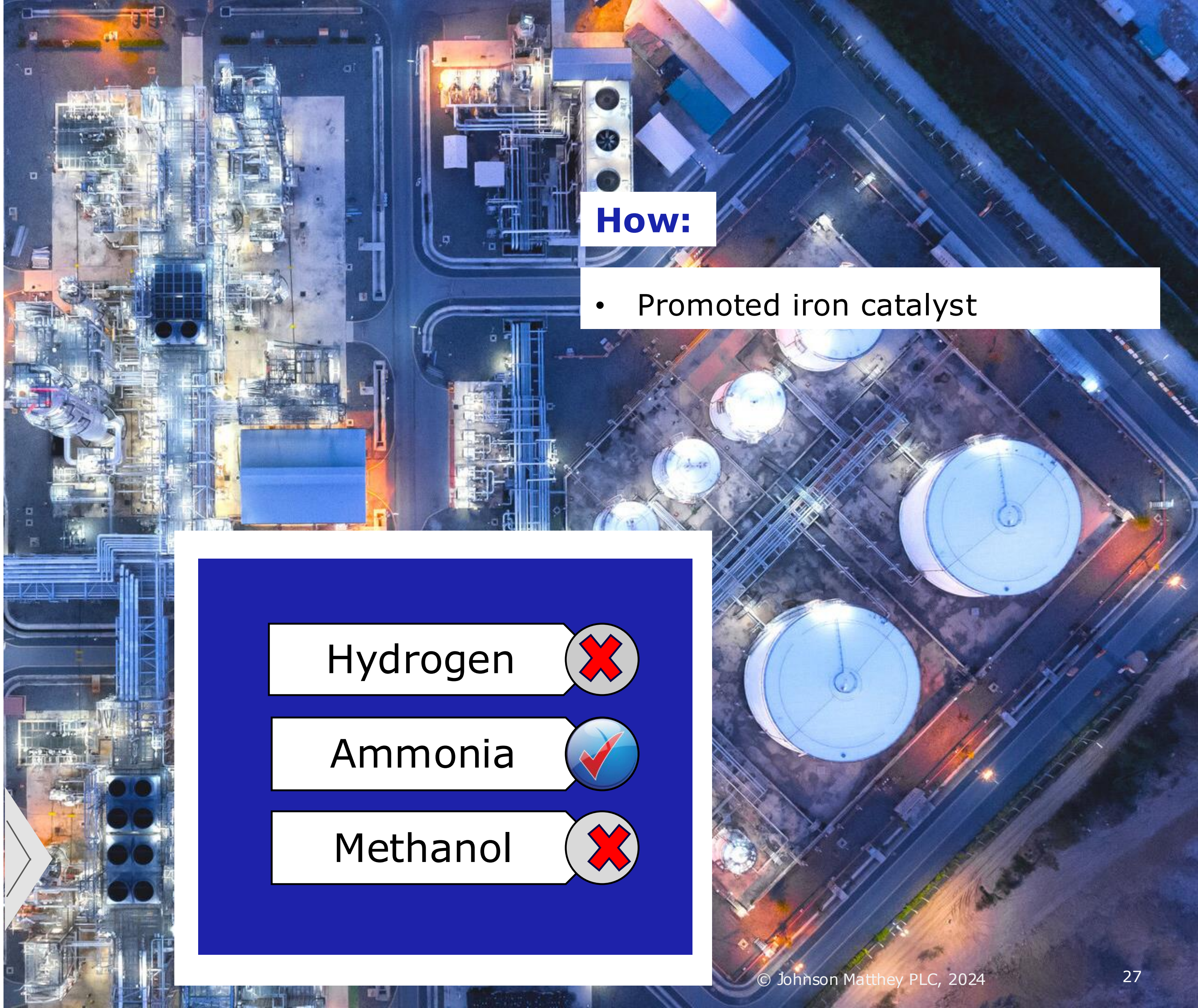
- N/A

Ammonia synthesis

Function:

1 Convert H_2 and N_2 (3:1) into ammonia in a high-pressure loop

Technology used



How:

- Promoted iron catalyst

Hydrogen ✗

Ammonia ✓

Methanol ✗

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Operating conditions

Possible unit operations	JM material?	Hydrogen operating temperature °F (°C)	Hydrogen operating pressure psig (barg)	Ammonia operating temperature °F (°C)	Ammonia operating pressure psig (barg)
Purification	Yes	302-752 (150 – 400)	290-435 (20 – 30)	302-752 (150 – 400)	290-580 (20 – 40)
Pre-reformer	Yes	842-932 (450 – 500)		842-932 (450 – 500)	
Steam reformer	Yes	Inlet: 842- 1202 (450 – 650) Outlet: 1382- 1562 (750 – 850)		Inlet: 842- 1202 (450 – 650) Outlet: 1292-1562 (700 – 850)	
Secondary reformer	Yes			Inlet: 1292-1562 (700 – 850) Outlet: 1652-1832 (900 – 1000)	
High temperature shift	Yes	608-662 (320 – 350)		644-716 (340 – 380)	
Low temperature shift	Yes	392 (200)		392 (200)	
CO_2 removal	No	176 (80)		176 (80)	
Methanation	Yes	482-662 (250 – 350)		482-662 (250 – 350)	
Ammonia synthesis	Yes			**662-968 (350 – 520)**	**1160-5076 (80 – 350)**

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Key reactions

Purification:	Organic sulphur + $H_2 \leftrightarrow H_2S$ + Hydrocarbon
	$RCl + H_2 \leftrightarrow HCl + RH$
Reforming:	$CH_4 + H_2O \leftrightarrow CO + 3H_2$ (ΔH = +206 kJ/mol)
Water gas shift:	$CO + H_2O \leftrightarrow CO_2 + H_2$ (ΔH = -41 kJ/mol)
Combustion:	$2H_2 + O_2 \rightarrow 2H_2O$
	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Methanation:	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ (ΔH = -206 kJ/mol)
	$CO_2 + 4H_2 \leftrightarrow CH_4\ 2H_2O$ (ΔH = -165 kJ/mol
Methanol synthesis:	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ (ΔH = -50 kJ/mol)
Ammonia synthesis:	$N_2 + 3H_2 \leftrightarrow 2NH_3$ (ΔH = -92 kJ/mol)


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