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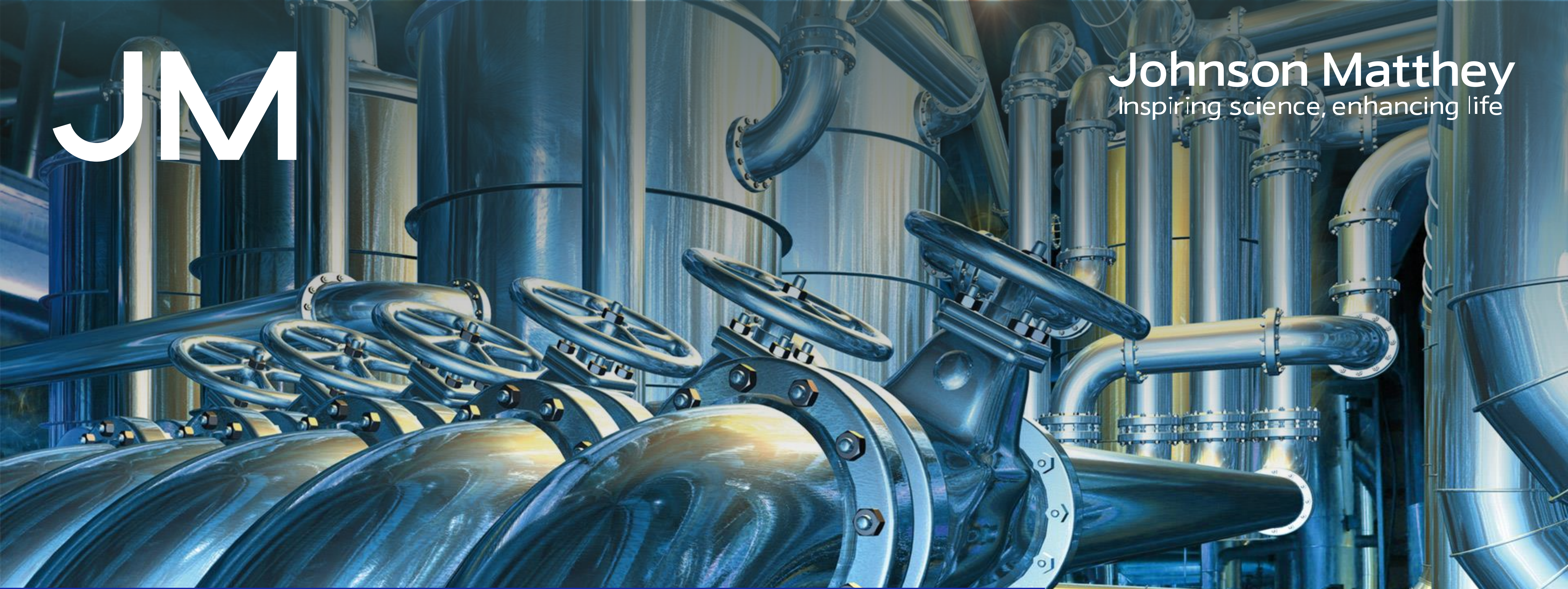
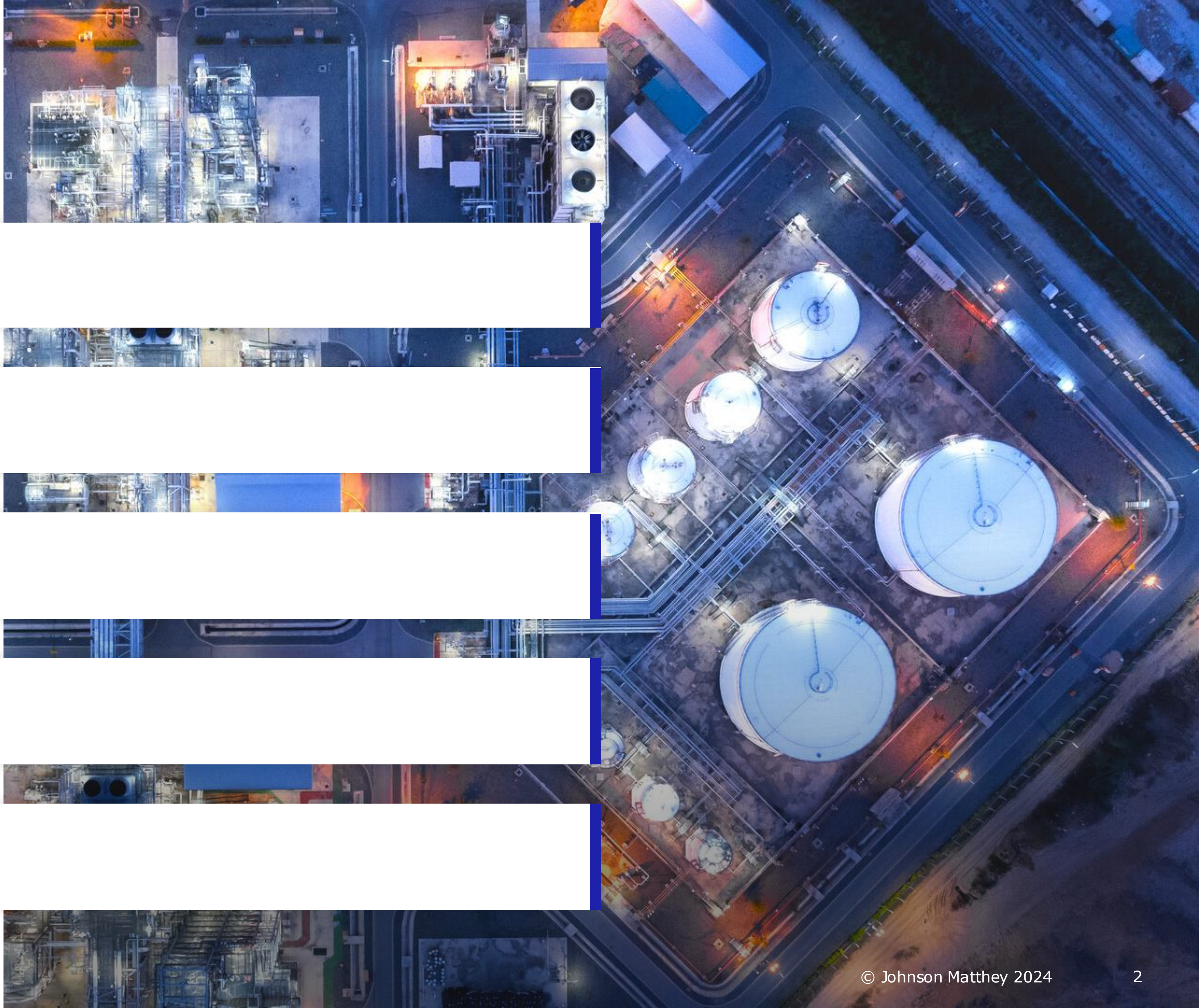


Americas hydrogen and syngas technical training seminar

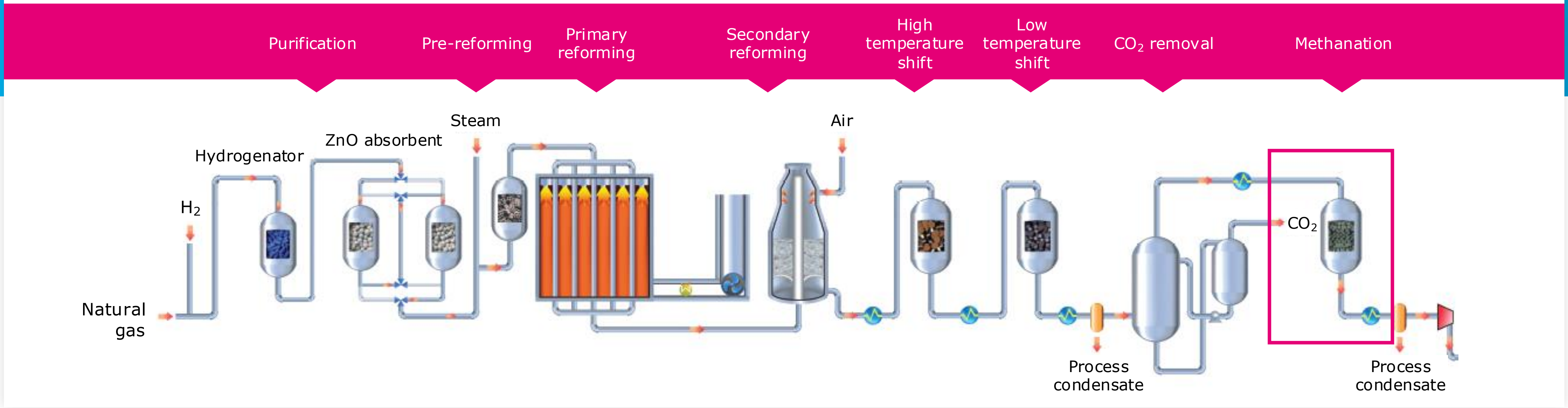
Methanation fundamentals

Ibrahim Tabanjah

Contents



Introduction



COx needs to be reduced to single figure ppm levels to avoid

1. Poisoning ammonia synthesis catalyst (throughput)
2. Forming ammonium carbamate (safety, downtime)
3. Freezing out in cold boxes (downtime, throughput)

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Methanation chemistry

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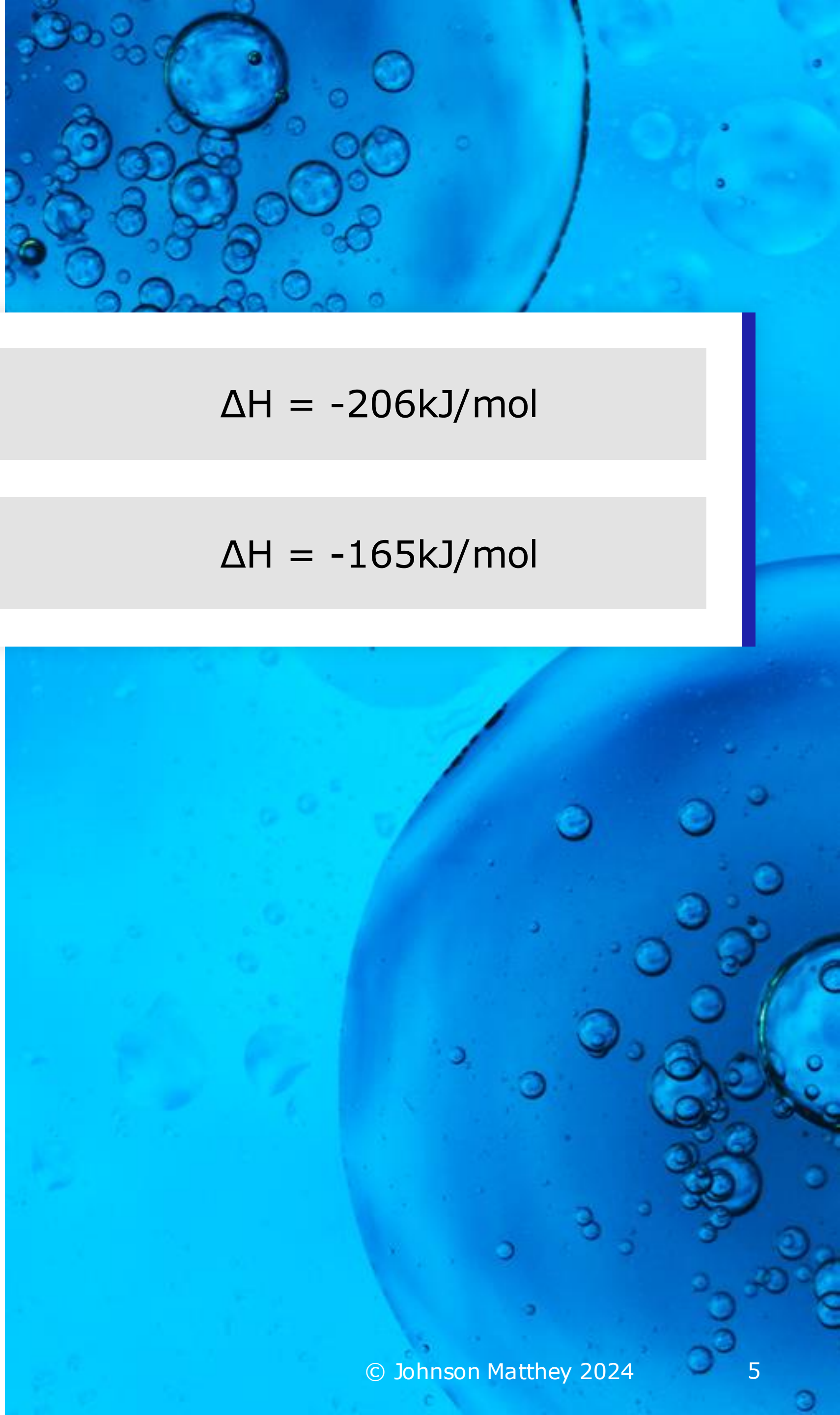
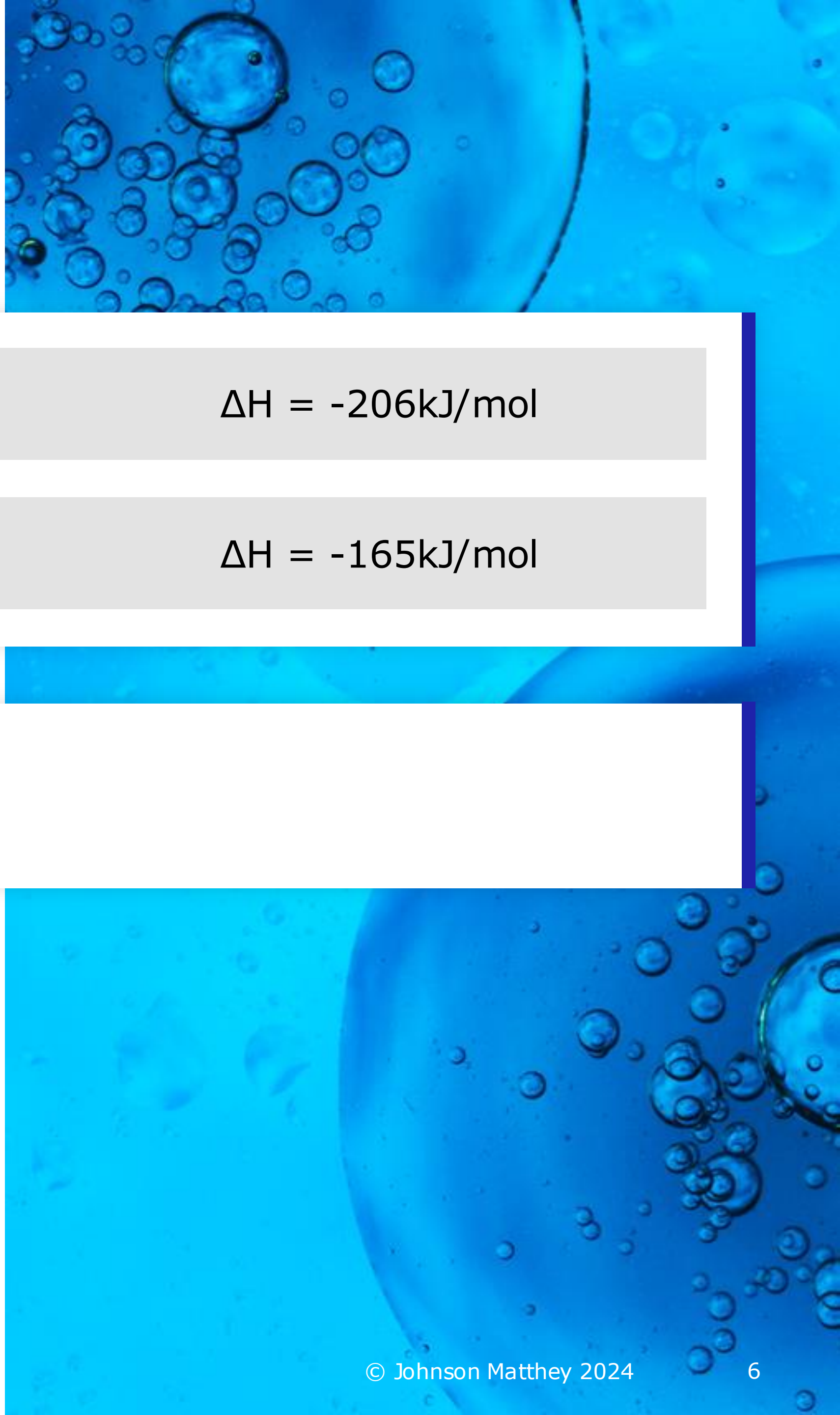
Theoretical aspects



Methanation reactions are strongly exothermic (and consume a lot of hydrogen!)

$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$\Delta H = -206 kJ/mol$
$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	$\Delta H = -165 kJ/mol$

Theoretical aspects



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Temperature rise

- 74°C (133°F) for each 1% of CO converted
- 60°C (108°F) for each 1% of CO_2 converted

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Temperature rise

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Conversion is not equilibrium limited, governed by kinetics

- CO is methanated first
- CO_2 only reacts when CO concentration is 200-300 ppm
- Methanation of CO_2 is a two-stage reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

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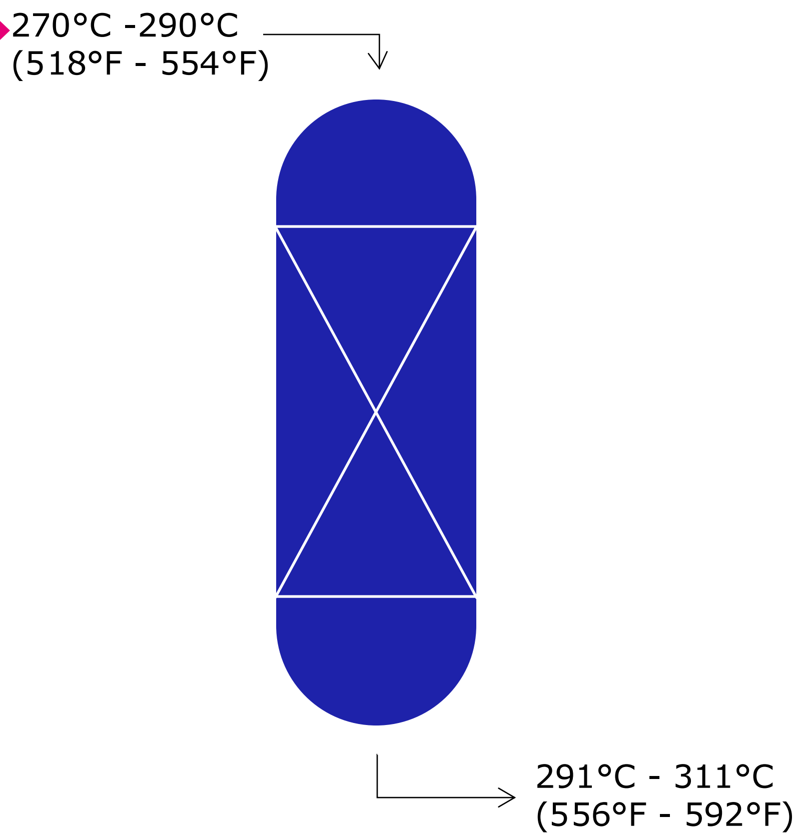
Typical process conditions

Inlet composition (%)	
CO	0.2
CO_2	0.1
H_2	93.9
CH_4	3.3
H_2O	2.5



Outlet composition (%)	
CO	<5 ppmv
CO_2	<5 ppmv
H_2	93.5
CH_4	3.6
H_2O	2.9

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Methanation reaction

Good methanation catalyst will demonstrate

1

High conversion

COx slip <5ppm standard, 1-2 ppm common

2

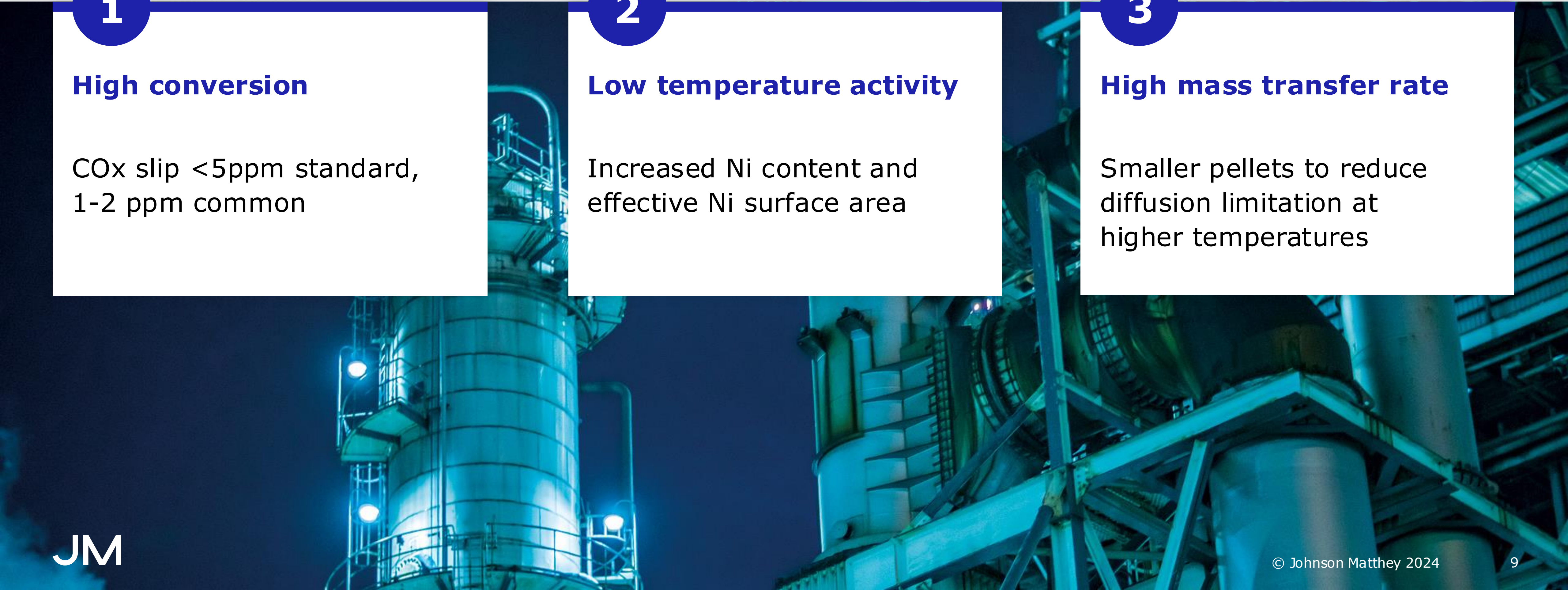
Low temperature activity

Increased Ni content and effective Ni surface area

3

High mass transfer rate

Smaller pellets to reduce diffusion limitation at higher temperatures



Reaction zones

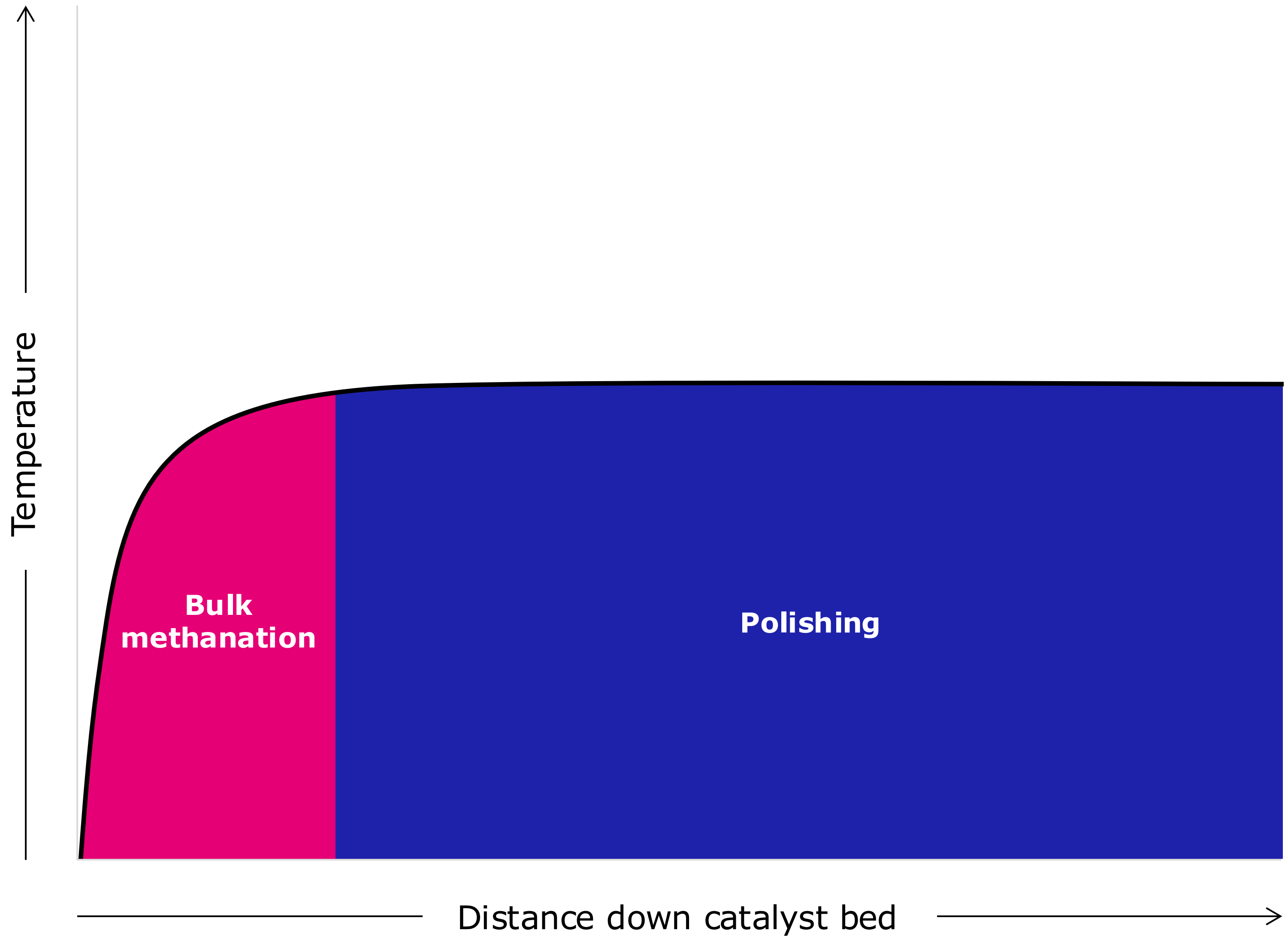
Reaction can be considered as 2 zones

1

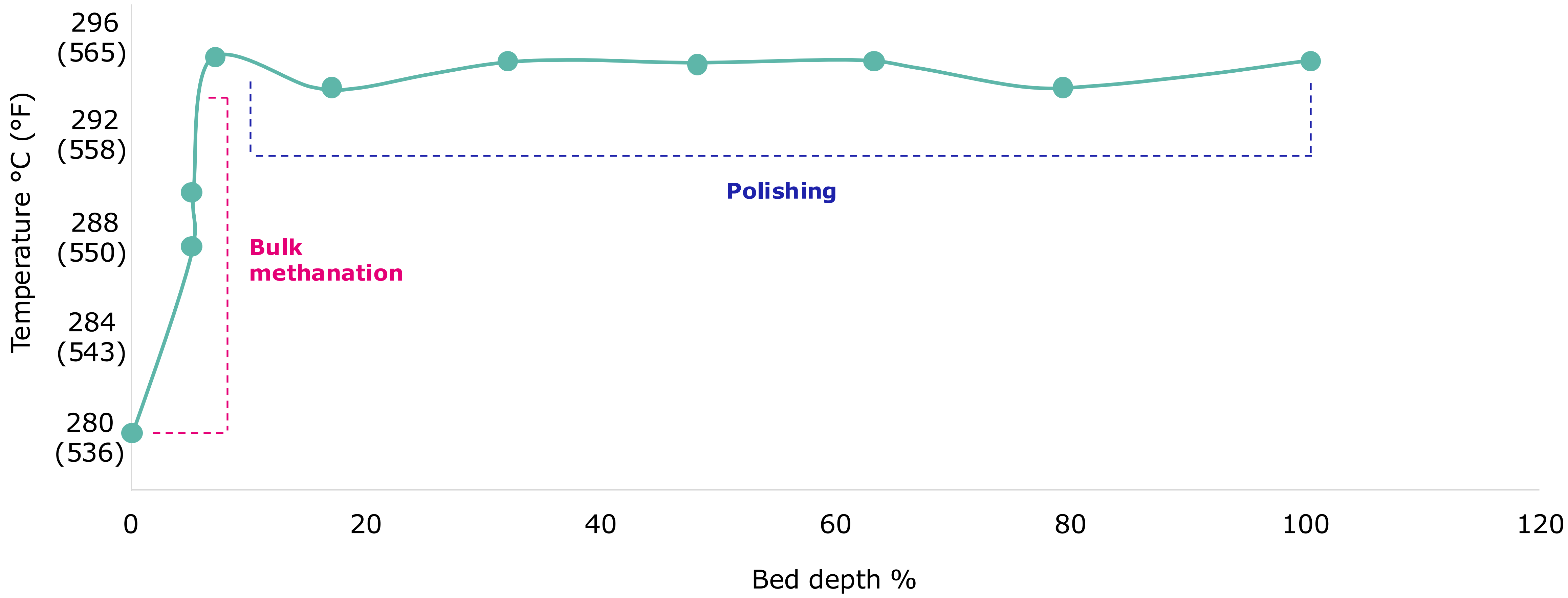
'Bulk methanation' quickly reduces carbon oxides <0.05% while increasing gas temperature

2

'Polishing' zone for required exit specification



Typical data



KATALCO 11-series

KATALCO™ 11-series

- Inlet temperature is plant-specific (design & operating conditions)
- Catalyst inlet temperature can be as **low as 210°C** (Formation of $Ni(CO)_4$ and Fisher-Tropsch by products formation to be considered)
- Lifetimes **20-30 years** due to high and stable activity
- **Low and stable** pressure drop
- **High** thermal stability
- **Robust enough** to withstand back washing in the event of external contamination

KATALCO 11-series 'R'

- **Pre-reduced** and **stabilized**
- Ideal for the top **20%-30%** of the catalyst bed
- **Simplifies** start up
- Saves up to **12 hours**

Pre-reduced catalyst

Can use **KATALCO** 11-series pre-reduced and stabilized variants

Made under carefully controlled conditions to give the highest possible activity

Solves problem of slow heat up by initiating methanation reaction early

Alternate loading options

1

100% bed pre-reduced
(more expensive)

Fully pre-reduced

2

20%-30% of catalyst bed
(cost effective)

20-30% pre-reduced

Option 2 top layer strikes fast; simplifies start up saving ~12 hours compared to fully oxidic charge

KATALCO 11-5MC / 11-6MC

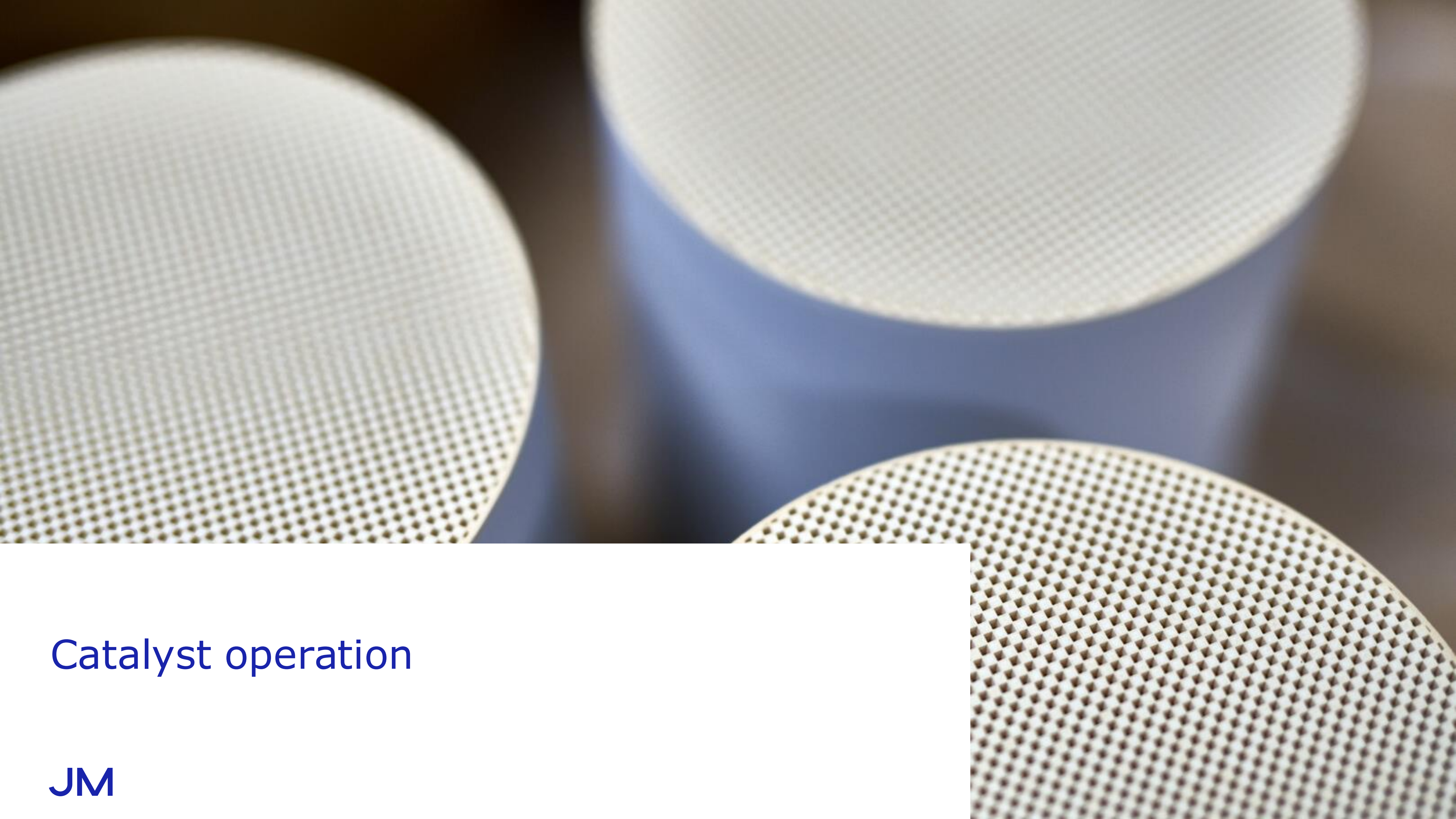
Very low pressure drop dry methanation catalyst due to specialized shape

Pressure drop governed by equivalent diameter and voidage

High voidage, hence low pressure drop

Relative PD estimate

Shape	Relative pressure drop
3-6 mm sphere	103%
KATALCO 11-4	100%
5 mm diameter ring	41%
KATALCO 11-5MC **KATALCO** 11-6MC	30%



Catalyst operation

Methanation start-up: example of bed reduction

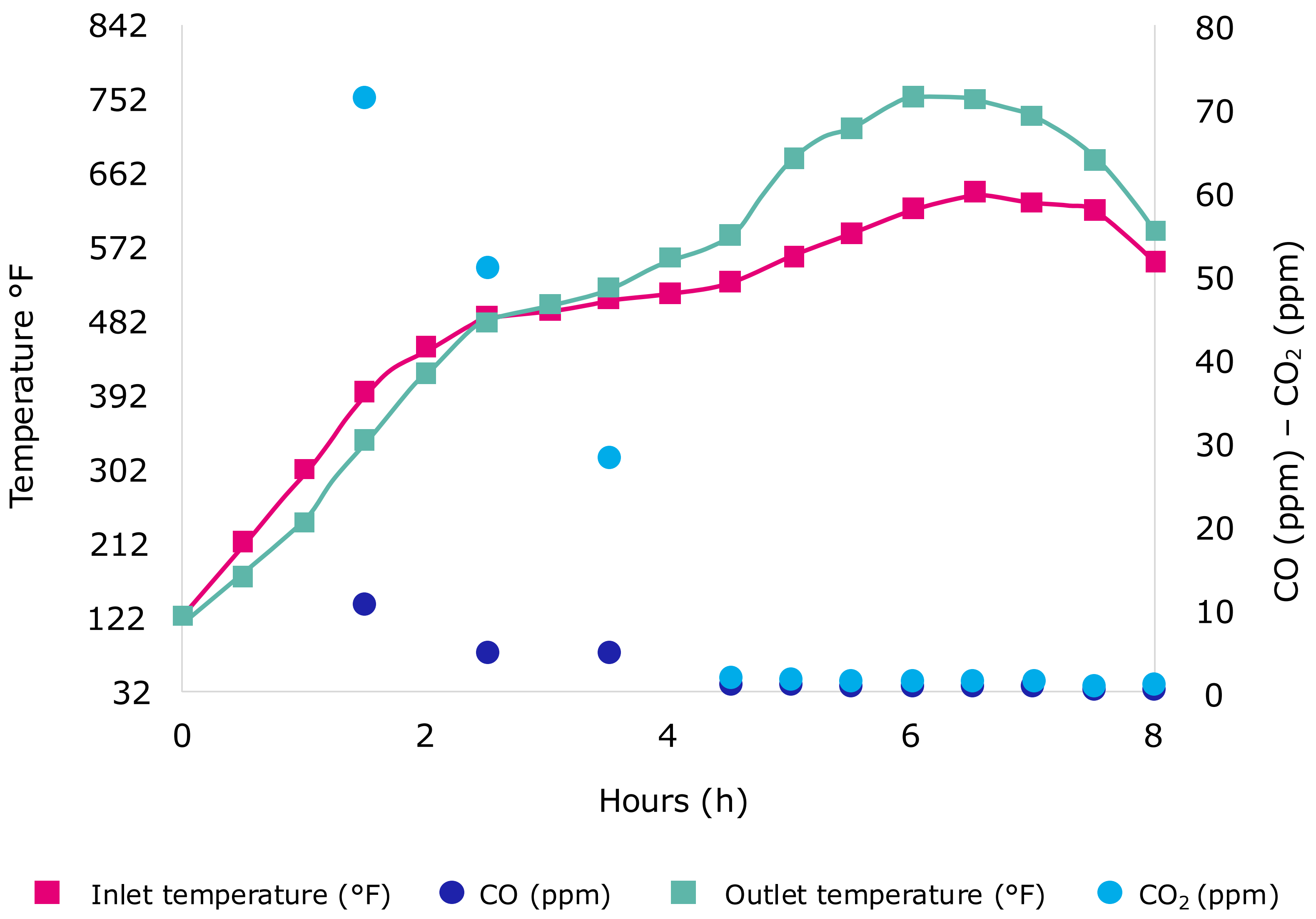
30 % pre-reduced KATALCO 11-4R

For quick 'strike'

Rapid reduction of bottom bed at 400ºC (752 ºF)

Minimize risk of nickel carbonyl formation

Ensure maximum catalyst activity achieved



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Normal operation

- High catalyst activity designed for long life
- Most reaction in top of bed
- Temperature profile moves down the bed
- Polishing to low ppm levels
- Catalyst lives 10-15+ years
- Change out is typically determined by vessel inspection schedule

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High catalyst activity designed for long life

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Feed COx increases:

➔ reaction rate increases

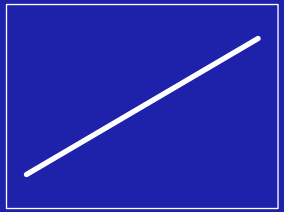
➔ COx slip decreases

➔ exit temperature increases

Lower inlet temperature to avoid high temperature plant trip

Abnormal conditions

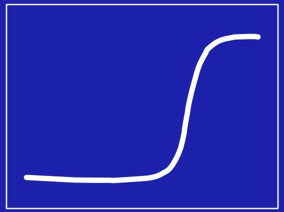
Gradual steady rise across whole bed



Inadequate reduction?

Fouling

Sudden movement of reaction zone with no change in slope



Poisoning/fouling of top?

Poor reduction of top?

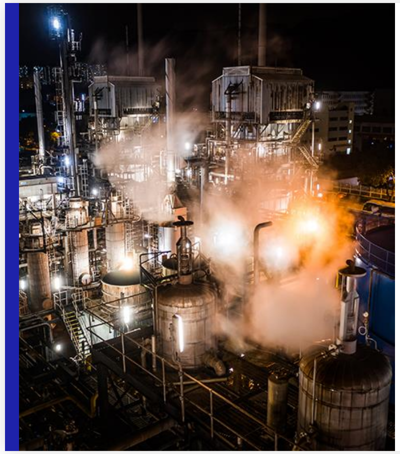
Normal temperature profile, high outlet carbon oxides

Channelling through bed?

Mechanical problems? (bypass valve, heat exchanger)

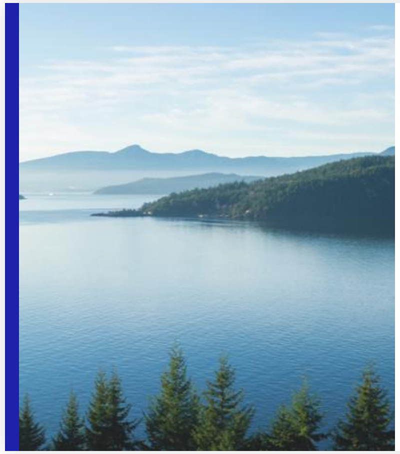
Analytical problems?

Unusual operating conditions



High COx levels

- CO2 System Upset / LTS bypassed
- Total concentration of carbon oxides < 3%
- Inlet temperature 210-250°C (410-480°F)
- If necessary, increase S:C ratio and/or lower plant rate



High water levels

- Normal level 2-3% water in inlet gas
- If > 3%, can lead to high CO_2 in exit gas
- Might need to increase bed inlet temperature
- Operating experience up to 7% water

Plant mal-operation

Normal catalyst maximum exit temperature is 450°C (840°F)

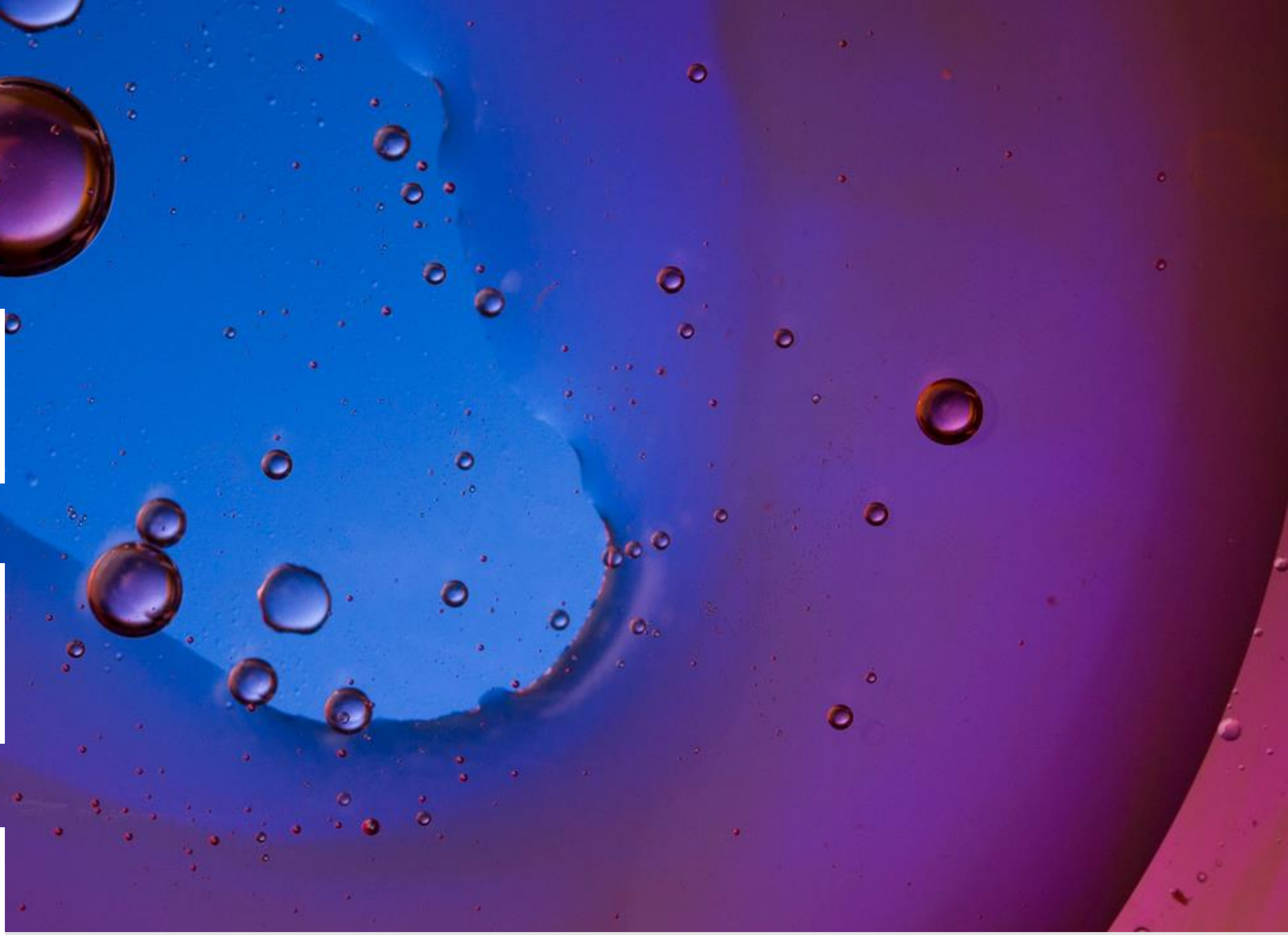
Excursions up to 600°C (1100°F) for several hours can be tolerated – check vessel integrity

In the event of a temperature runaway, the operator may take some steps to protect the vessel[1]:

- Isolate on inlet side
- Blow down to atmospheric
- Purge with nitrogen to aid cooling
- Exclude air to avoid exothermic oxidation

[1] The steps described above is an example of steps operators may take to protect vessels and should not be taken as a recommendation of specific actions to be taken in the case of a temperature runaway.

Catalyst poisons



Most poisons **originate from CO_2** removal system

Carry-over of a **small amount of liquid** not generally serious

Large volumes of liquid carry-over will have a **serious effect**

Sulfur is a **poison**, but normally **absent** unless LTS bypassed

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CO_2 Solvent Carryover	Effect
K_2CO_3	Blocks pores; removable
As_2O_3	Serious; irreversible poisoning
Sulpholane	Decomposes to S; poison

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Some operators have successfully recovered from liquid carryover by condensate back-washing the bed

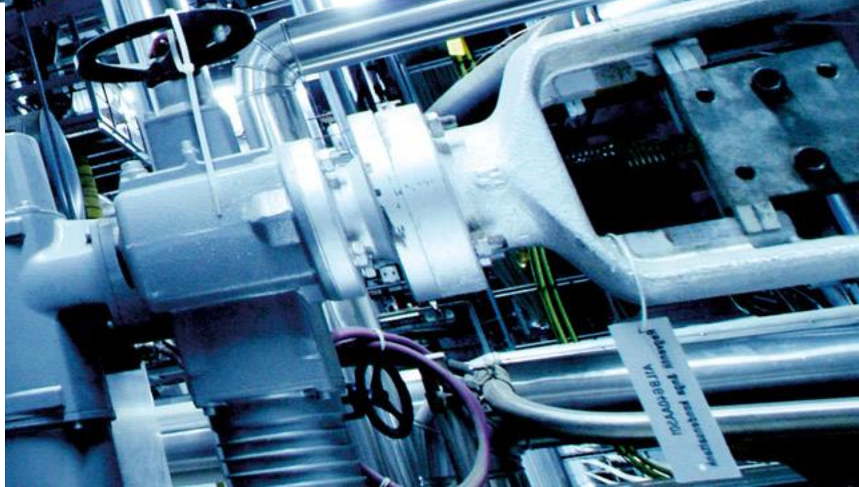
Shutdown

If process gas temperature > 200°C (390°F), can be left in atmosphere of process gas for short periods

Below 200°C (390°F), must be purged with an inert to prevent carbonyl formation

Reduced catalyst pyrophoric; oxidation very exothermic:

- Have appropriate firefighting kit available
- Transport in metal skips/metal-sided trucks



Nickel carbonyl

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Nickel carbonyl hazard

Formation of $Ni(CO)_4$ is a potential hazard

- Extremely flammable liquid and vapor
- Fatal if inhaled – 2ppmv (IDLH by NIOSH)
- Target daily average concentration 0.001ppmv (PEL by OSHA)

Nickel carbonyl is a colourless liquid

Flammable in air, insoluble in water

Nickel carbonyl boils at 43°C (109°F)

*Operators should review relevant SDS for exposure limits as they may be different for each country/jurisdiction.

Avoiding $Ni(CO)_4$ formation

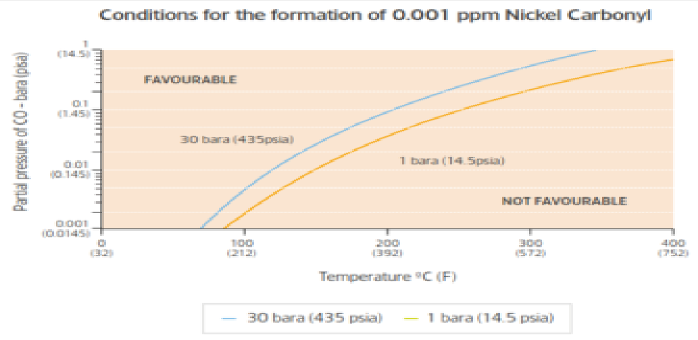
Under normal operating conditions

Steam reformer has a high CO and high Ni, but high temperatures

After LTS, temperatures low, but low CO and low Ni

Under normal operating conditions

Start up, shutdown, etc. – it is possible to form $Ni(CO)_4$

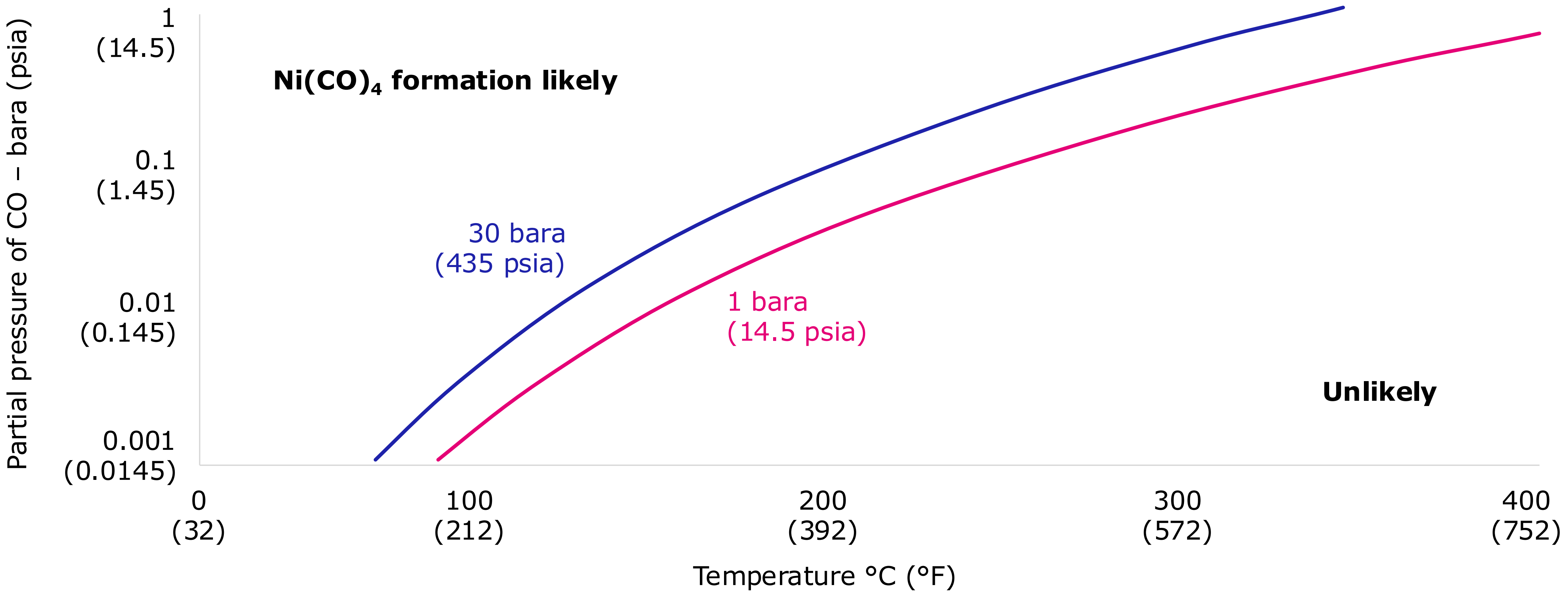


To avoid formation of $Ni(CO)_4$

Keep the temperature above 200°C (392°F) when the methanation catalyst is exposed to gas containing CO (refer to JM operating manual or the graph in the next slide)

Nickel carbonyl formation

Conditions for the formation of 0.001 ppm nickel carbonyl*



*An appropriate safety margin should be added to the predicted boundary

Summary

Methanation summary

Key performance variables

- Inlet temperature
- Exit temperature
- Pressure drop

1

Performance trends

- Temperature profile movement through the bed
- Pressure drop
- $CO + CO_2$ slip from bed

2

End of life criteria

- $CO + CO_2$ slip from bed
- Pressure drop
- Vessel statutory inspection

3

Optimisation

- Inlet temperature

4

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Methanation summary

Methanation is last purification step in Ammonia & Hydrogen production

Ensures long ammonia synthesis catalyst life and high hydrogen purity

KATALCO
11-4 methanation catalyst

- Available pre-reduced and stabilized
- Robust, offering low stable pressure drop
- High activity and ability to operate at lower temperatures

KATALCO
11-5MC/11-6MC methanation catalysts

- Same performance benefits as **KATALCO** 11-4 with significantly lower pressure drop
- Product selection is dependent on plant drivers

Ability to withstand abnormal operation


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