Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Principals of pre-reforming technology
Scott Commissaris

Contents

Pre-reformer

Assurance in experience and capability

A long heritage and strong credentials in pre-reforming

Technology licensed by **Davy Process Technology**

Over 60 years of **catalyst manufacturing experience**

More than **150 active reference**

Knowledge and expertise in operations

An introduction to pre-reforming

Pre-reforming is the process by which **heavier hydrocarbons and methane** are steam **reformed adiabatically** and the products of the heavier hydrocarbon reforming are methanated

Pre-reforming can be used for low temperature steam reforming of a range of hydrocarbon feedstocks from **natural gas through to naphtha**. The process **duty in a downstream fired steam reformer is made less arduous** by converting higher hydrocarbons into methane using a highly active catalyst

Steam reforming (example of methane)

$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	$\Delta H = +206$ kJ/mol

Water-gas shift

$CO + H_2O \Leftrightarrow CO_2 + H_2$	$\Delta H = -41$ kJ/mol

Methanation

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

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Remaining competitive against the challenges of increasing gas prices and use of cheaper feedstocks

Increasing efficiency, flexibility and throughput

Pre-reforming is utilized in new plants when

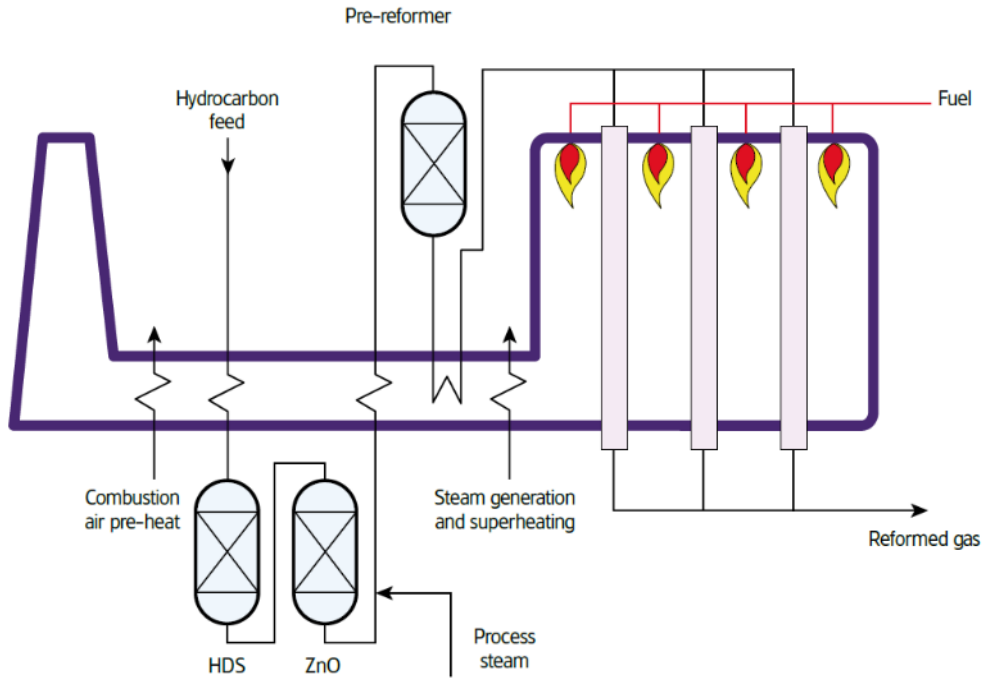
- A plant requires the **flexibility** to process multiple feeds
- **More CO** production is required (HyCO)
- Less export steam is required
- A **smaller primary reformer** is desired

Pre-reforming an also be used in revamps to

- Increase plant rate, typically **10% to 15%** rate increase
- Or provide feedstock flexibility

Considerations for pre-reforming include

- Adds another process step to the flowsheet, complicating **start-up and process control**
- Requires **good operation** and management
- Assurance of **purification** performance



Maximizing flexibility of your plant

Feedstock flexibility

Unlike the steam-methane reformer, a pre-reformer is **able to operate with a wide variety of feeds** with a single catalyst type

Gaseous:

Natural gas, associated gas, refinery gas, synthesis gas derived from coal or oil gasification

Liquid:

Natural gas liquids, LPG, naphtha, kerosene, methanol, ethanol

Operational flexibility

Pre-reformers are also able to operate with more aggressive steam:carbon ratios than a steam-methane reformer, thereby enabling **better plant efficiency**

Operating pressure

Up to 70 bar (1015 psi)

Operating temperature

300-650°C (480-1200°F)

Steam to carbon ratio

0.3-5.0 (w/w)

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Case Study: benefit of a pre-reformer

- Case 1 –Basis: no pre-reformer installed
- Case 2 –Pre-reformer installed
- Case 3 –Pre-reformer installed, and plant rate increased until firing on the reformer is the same as Case 1

	Units	Case 1	Case 2	Case 3
Plant rate	[%]	100	100	109
Methane slip	[mol % dry]	12.84	12.76	12.79
ATE	[°C]	1.8	1.1	1.3
Pressure drop	[bar]	1.26	1.28	1.49
Max. TWT	[°C]	809	803	807
Flue gas temp	[°C]	898	885	898
Radiant efficiency	[%]	68.7	69.4	68.7
Fuel rate change	[%]	0	-8.8	0

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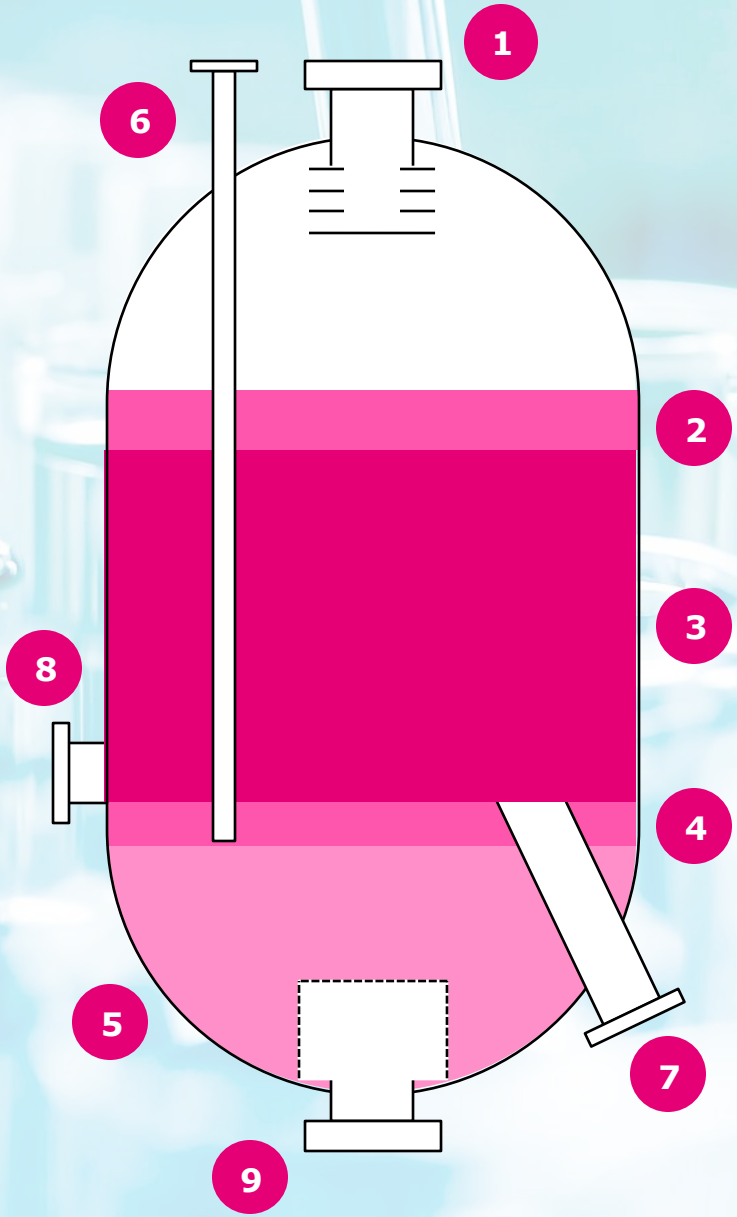
A typical features of a pre-reforming unit

1. Inlet nozzle and distributor, prevents bed disturbance and enables good gas distribution through the catalyst bed
2. High purity alumina hold down material, to prevent bed disturbance and prevent fouling of the catalyst
3. Catalyst bed
4. High purity alumina support material, the initial interface layer is designed to prevent penetration of the catalyst
5. Bottom dished end, usually loaded with high purity alumina supports around the gas collector, to minimize pressure drop
6. Travelling or multi-point thermocouple, for monitoring catalyst deactivation
7. Catalyst discharge nozzle (typical)
8. Catalyst discharge nozzle (alternative)
9. Gas collector to outlet



Best practice for pre-reforming catalyst management :

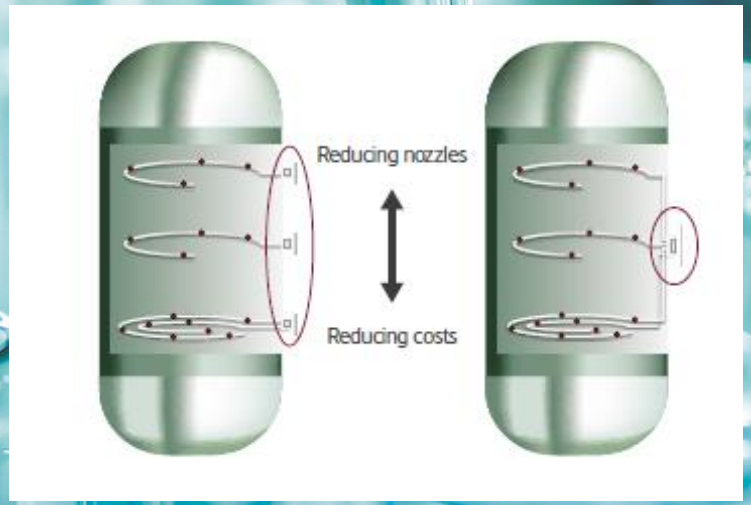
CatTracker® catalyst temperature tracking system

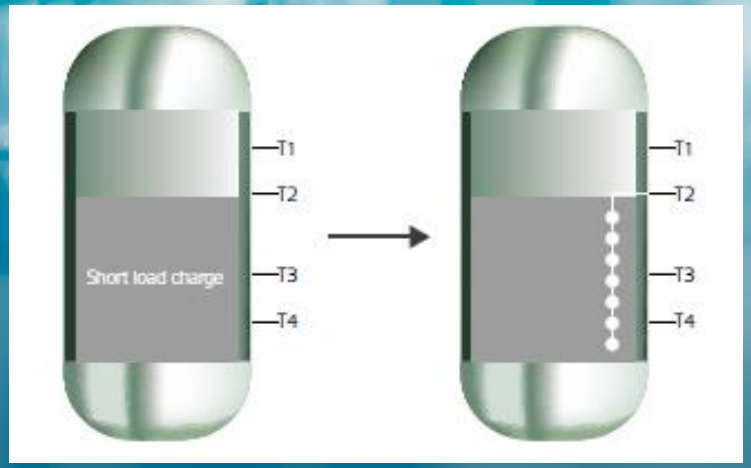
First introduced by Daily Thermetrics at commercial scale as a patented technology

Installed in hundreds of vessels over five continents

Rugged yet flexible temperature probes designed to be in direct contact with the process.

CatTracker® temperature sensors are engineered to withstand the harshest of environments and the most strenuous temperature demands.





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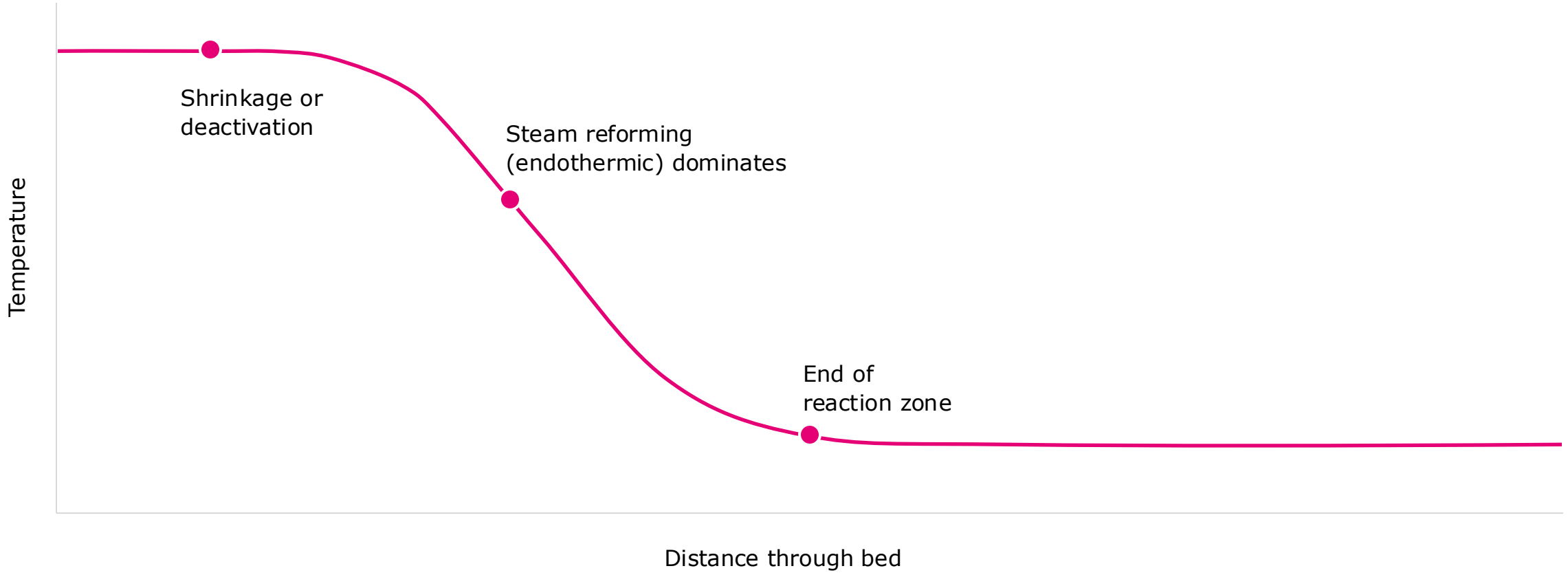
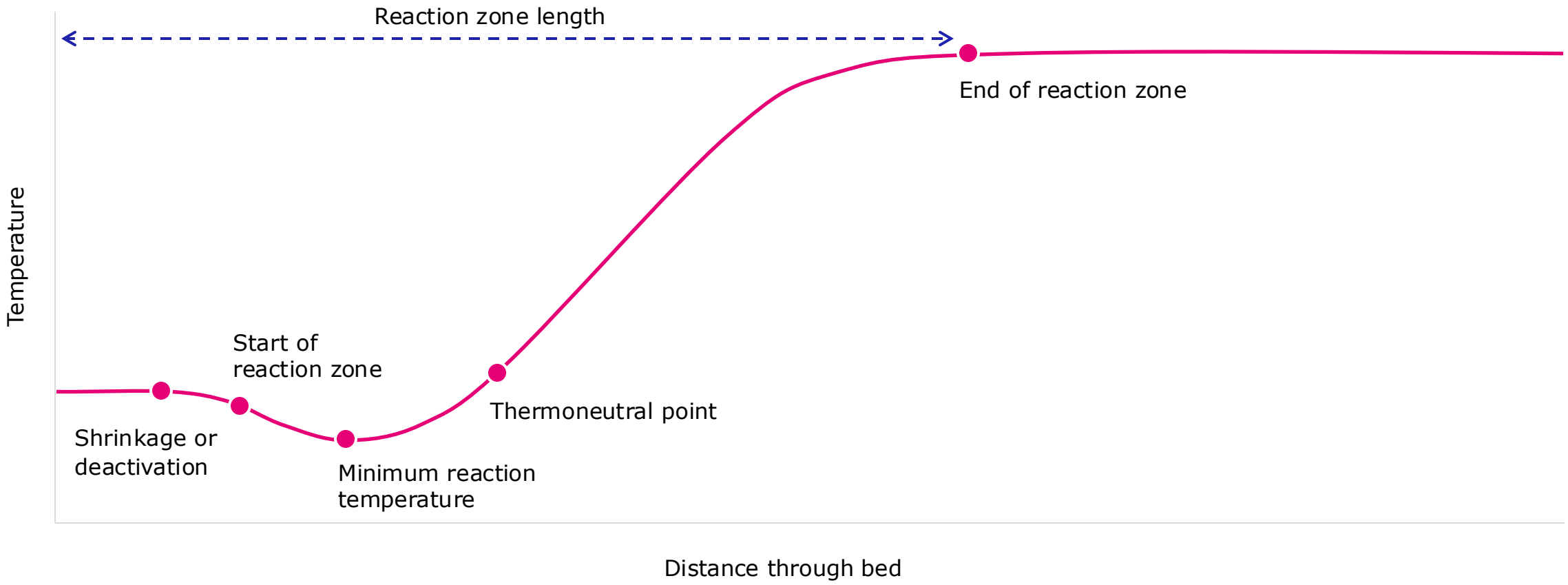
Reaction profile

Natural gas



Reaction profile

Naphtha



Maximising the life of high activity Ni catalysts

The high activity of pre-reforming catalysts is achieved through a high Ni loading, for which sulfur is a virulent poison

Careful **management of the purification and steam system** are necessary to minimize potential for poisoning the pre-reformer

It is recommended the feed to the pre-reformer has **less than 100 ppb wt sulfur** throughout life

Ultra-purification is recommended for where sulfur poisoning is the dominant deactivation mechanism

Maximising the life of high activity Ni catalysts

Recommended feed specifications

Feed poisons

Sulfur	<100 ppb wt
Chloride	<100 ppb wt
Heavy metals	<10 ppb wt

Cyclic compounds

Aromatics	<25 vol%
Naphthene	<40 vol%
Together	<35 vol%
Aromatics	*<10 vol%*
Naphthene	*<25 vol%*

Steam quality

Sodium	<100 ppb wt
Chloride	<50 ppb wt
Sulfide	<50 ppb wt
Silica	<100 ppb wt

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Confidently operating to achieve targeted production targets and turnaround periods

Quality, performance and reliability

CRG-LH:

A well established and recognized catalyst for pre-reforming, offering strong performance through the life of the catalyst with high thermal stability

CRG-F:

A premium high activity product, specifically designed for high performance and low temperature applications

KATALCO™ 65-3X:

Our latest catalyst features the same ease of operation and reliability as the established CRG-LH, but with enhanced thermal stability to provide a longer life

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Simplifying operations and solutions for your specific needs

Overcome **equipment constraints** and simplify the **start-up**

CRG-LH is available in **reduced** and **passivated** forms for easy start-up and optimized performance

Reduce pressure drop to **increase throughput** or **reduce energy consumption**

CRG-LHC is a shaped variant featuring **low pressure drop** in **reduced** and **passivated** forms for easy start-up and optimized performance

Extend catalyst cycle length and **reduce operating costs**

KATALCO 65-3X is a high stability catalyst with reduced and passivated forms for easy stat-up and longer cycle length

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Demanding more from the pre-reformer with **KATALCO** 65-3X

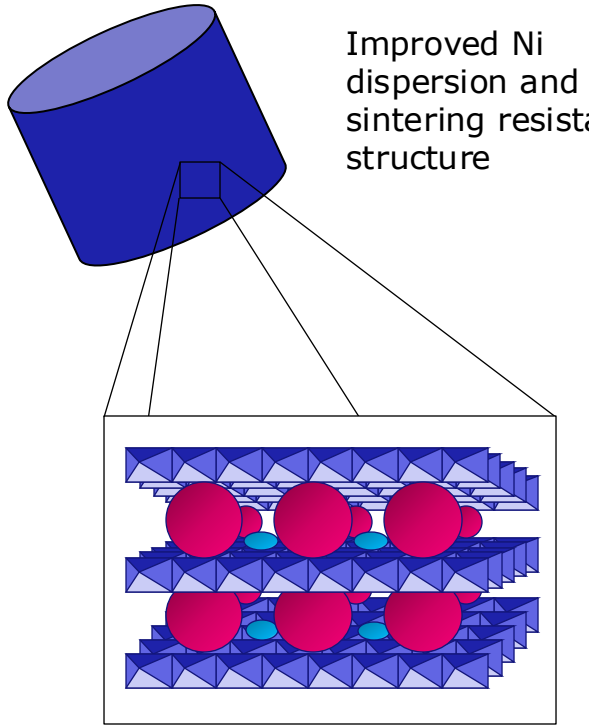
Stronger performance maintained deeper into the operating cycle

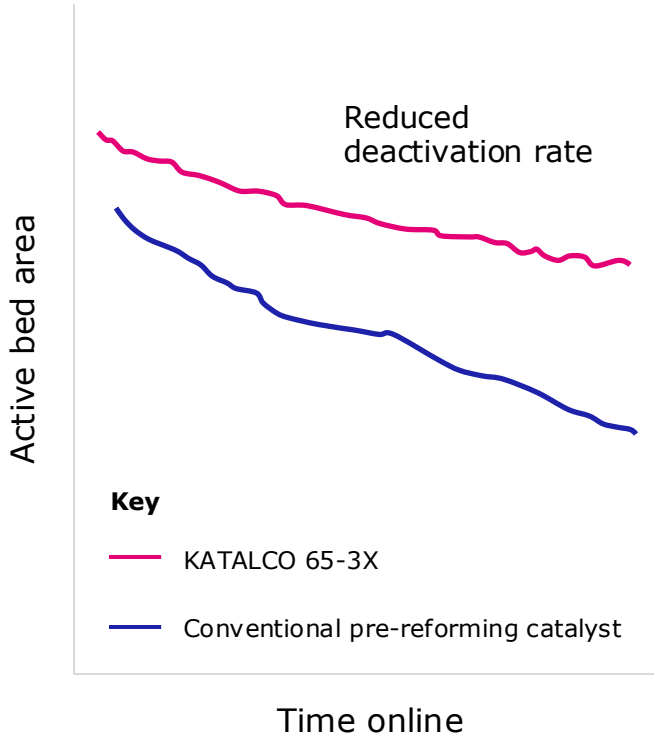
KATALCO 65-3X

Optimized Ni-structure and promotors for high retained active Ni surface area

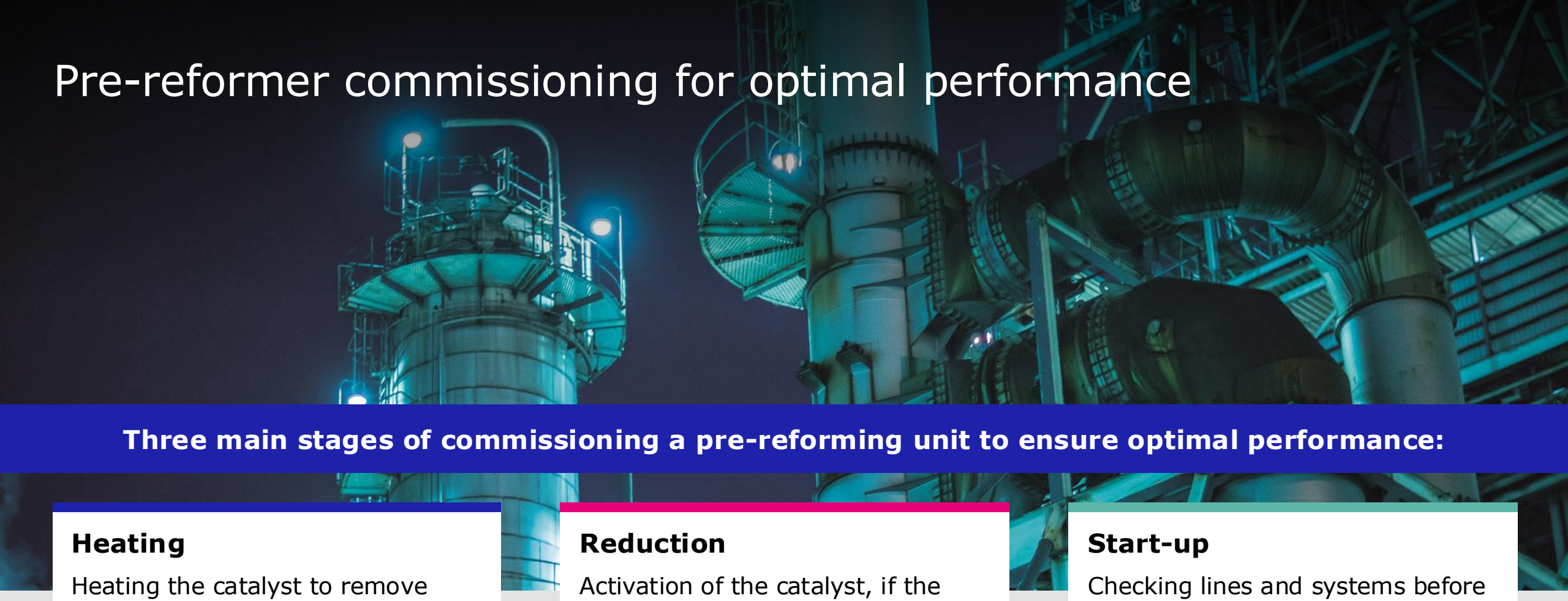
Longer bed lives from increased thermal stability

Improved EHS properties, with a Cr-free formulation





Pre-reformer commissioning for optimal performance



Three main stages of commissioning a pre-reforming unit to ensure optimal performance:

Heating

Heating the catalyst to remove absorbed moisture and bring to activation temperatures

1

Reduction

Activation of the catalyst, if the catalyst is not in the reduced and passivated form

2

Start-up

Checking lines and systems before bringing the pre-reformer online

3

Commissioning with hot nitrogen

The presence of moisture can impact during the start-up can damage the catalyst

Mitigation of the impact of moisture is done by a controlled heating procedure:

Typically heating/drying is done using **nitrogen**

Initial heating rate, **50°C/h (90°F/h)** from ambient to 200°C (390°F)

At 200°C (390°F) typically there will be a hold to ensure no further adsorbed water is evolved, after which the heating rate may be increased to **70°C/h (130°F/h)**

Maximum temperature differential of 100°C (180°F) between catalyst and circulating gas is recommended

Heating till **peak of 400°C (750°F)** is achieved, min 370°C (700°C)

High circulation rate is recommended for good gas distribution, but a maximum pressure drop of 2 bar must not be exceeded to avoid catalyst damage

Additional drying may be required if the catalyst has been exposed to low temperatures

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Start-up of pre-reforming catalyst

Once the pre-reforming catalyst has been brought to temperature, it can be put online but some precautions are required

- Check for build-up of **carbon oxides and hydrocarbons**, to ensure no unwanted side reactions occur
- Add 10-25 mol% **hydrogen** in small steps into circulating gas to prevent catalyst oxidation and sintering
- Introduce **steam** if heating has been done with nitrogen and steam has not already been added. The steam should initially be vented to atmosphere before cutting in, thus minimising condensation onto the catalyst bed
- Introduce **process feed**, maintain safe steam:feed ratio
- Ensure feed lines have been **drained and warmed** to avoid carry forward of condensate onto the bed

Good monitoring of the pre-reformer is vital

Detecting and resolving problems early to maximize value for a catalyst charge

Feed composition

Gas and LPG feeds

- Full composition
- Level of impurities

For naphtha feeds

- PONA analysis
- Level of impurities
- C/H ratio and molecular weight
- FBP

Operating conditions

- Temperatures inlet and outlet the bed
- Temperature profile through the bed
- Gas analysis inlet and outlet bed
- Feedstock and steam flows inlet bed
- Bed pressure drop trend
- Purification beds analyzed

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Good monitoring of the pre-reformer is vital

Detecting and resolving problems early to maximize value for a catalyst charge

Pre-reforming requires a **high activity** catalyst. High activity catalysts are more sensitive to **poisons and fouling**

Careful monitoring of a pre-reformer allows problems to be **detected and rectified** early, thereby **minimizing impact on the pre-reforming catalyst life**

Sulfur

Poisoning via sulfur can lead to a rapid loss in active bed volume and the poisoning is not reversible as it is for primary reforming

Fouling/Oxidation/Wetting

Oxidation of reduced catalyst, agglomeration by wetting and fouling by carbon, can lead to a loss in performance which may be resolved by skimming or other

Remnant life

Careful monitoring the pre-reforming performance is important to determine the remnant life and help with planning for changeouts

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Reaction temperature profiles

By monitoring the movement and shape of the temperature profile we can:

1. See if there is **sulfur poisoning**
2. See if there is **excessive nickel sintering**
3. See if there is **mal-distribution**
4. See if there is **carbon laydown**
5. Determine what **corrective action** is needed

But:

Plant rate changes will also **affect the shape of the temperature profiles** so this needs to be recognized too

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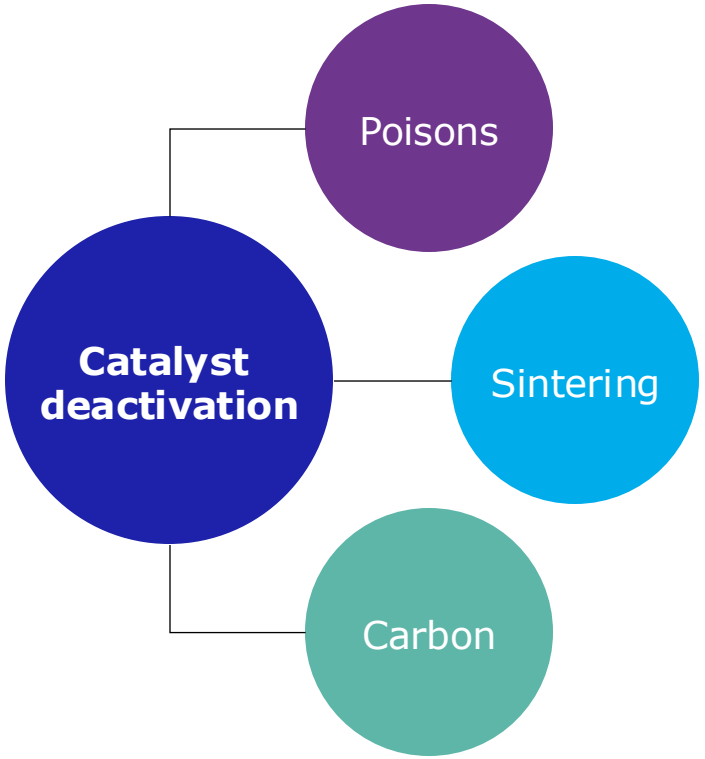
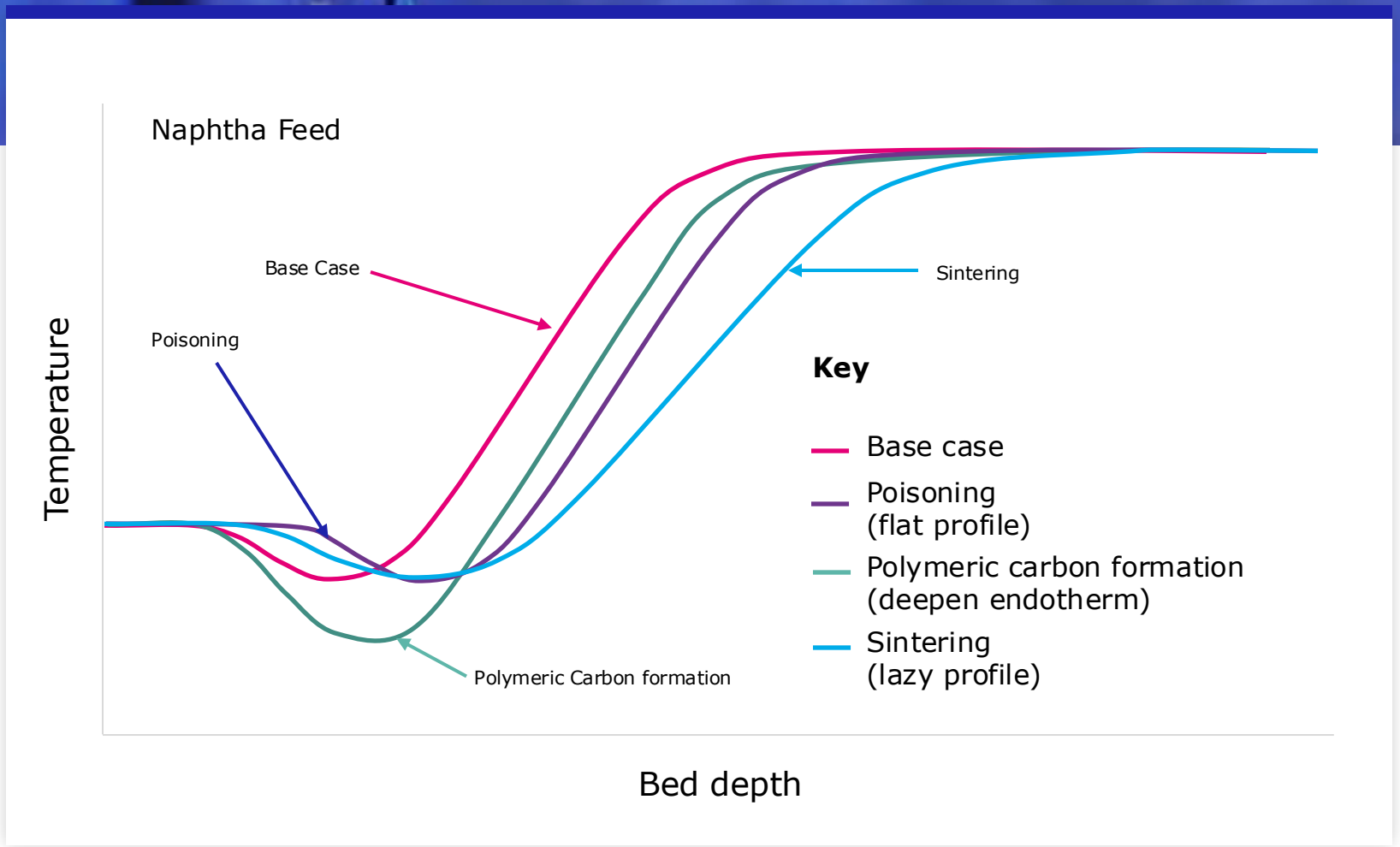
Managing catalyst deactivation mechanisms

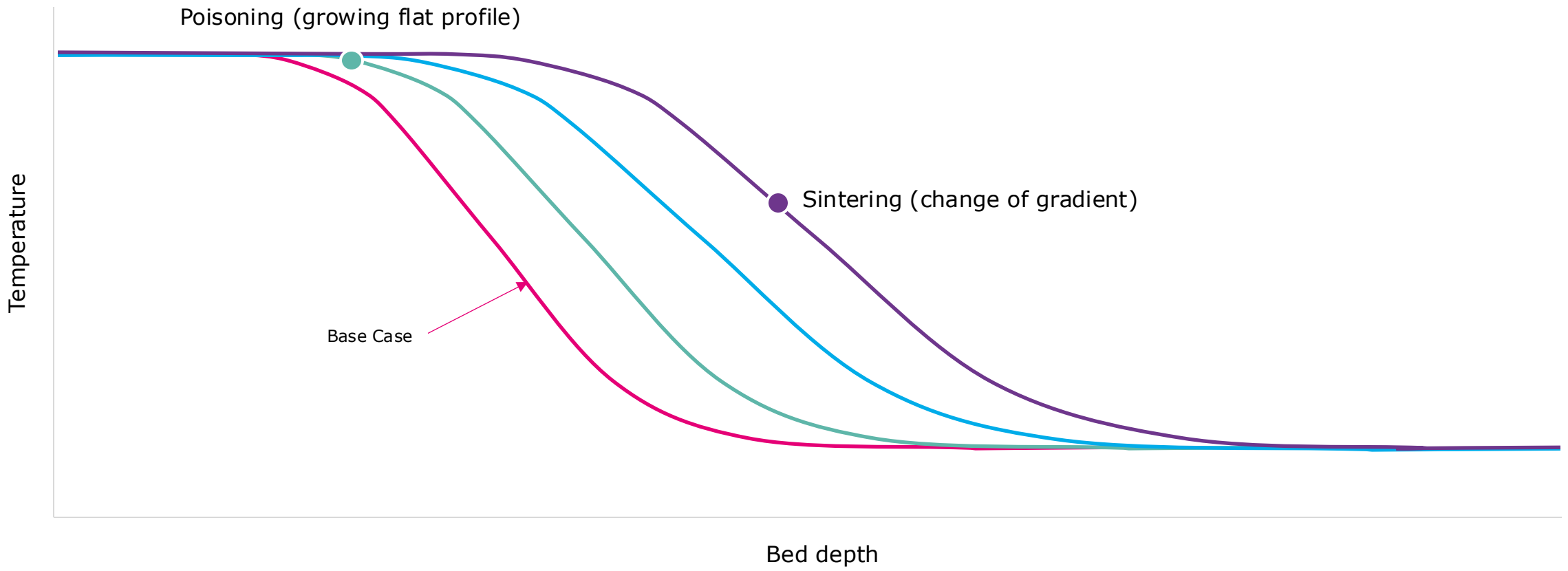
Pre-reforming requires high activity catalysts that perform at low temperatures





Temperature profile

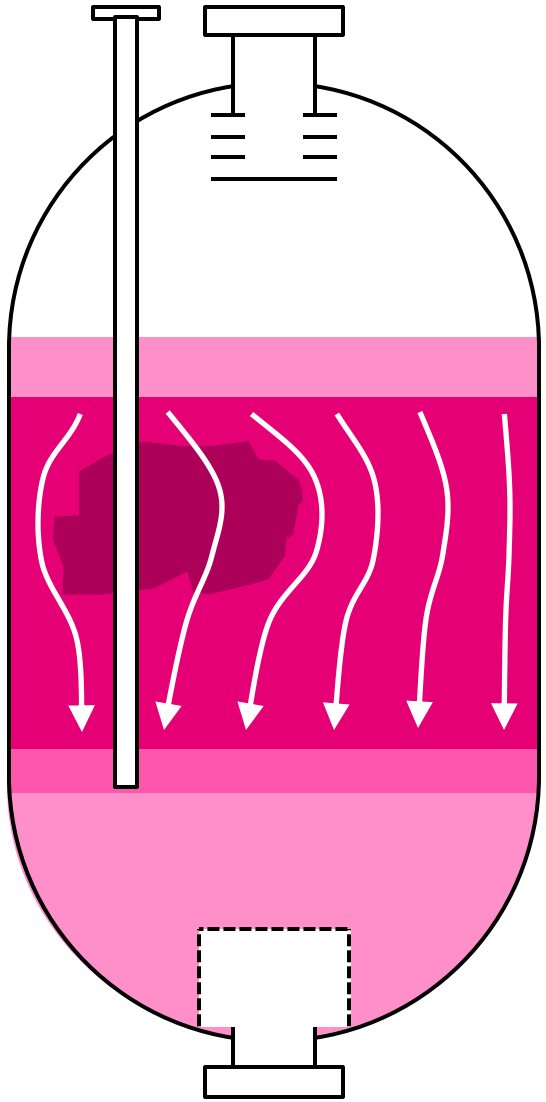
Natural gas



Temperature profiles

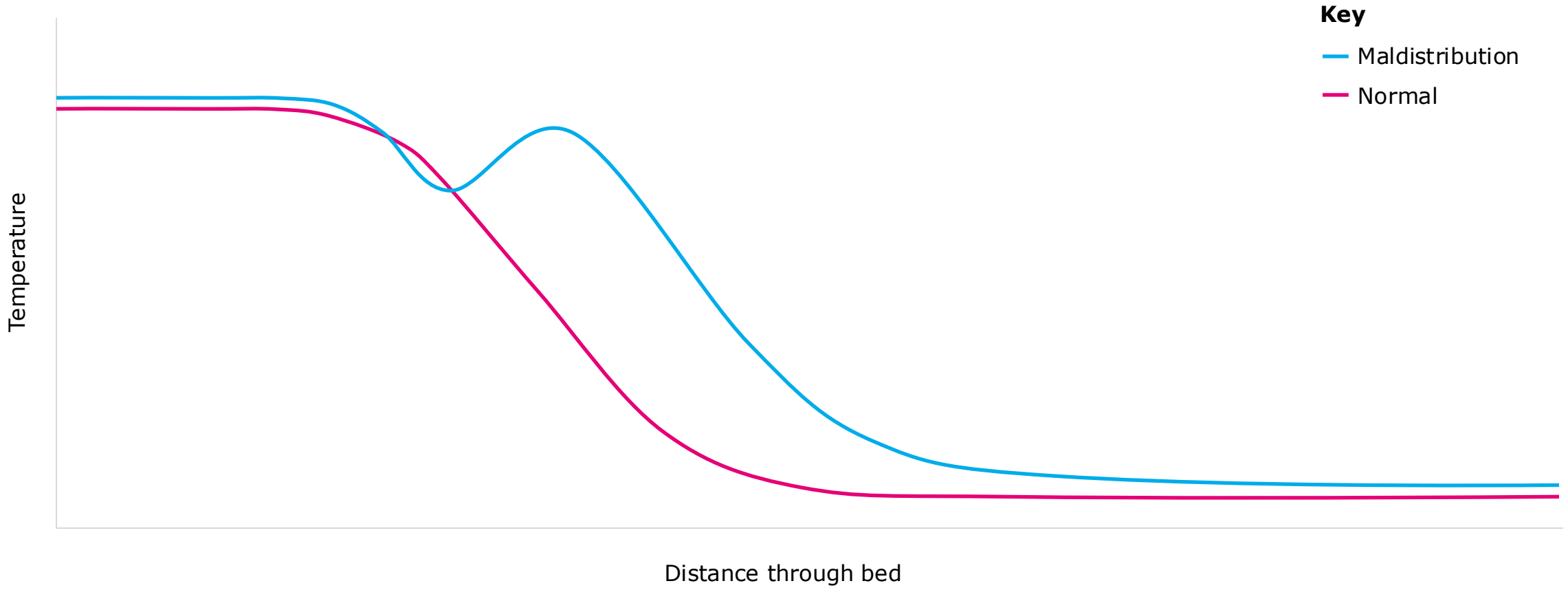
Maldistribution

Maldistribution due to wetting/agglomeration



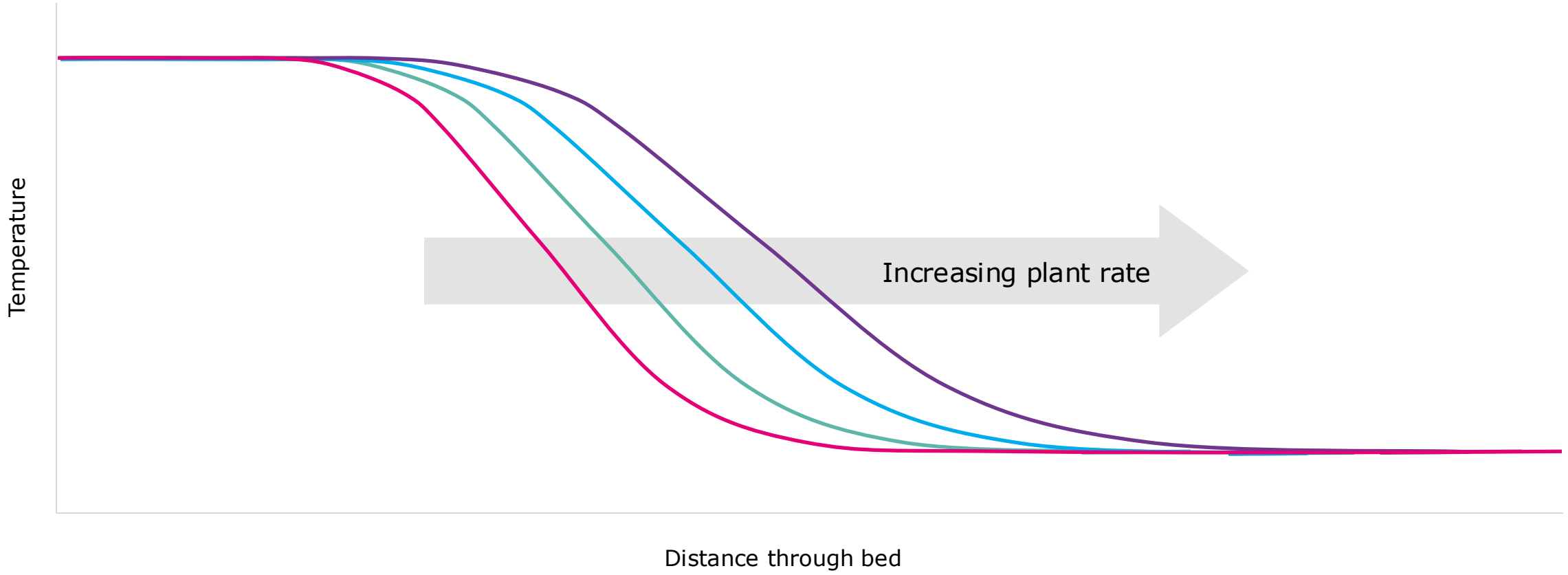
Temperature profile

Natural gas maldistribution



Temperature profile

Natural gas plant rate

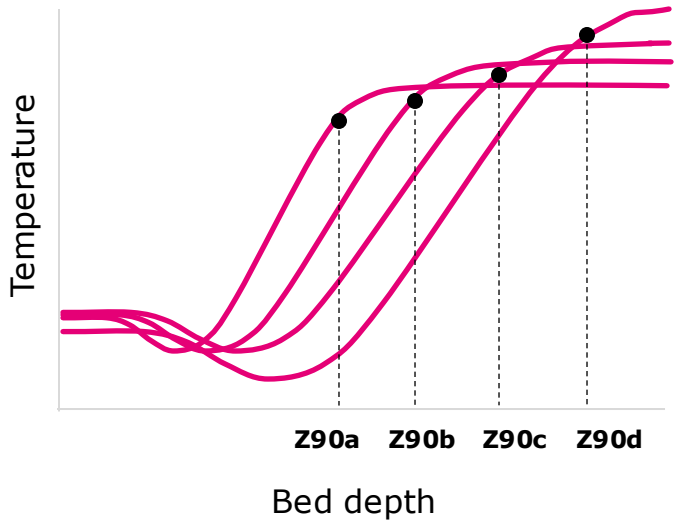


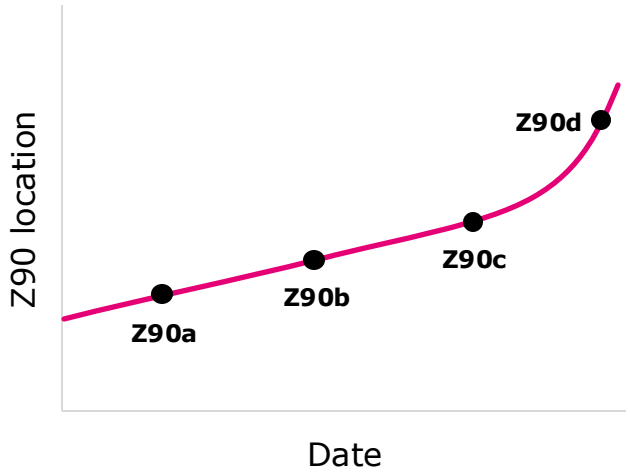
Best practice for pre-reforming catalyst management

Generally, the limit for the pre-reformer are:

- When **feed preheat or reheat limitations** are reached
- When **C_{2+} slip** is unacceptable for reforming catalyst

Waiting for ethane or higher hydrocarbon slip as an indicator for the need to change the catalyst is typically too late





Recommendations:

- Regularly record and **plot the temperature profile**
- Examine the profile for **poisoning, carbon polymer formation and sintering**
- Plot the end of the reaction zone against time. As the end of the reaction zone can be difficult to accurately locate, the **Z90** is commonly used. The Z90 is the position at which the temperature profile is at 90% of the overall change

Technical service model built around customers

Responsive and quality technical support

Global pool of engineers

We have a large community of engineers, with our strength in technical support a key highlight in customer feedback surveys

Subject matter experts

Our subject matter experts can provide deep insight to help define solutions to the most complex of problems

Local presence

Our engineers are physically located around the world and can respond expertly and swiftly, often in your local language

On site presence

We can bring our experts to your site to assist with loading, discharging, passivation, skimming, start-up and troubleshooting

Modeling tools

Our advanced modelling capabilities for pre-reforming enable us to provide you with optimized solution and performance predictions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