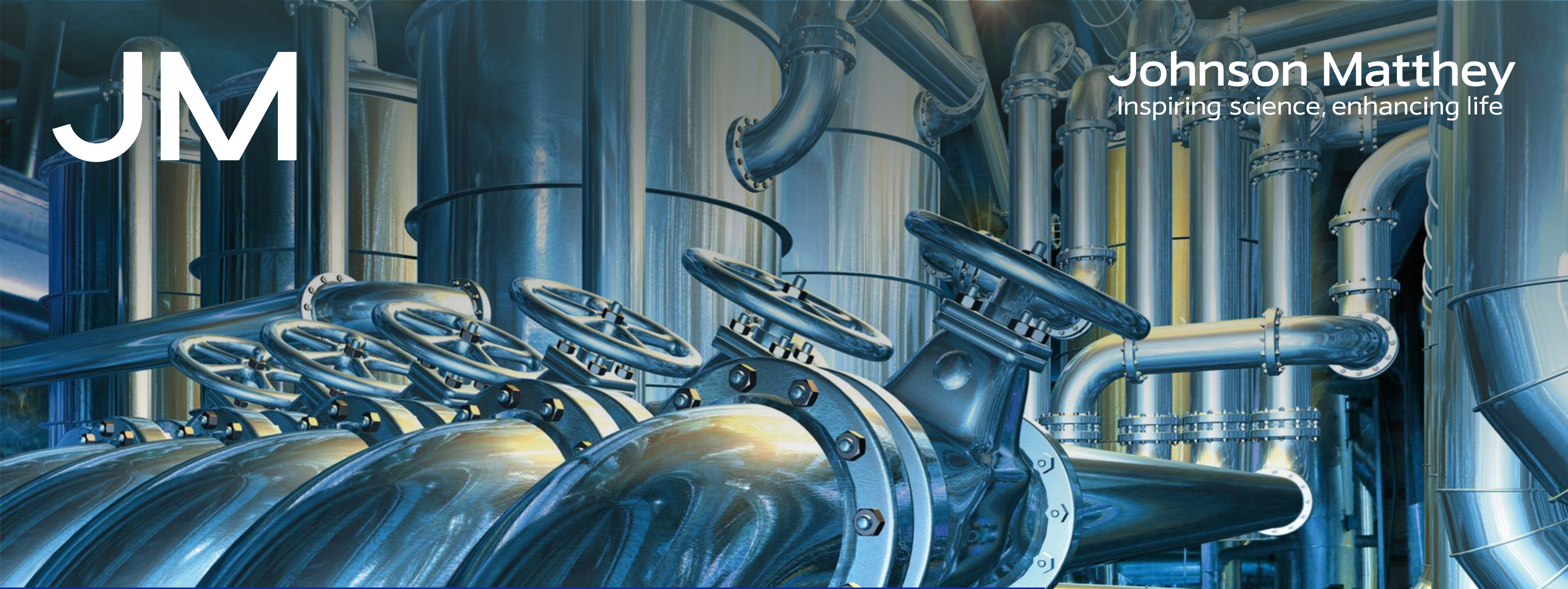

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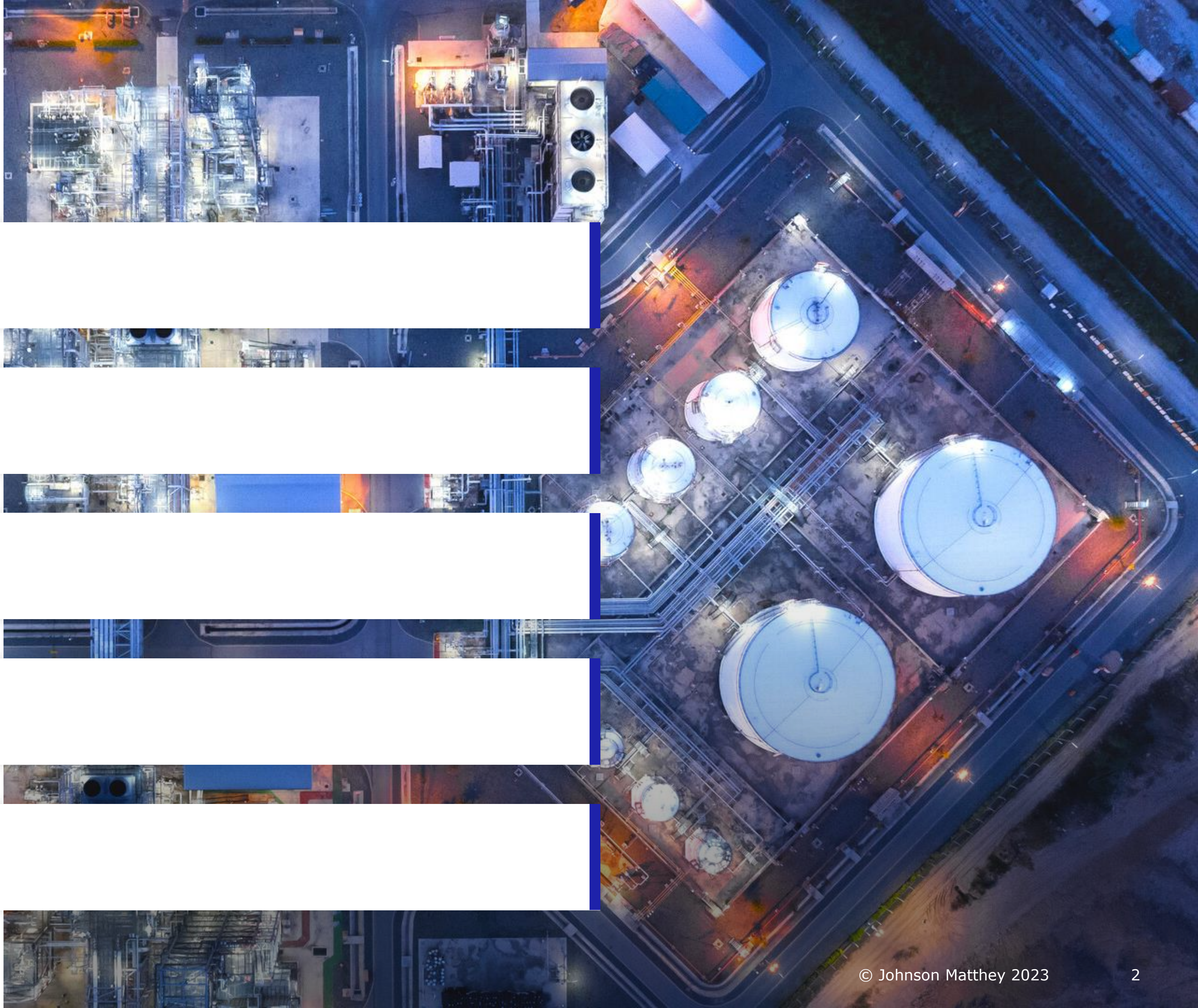
Americas hydrogen and syngas technical training seminar

Methanation fundamentals

Scott Commissaris

Contents



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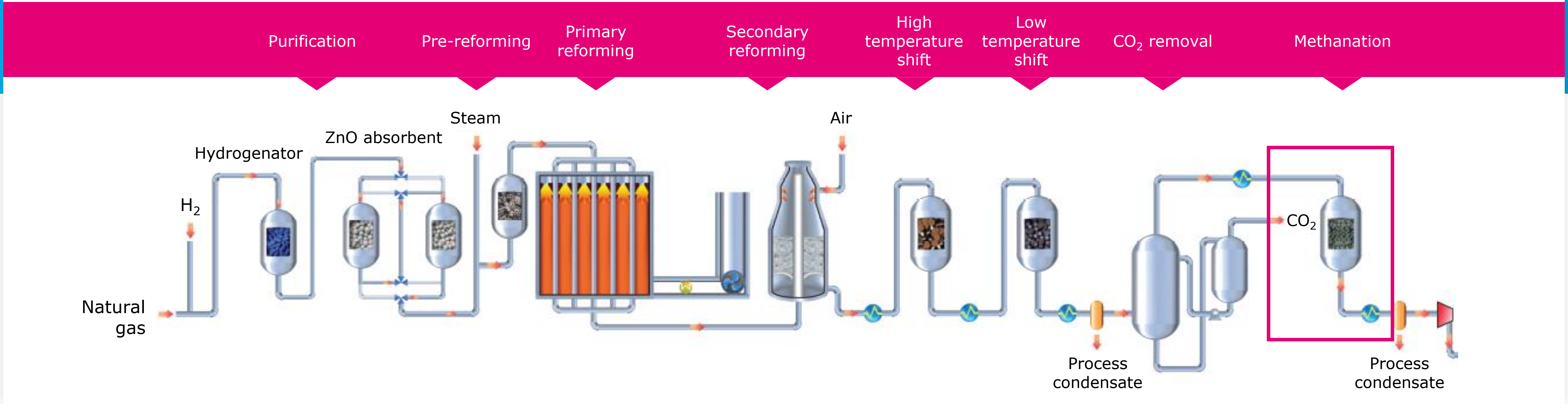
Introduction

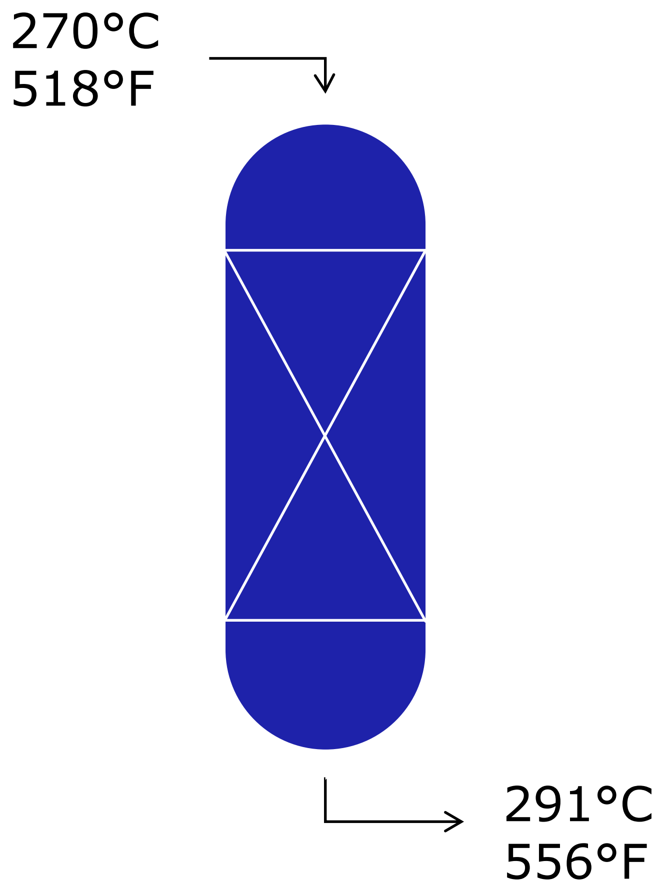


COx needs to be reduced to single figure ppm levels to avoid

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

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

Methanation chemistry

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Theoretical aspects

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

$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ ΔH = -206kJ/mol

$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ ΔH = -165kJ/mol

Temperature rise

- 74°C for each 1% of CO converted
- 60°C for each 1% of CO_2 converted

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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Methanation reaction

Good methanation catalyst will demonstrate

1

High conversion

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

2

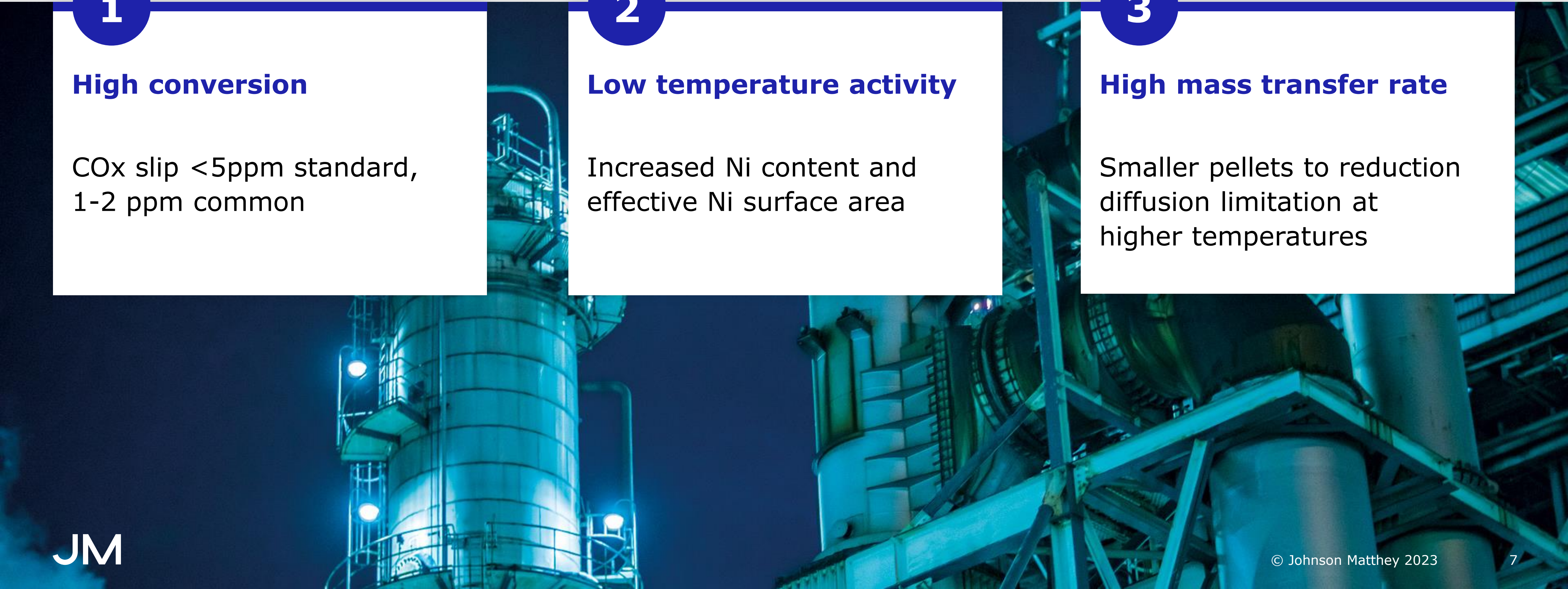
Low temperature activity

Increased Ni content and effective Ni surface area

3

High mass transfer rate

Smaller pellets to reduction diffusion limitation at higher temperatures



Reaction zones

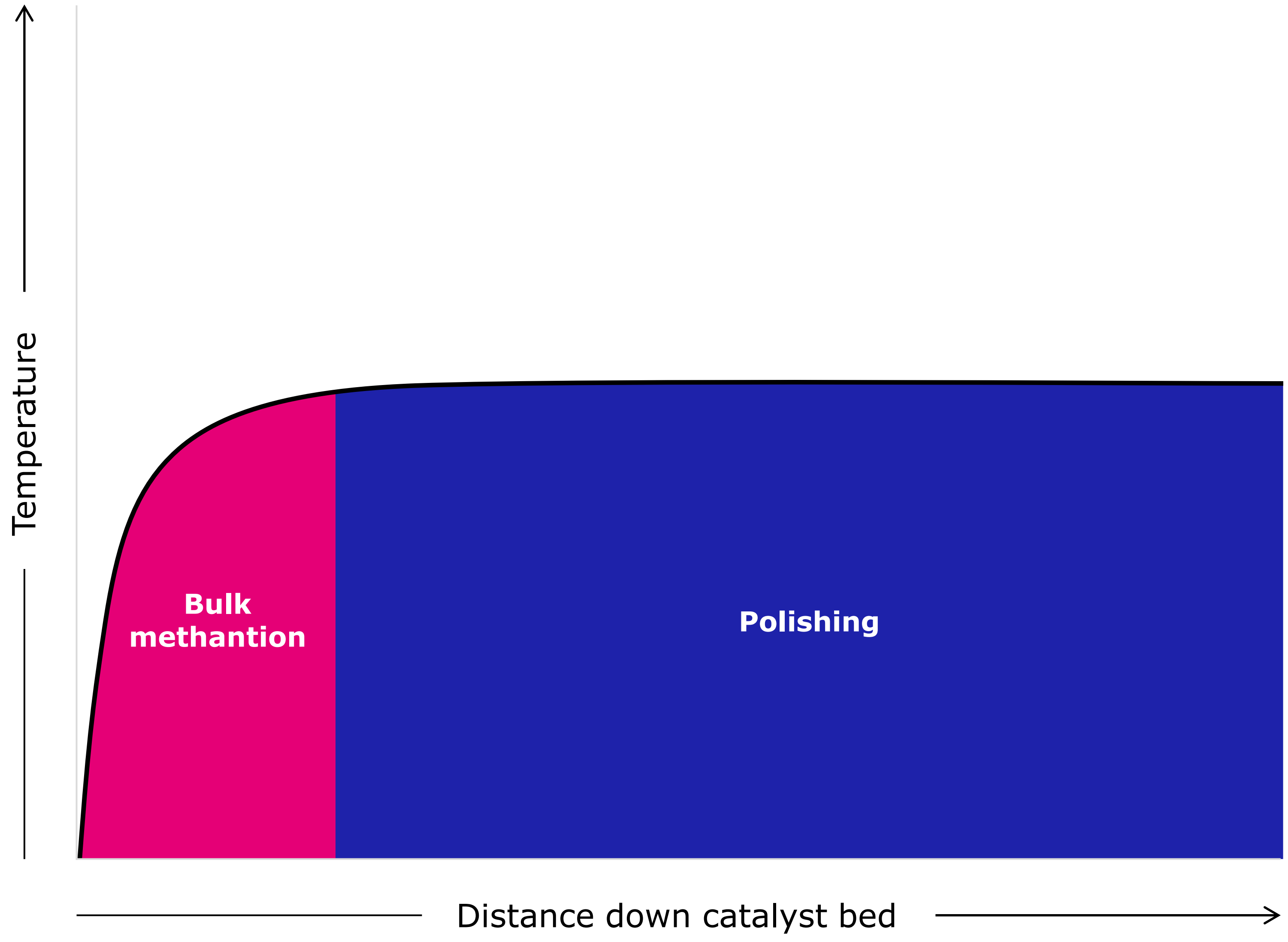
Reaction can be considered as 2 zones

1

'Bulk methanation' quickly reducing carbon oxide <0.05% increasing gas temperature

2

'Polishing' zone for required exit specification



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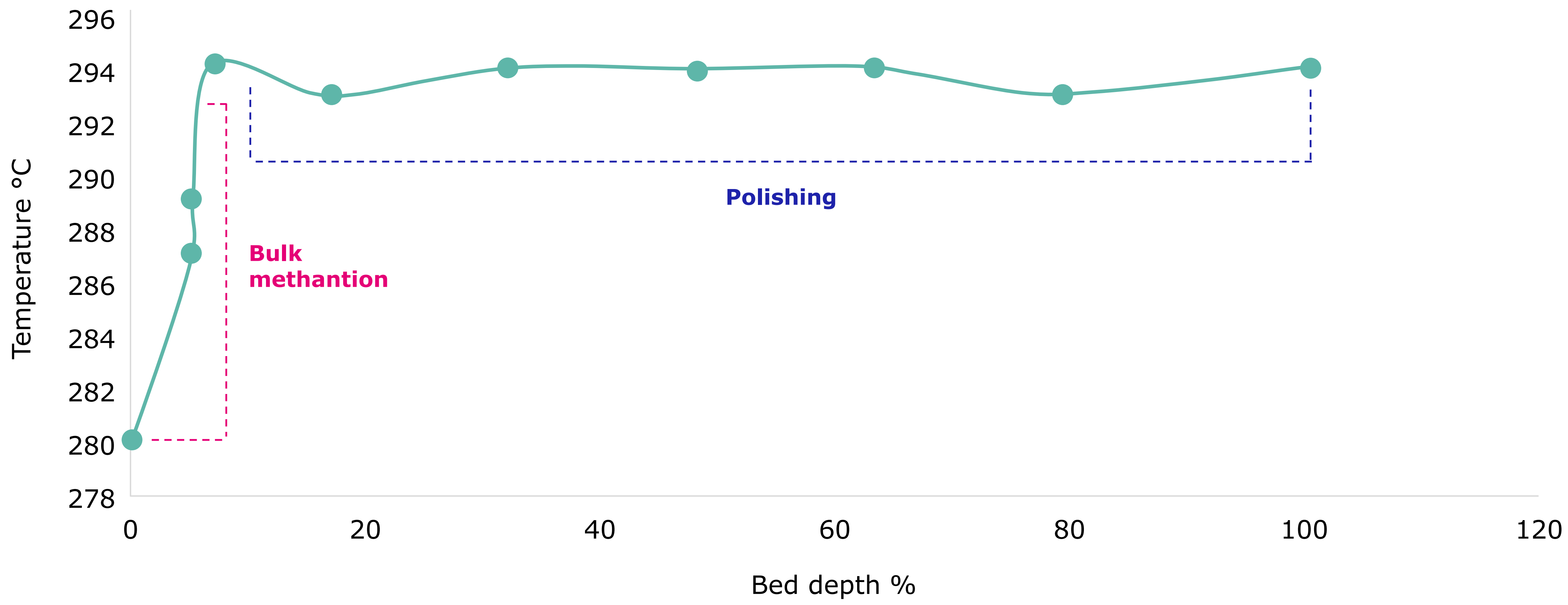
Typical data



KATALCO 11-series

KATALCO™ 11-series

- Can run at inlet temperatures as **low as 200°C**
- 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**

KATALCO 11-5MC / 11-6MC

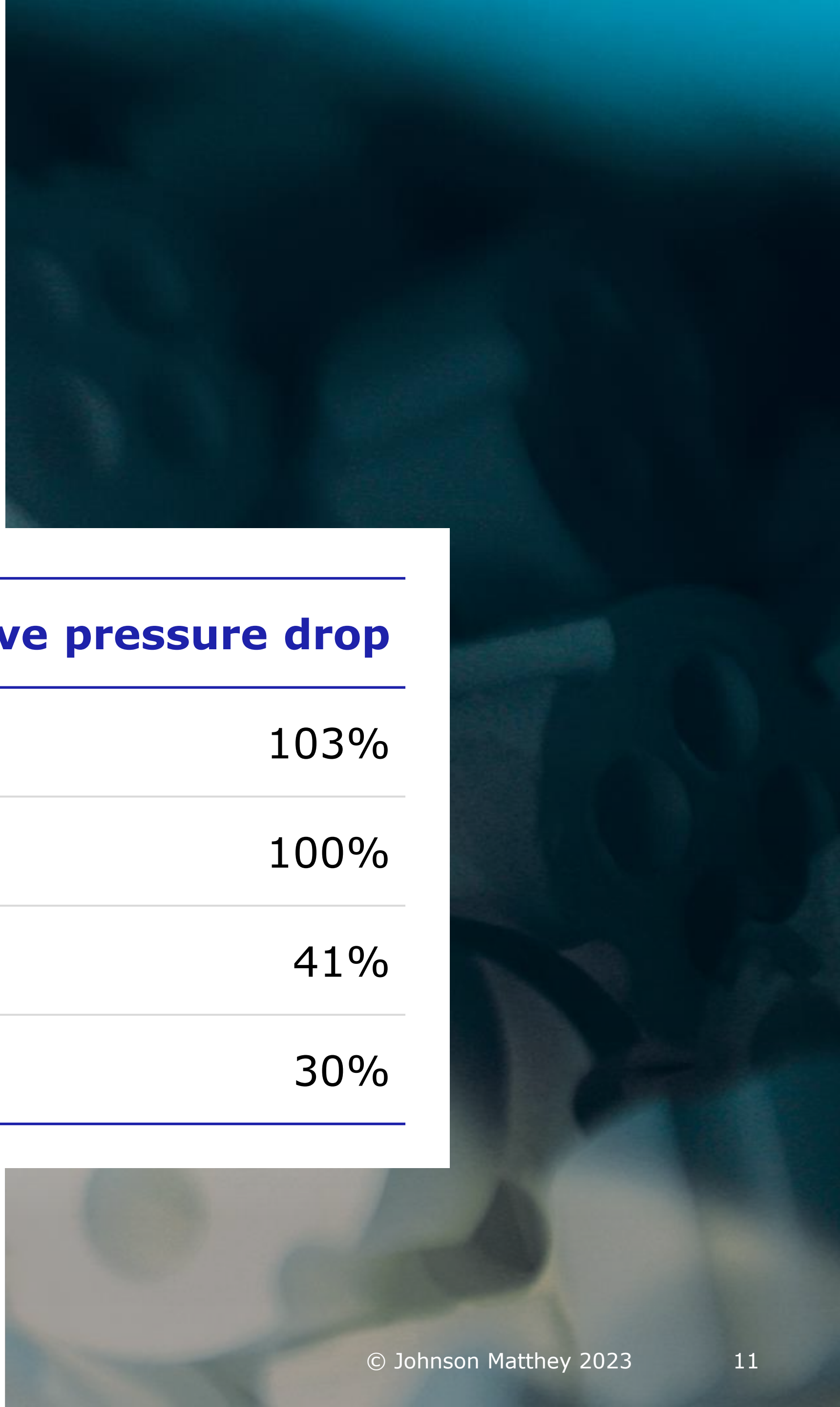
Very lowest pressure drop dry methanation catalyst due to specialized shape

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	30%



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Catalyst operation

Pre-reduced catalyst

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

Made under carefully controlled conditions to give the highest possible activity

Alternative options to use

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

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Methanation start-up: example of bed reduction

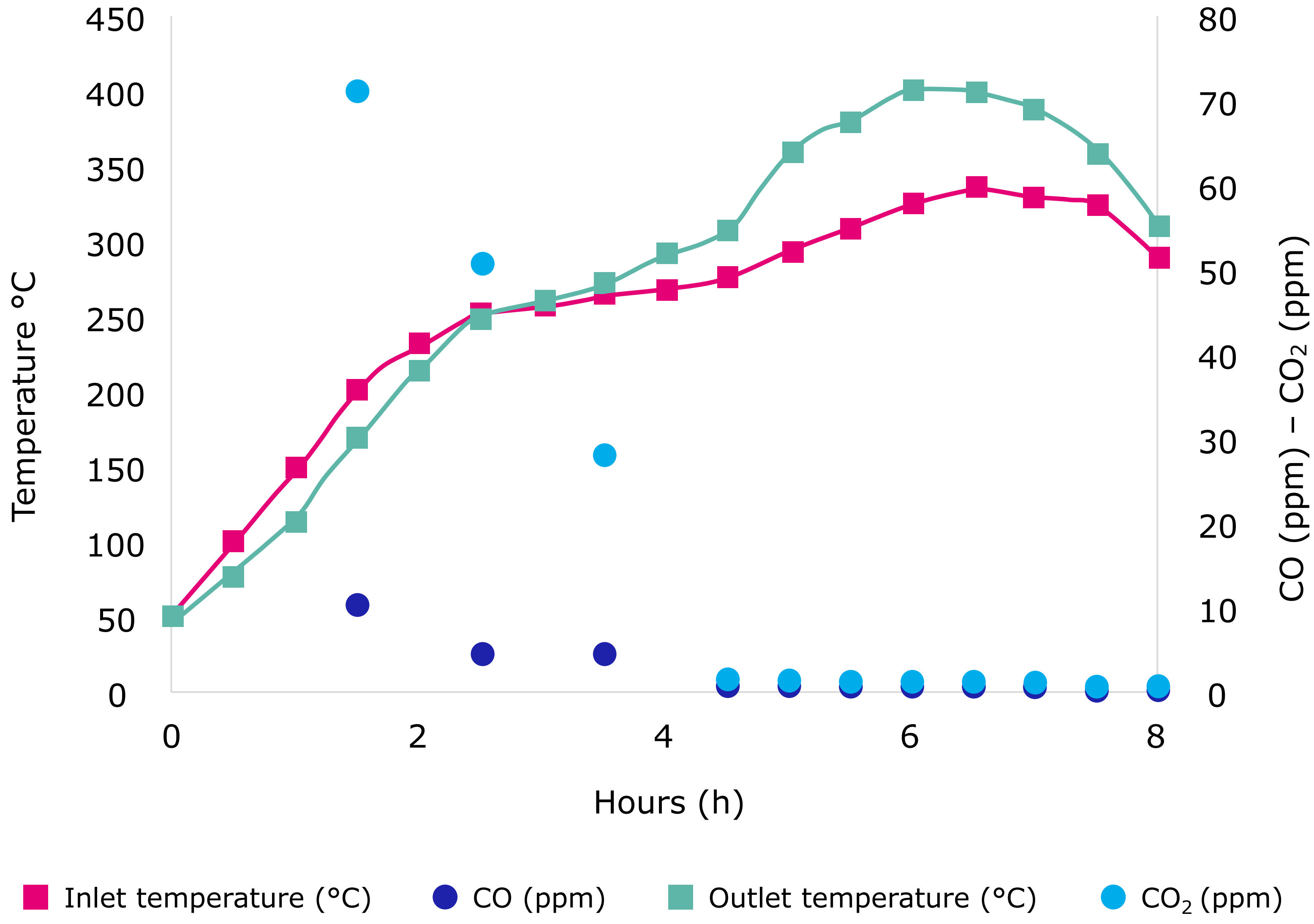
30 % pre-reduced KATALCO 11-4R

For quick 'strike'

Rapid reduction of bottom bed at 400ºC

Minimize risk of nickel carbonyl formation

Ensure maximum catalyst activity was achieved



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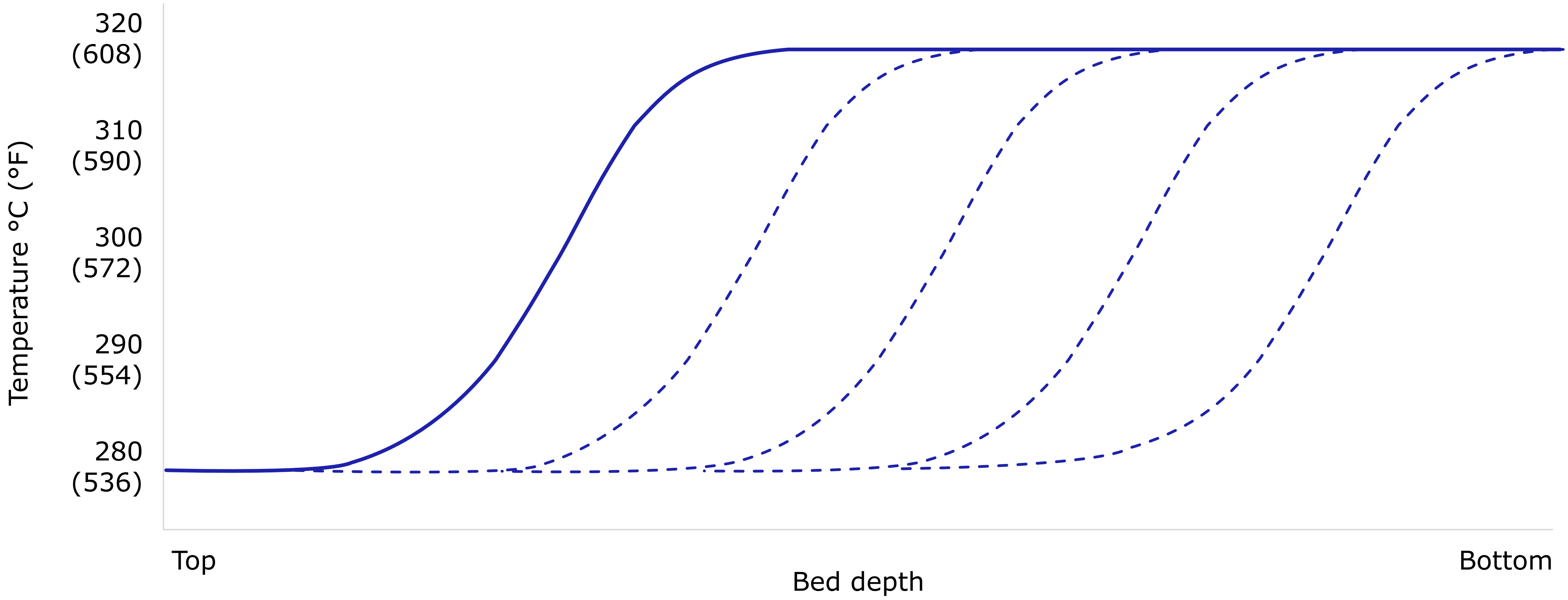
Normal operation

- Originally over-designed, high catalyst activity
- Most reaction in top of bed
- Aging mechanism is gradual poisoning
- Profile moves down the bed
- Catalyst lives 10-15 years
- Conversion of carbon oxides dependent on outlet temperature

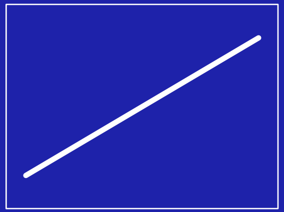
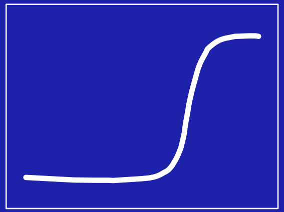
If CO inlet increases, exit temperature also increases, reaction rate increases and exit carbon oxide level decreases

this may allow a reduction in inlet temperature

Methanation catalyst aging



Abnormal conditions

Gradual steady rise across whole bed		Inadequate reduction? Poisoning
Sudden movement of reaction zone with no change in slope		Poisoning of top? Poor reduction of top?
Normal temperature profile, high outlet carbon oxides		Channelling through bed? Mechanical problems? (bypass valve, heat exchanger) Analytical problems?

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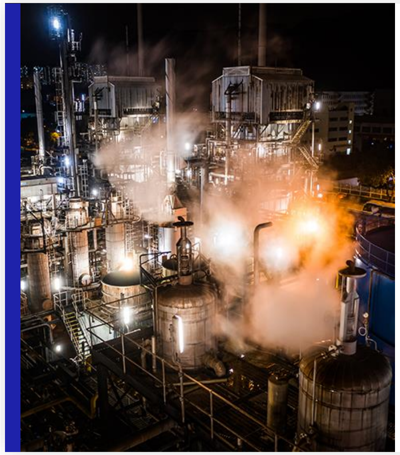
Unusual operating conditions



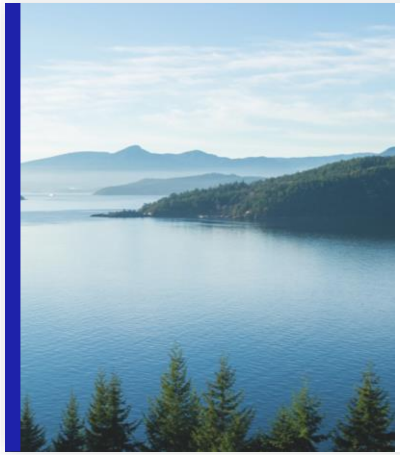
High CO levels

LTS bypassed

Total concentration of carbon oxides < 3%

Inlet temperature 210-250°C (410-480°F)

If necessary, lower rate through HTS and increase S:C ratio



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

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Plant mal-operation

Normal maximum exit temperature is 350°C (660°F)

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

In the event of a temperature runaway, the vessel must be protected:

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

Catalyst poisons

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

Most poisons **originate from CO_2** removal system

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

Large volumes will have a **serious effect**

Common poisons	Effect
K_2CO_3	Blocks pores; removable
AS_2O_3	Serious; irreversible poisoning
Sulpholane	Decomposes to S; poison

Shutdown

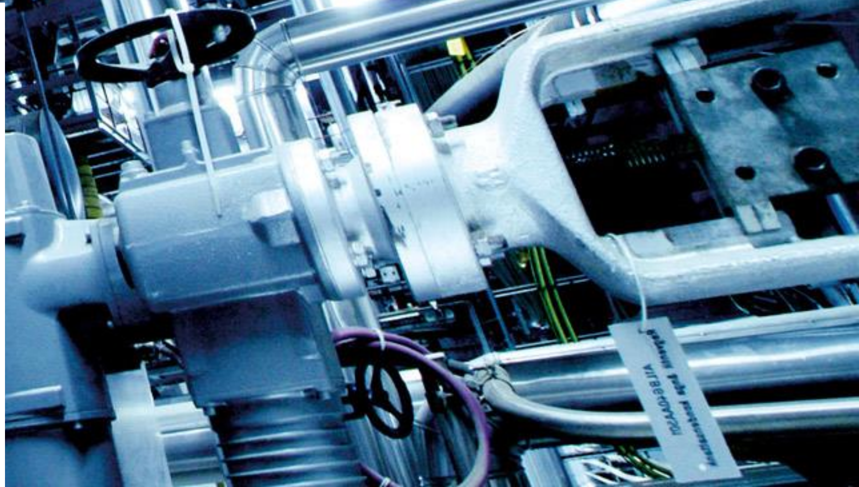
If process gas temperature > 200°C (390°F), can be left in atmosphere of process gas for short periods

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

Reduced catalyst pyrophoric; oxidation very exothermic:

- Spread catalyst thinly on ground
- Have water hoses available
- Transport in metal skips/metal-sided trucks

Nickel carbonyl



Nickel carbonyl hazard

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

- Exposure to 4ppm v/v for one minute gives severe toxic effects
- Exposure to 2ppm v/v for a short time causes illness
- Target daily average concentration 0.001ppm v/v

Nickel carbonyl is a colourless liquid

Flammable in air, insoluble in water

Nickel carbonyl boils at 43°C

IS THE HEADING MEANT TO BE REPEATED TWICE

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

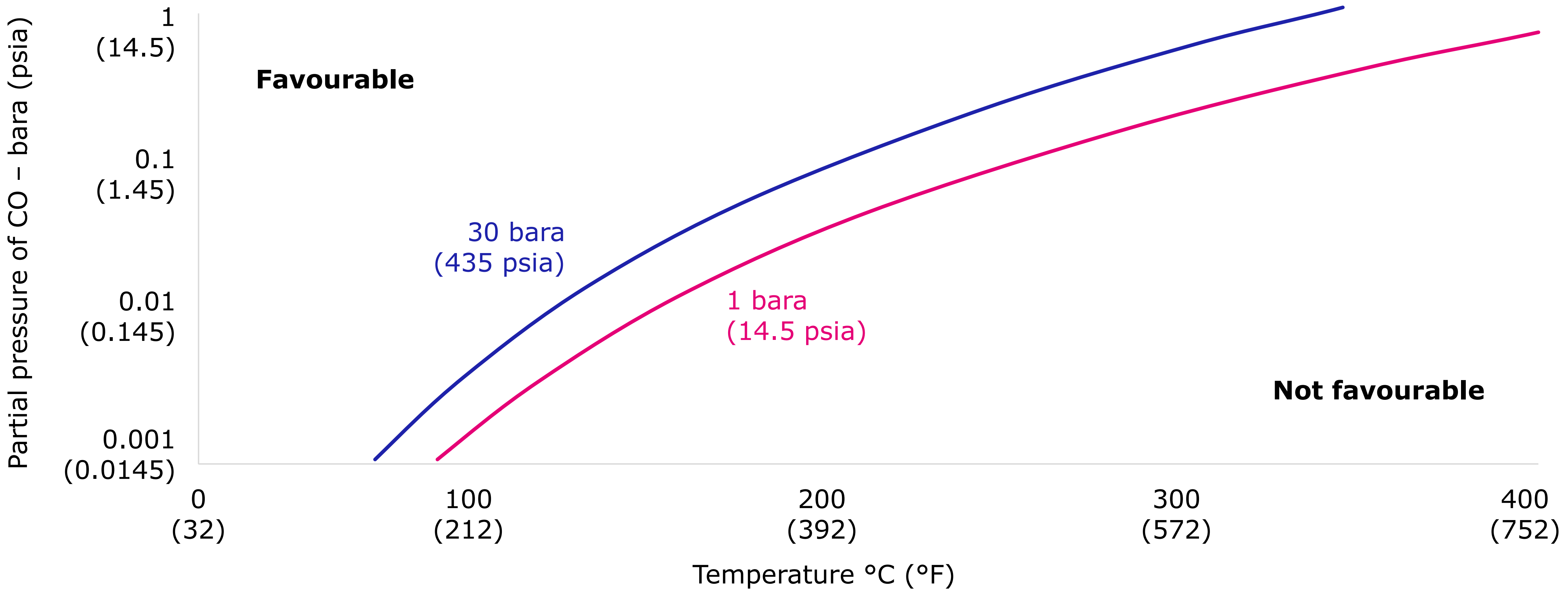
Start up, shutdown, etc. – it is possible to form $Ni(CO)_4$

To avoid formation of $Ni(CO)_4$

Keep the temperature above 200°C when the methanation catalyst is exposed to gas containing CO (check design guide graph)

Nickel carbonyl formation

Conditions for the formation of 0.001 ppm nickel carbonyl



Summary

Methanation summary

Methanation is last purification step in ammonia production

Low carbon oxide slip ensures long ammonia synthesis catalyst life

KATALCO
11-4 methanation catalyst

- Available pre-reduced and stabilized
- Robust, offering low stable pressure drop
- Has been back-washed often without problem
- High activity and operate at temperatures down to 210°C

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

- Same performance benefits as KATALCO 11-4 with significantly lower pressure drop
- Selection optimized for typical and lower temperature operation

Abnormal catalyst operation

Catalyst poisons and the nickel carbonyl hazard

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

3

Optimisation

Inlet temperature

4

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