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Inspiring science, enhancing life

Americas Hydrogen and Syngas Technical Training Seminar

Autothermal/Secondary reforming

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Agenda

Secondary and Autothermal Reforming Concept

The secondary reformer in the ammonia plant plays an important role:

- Further converting methane (0.3 – 0.5% CH_4)
- introducing nitrogen into the process by the addition of air
- generate heat for HP steam in waste heat boiler
- helps down-size the primary reformer

Combustion of hydrogen provides the heat required to achieve a very low exit methane concentration

Oxygen fired autothermal reformers (ATR) are increasingly common in hydrogen and methanol plants

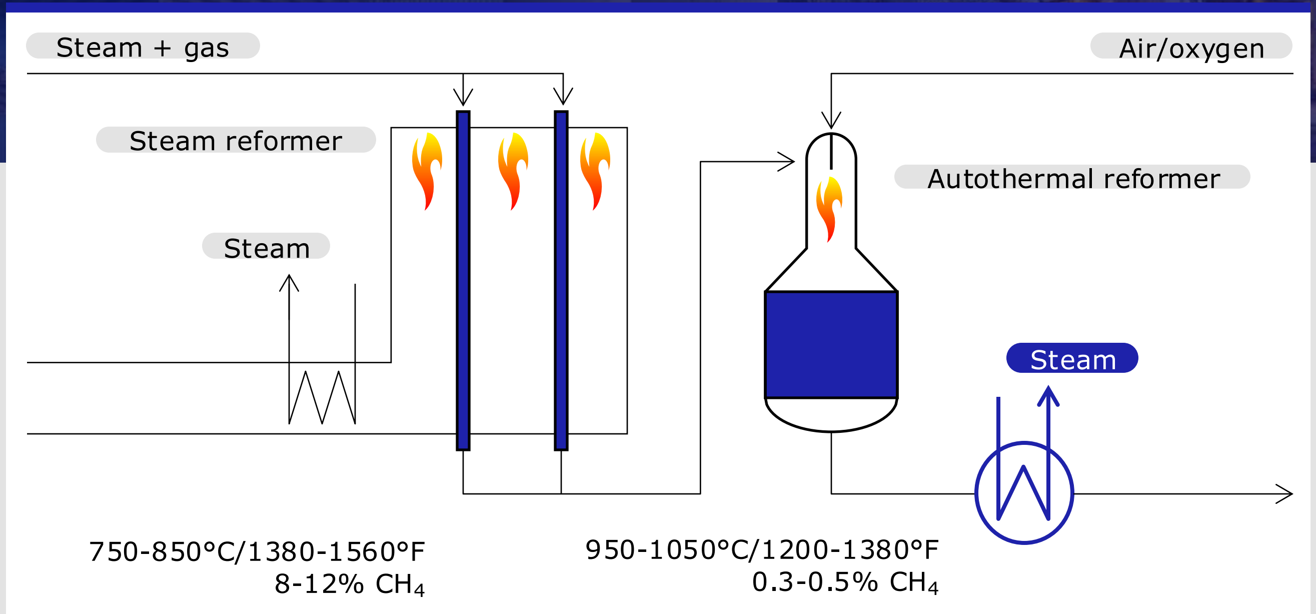
- Helps reduce capex in larger plants by reducing the required duty of the primary reformer
- Enables alternative feeds such as coke oven gas

Brings several benefits

- Low methane slip due to high temperature
- Stoichiometric synthesis gas for ammonia.

Typical Reactions and Reforming configuration

Combustion	$2H_2 + O_2 \Rightarrow 2H_2O$ $CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$	**Exothermic**
Steam reforming	$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$	**Endothermic**
Water gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$	**Slightly exothermic**



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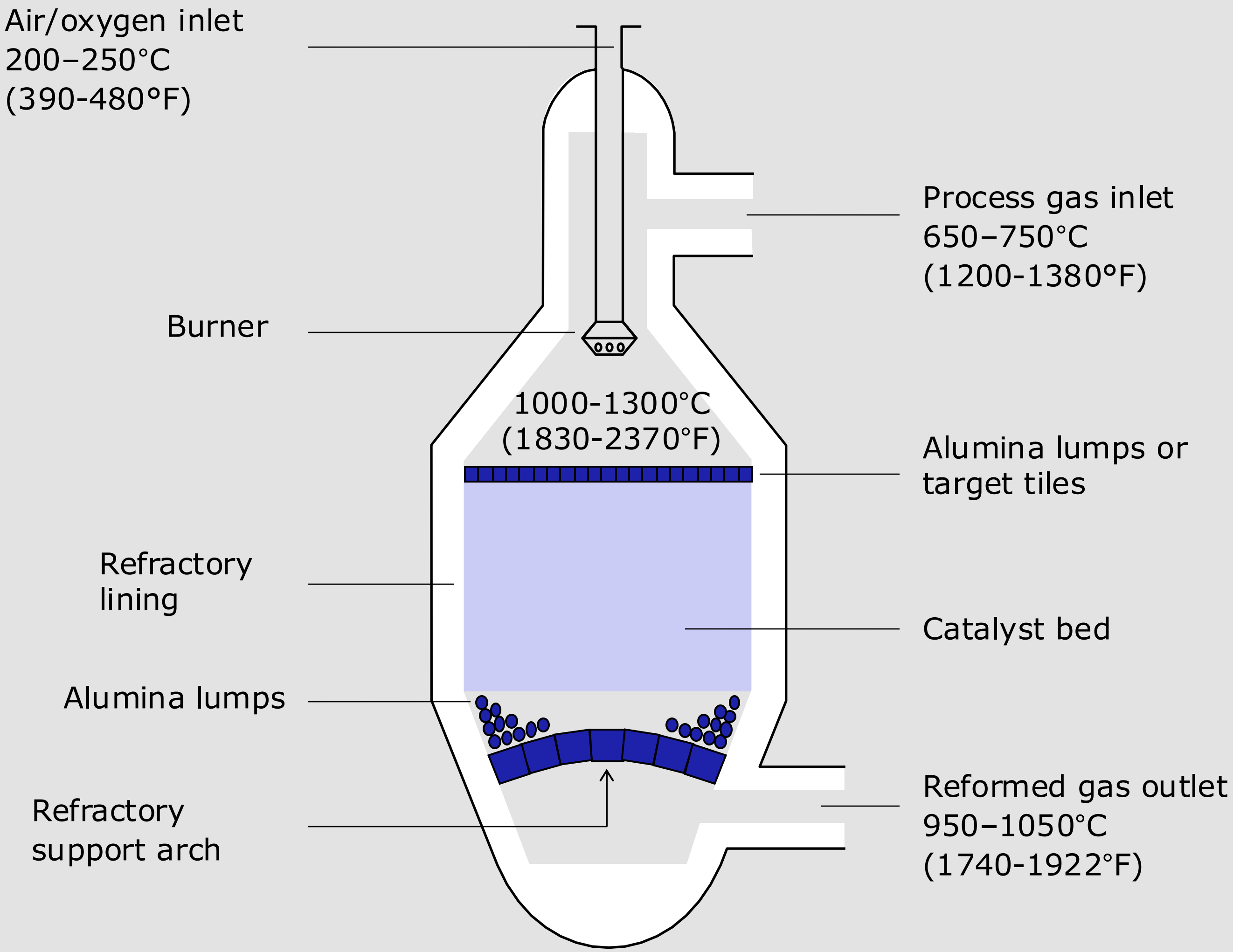
Vessel details

Mechanical features

1. Refractory lined pressure shell
2. Water jackets to keep shell cool
3. Combustion section in upper region
4. Fixed catalyst bed in lower region
5. Catalyst supported on brick arch

Loading features

1. Alumina hold-down lumps or tiles
2. Guard layer of large pellets of used
3. Main bed of standard catalyst



Autothermal Reformer Burners

Burner design and mixing volume

Air/oxygen injected at **high velocity**	**Forces mixing** of air and process gas	Combusts only **20%** of process gas	Must also mix in other **80%**	Should achieve a **uniform mixture**	Catalyst bed can affect **flow patterns**

Burner Design - Minimising the potential for damage

Combustion occurs in vessel neck

No risk of overheating catalyst bed

Reduces radiant heating of burner

Creates intimate mixing of gas and oxidant

Simple design of burner

No complex nozzles/swirlers

Self-cooled by oxidant flow

Oxygen Firing

Mass flow of oxygen = 20% of air

Oxygen jet creates **all the mixing**

Mixing more difficult with oxygen

Burner tends to use **higher velocities**

Oxygen can burn materials

Need to use **higher alloys** for burners

Higher flame temperatures result

More **arduous duty** for refractory lining

Alumina vaporisation can occur

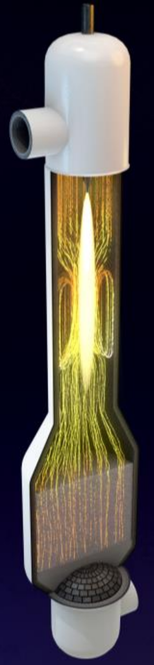
Efficient Combustion

Expertly designed for maximum throughput and minimum downtime

A clever and reliable “long neck” design which **maximises throughput** and **uptime**

Velocity control

Temperature control



High velocity

Aids feed and O_2 **mixing**

Low, uniform velocity

Prevents catalyst bed **movement**

No need for expensive heat shield **target tiles**

Full combustion

Perfect mixing of flame and process gas

Uniform temperature

Protects the catalyst from overheating

Avoids alumina **vaporisation** issues

A simple, **low-maintenance burner** with **exceptional performance** and **long life**

Simple and low maintenance

No complex nozzles or swirlers that may become blocked or damaged and lead to premature failure

Self-cooled by oxidant flow – No need for additional external cooling

12 years life with no maintenance

Optimised position in the reactor, protected from high radiant heating

Excellent performance

Delivers almost perfect mixing

40% turndown and even lower

Poor Gas Mixing

01
Gas contains hydrogen, mixes with oxygen

Gas feed >630°C (1165°F)

02
Ignites automatically

Auto-ignition >615°C (1140°F)

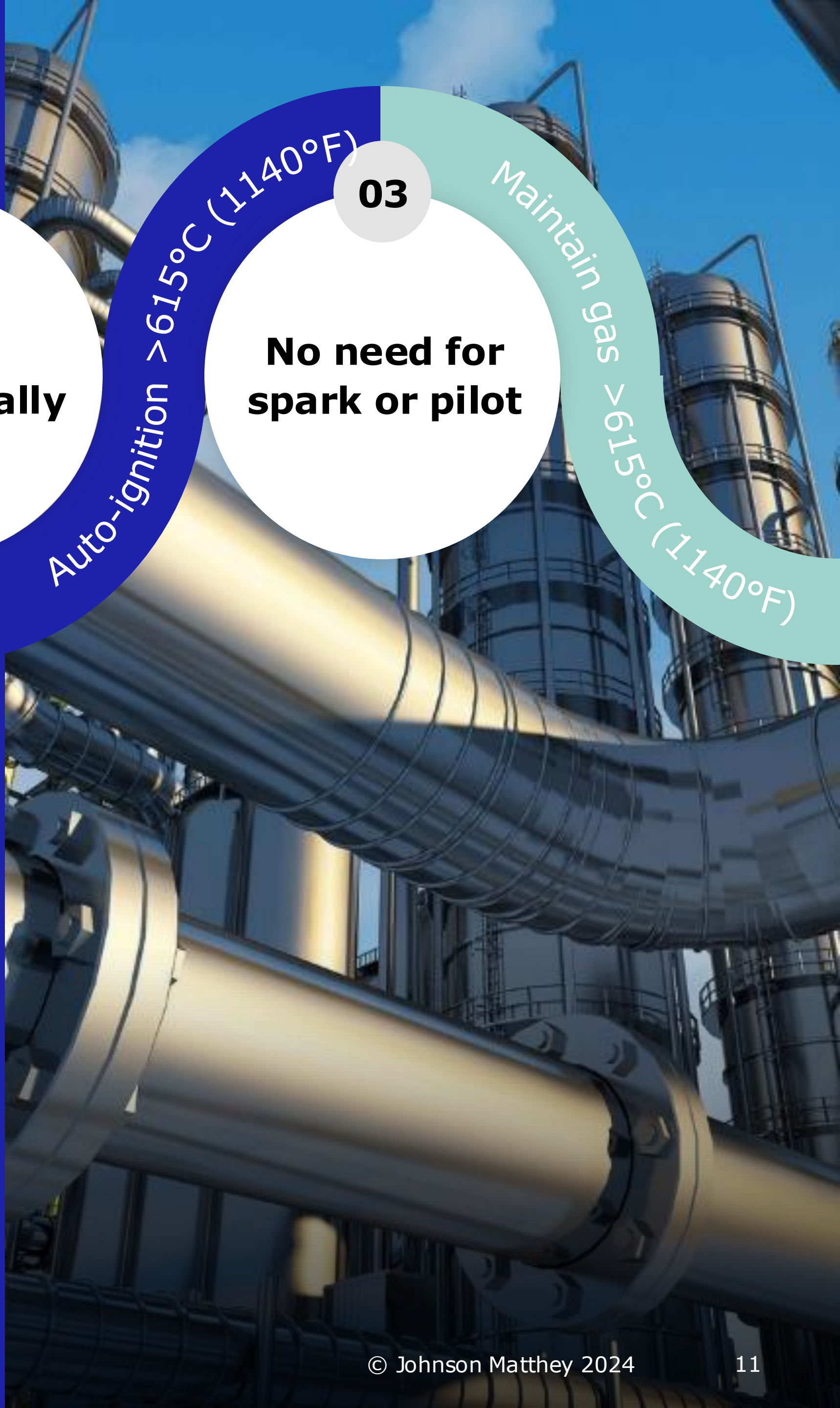
03
No need for spark or pilot

Maintain gas >615°C (1140°F)

Poor mixing in mixing zone gives **high approach** and **high methane slip**

Poor mixing can be due to

- Poor burner design
- Incorrect installation
- Insufficient mixing volume
- Burner gun failure



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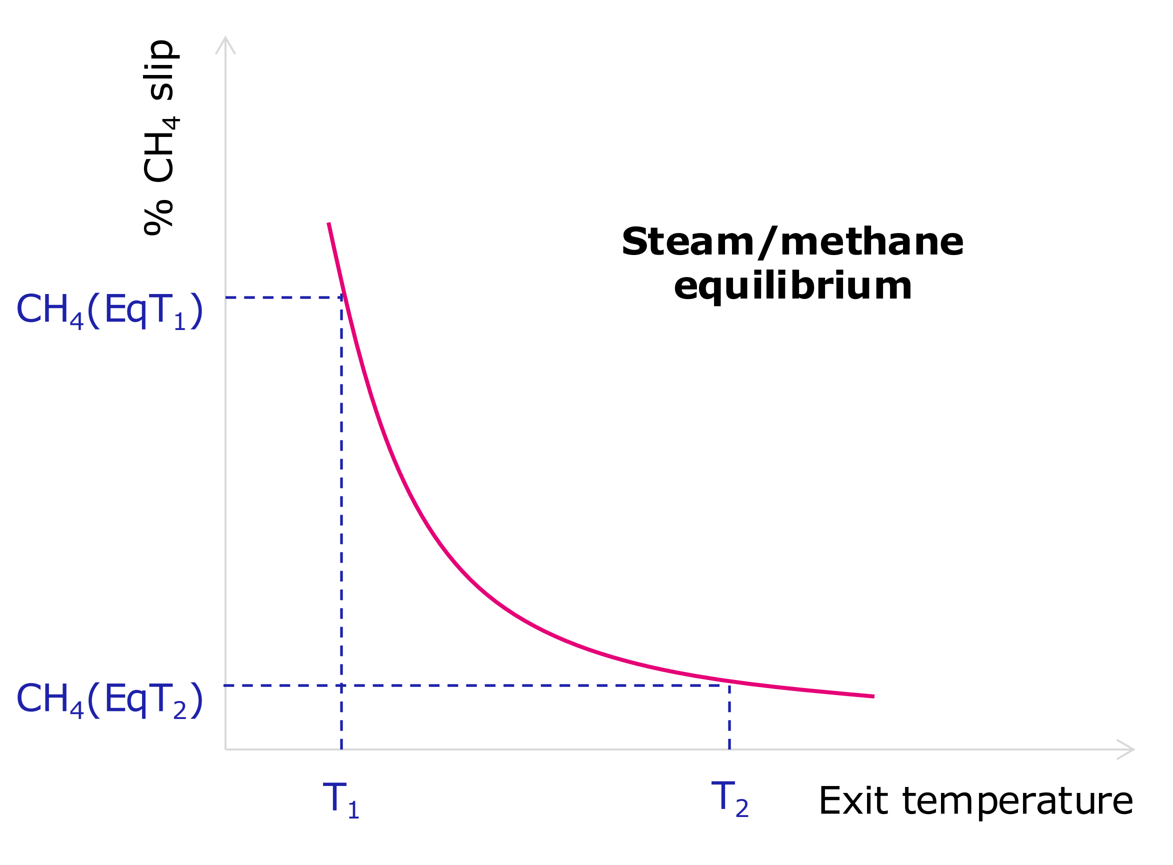
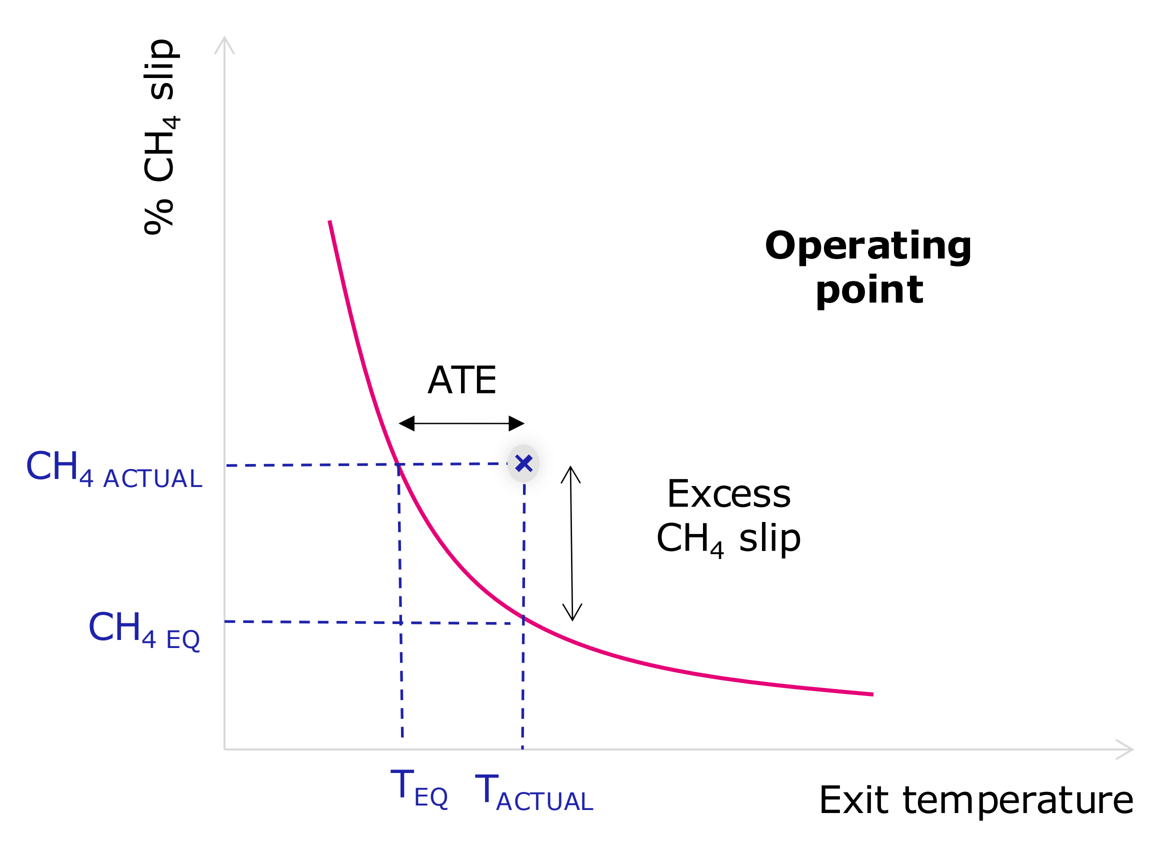
Inefficiency caused by poor process gas mixing in the catalyst bed





Effects of Poor Performance

Poor performance with 20-50°C ATE →

For **1 extra** mole CH_4 after secondary 4 moles H_2 are lost in the reformer and shifts

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

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

4 moles H_2 would form 2.66 moles NH_3

Value depends on whether the syn loop has hydrogen recovery

Value of reducing CH_4 slip by 0.1% on a 2000tpd ammonia plant

With H_2 recovery - approx. 14tpd ammonia

Without H_2 recovery - can be >30tpd ammonia

Minimise the autothermal reformer performance issues by following good practice in:

- Design and installation of burner
- Regular burner inspection and maintenance
- Right selection of refractory, catalyst, holddown and supports
- Maintain mixing zone length

Even skimming a bed can be costly in lost production time

- **30 hrs** to shut-down, cool and purge system
- **3 days** to effect entry, clear fouled catalyst, inspect and re-charge
- **30 hrs** to restart and be back on spec at rate

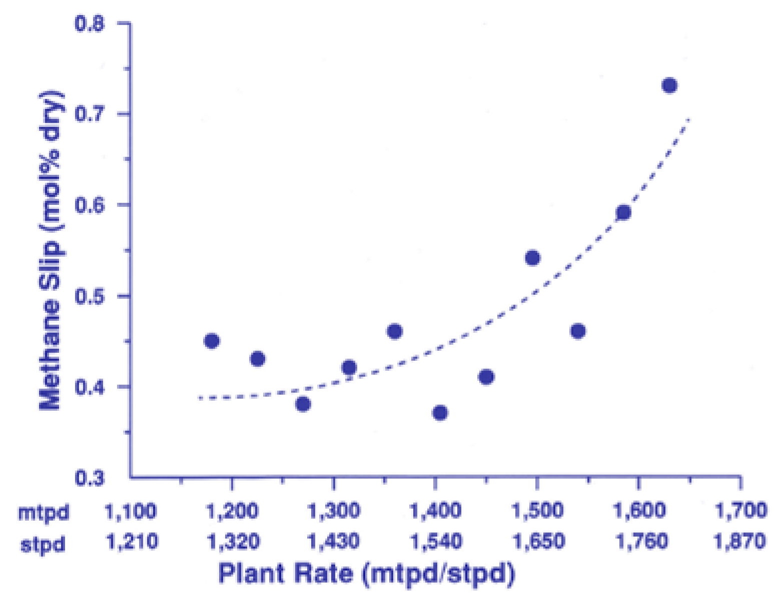
Case study – Reduced Performance due to poor mixing

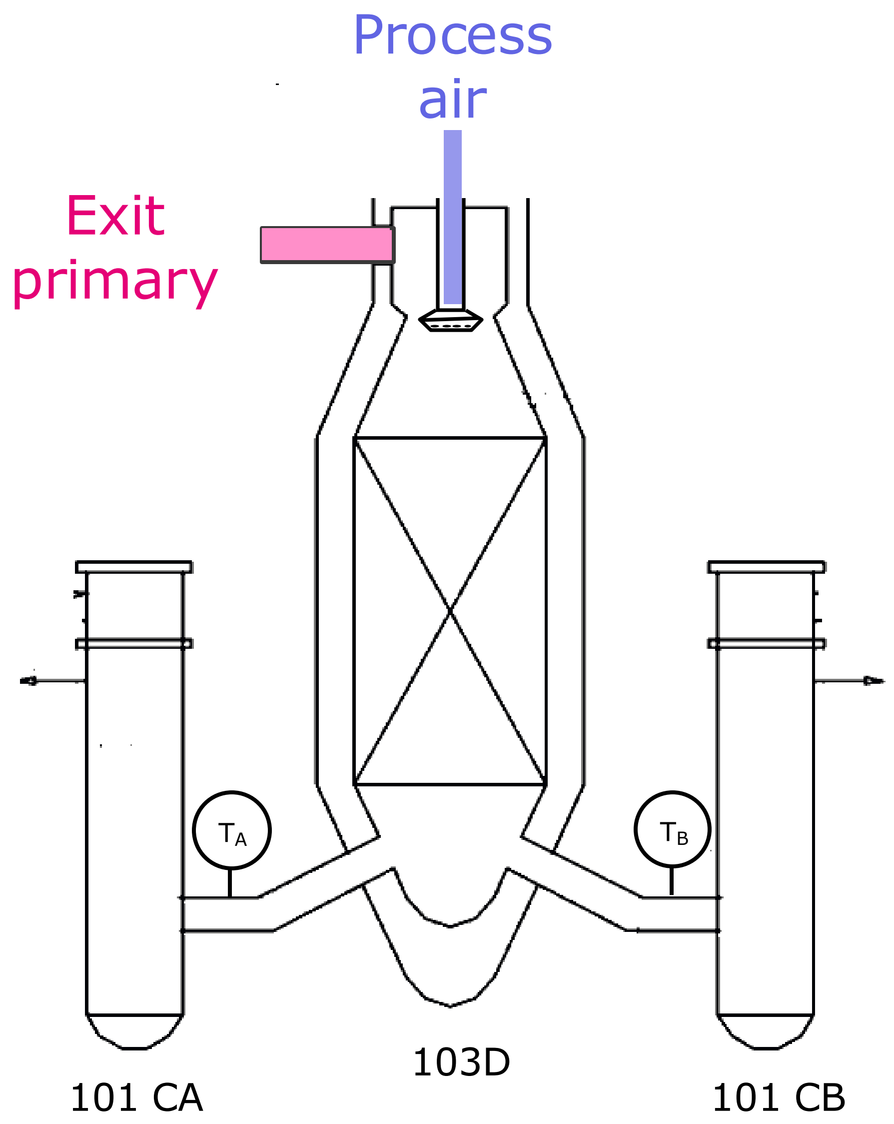
Standard Kellogg design ammonia plant

- 1960’s vintage, operating above design capacity

As rate increased

- Exit temperature to boilers 101-A/B diverted
- Methane slip increased



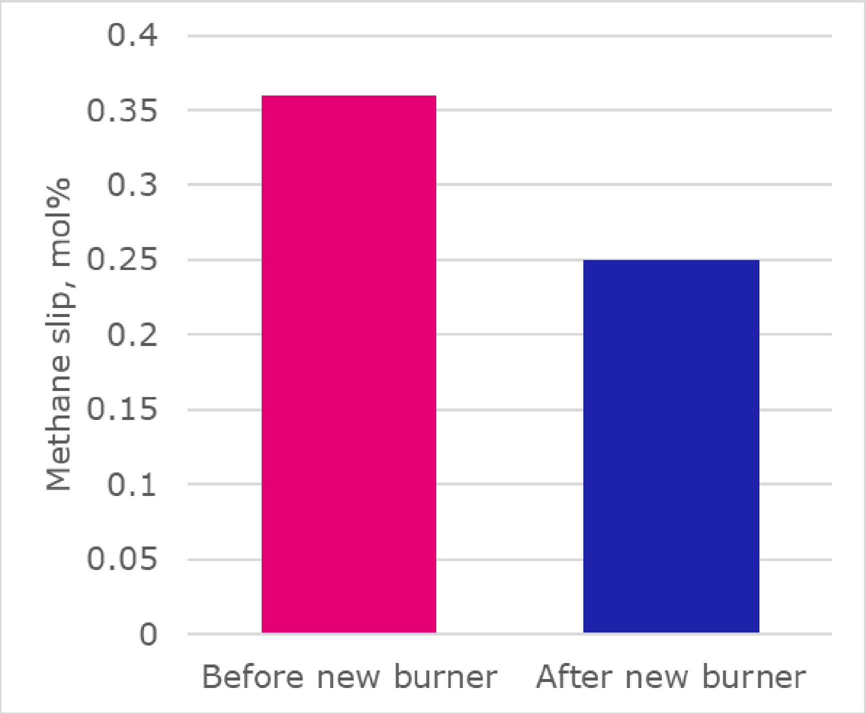


Case study - Improved Performance due to installation of new burner and catalyst

Ammonia plant installed both the Johnson Matthey high intensity ring burner and a short load of **QUADRALOBE™** catalyst

On restart the methane slip from the secondary reformer was reduced from 0.36 to 0.25 mol%

- Improvement allowed for a production increase of 15 mtpd
- Increased production at US$ 150/te margin, worth **US$ 820,000/year**



Alumina vaporization

Alumina reacts with steam →	$Al_2O_3(s) + 3H_2O(g) \rightleftharpoons 2Al(OH)_3(g)$	
As hot gas flows through target tiles and top catalyst →	Forward reaction occurs	
	$Al_2O_3(s) + 3H_2O(g) \rightarrow 2Al(OH)3(g)$	
	Alumina removed from top of catalyst bed	
	Gas becomes saturated with aluminium hydroxide	
As gas cools in the catalyst bed →	Reverse reaction occurs	
	$2Al(OH)3(g) \rightarrow Al_2O_3(s) + 3H_2O(g)$	
	Alumina crystallises out on colder catalyst surfaces	

Effects of alumina condensation:

- Increase in pressure drop
- Loss in activity due to physical binding of catalyst
- Maldistribution of process gas through ed, impacting efficient use of the catalyst
- Fouling of downstream waste heat boiler
- Difficulty in discharging the catalyst

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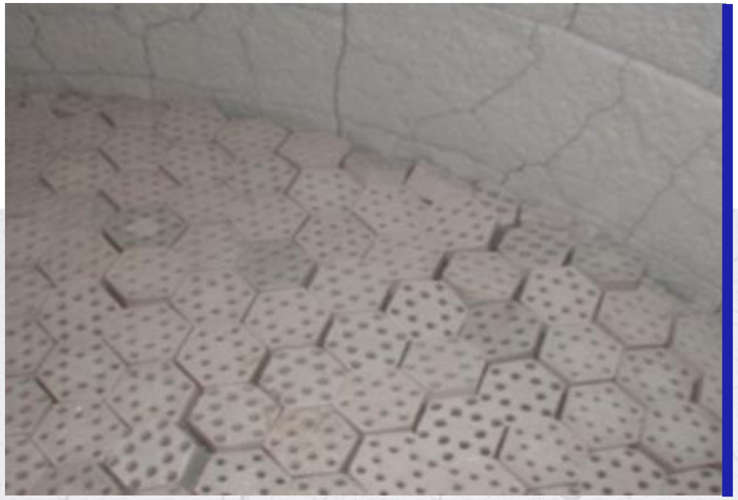
Signs of alumina vapourization



Target tiles
after operation

Vaporized tiles and
large catalyst

Severe fouling
of main bed

Ruby formation on
holddown material

Startup and Shutdown

1 Maintain **auto-ignition conditions within ATR**

2 Maintain **control during ignition – start-up**

3 **Control and trip system** design – **shut-down**

4 No **steady-state fired heater** requirement

ATR catalysts – requirements

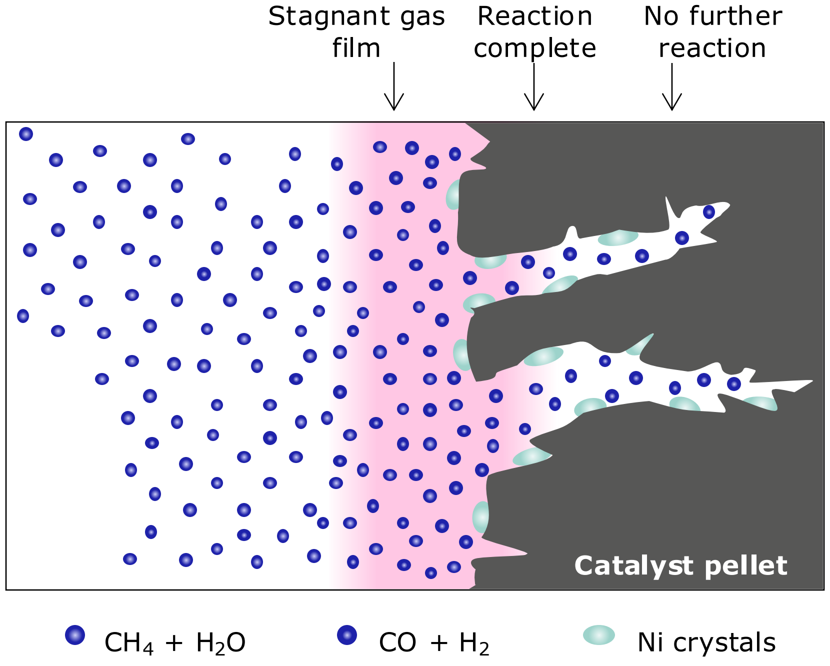
Four key requirements

1. **Low** pressure drop
2. **High** activity
3. **Chemical** stability
4. **Mechanical** stability

Increased severity of conditions

Oxygen firing
Reduced steam ratios
Higher exit temperatures
Higher space velocities

Activity ∝ geometric surface area (GSA)



Reaction at catalyst surface – **very fast**

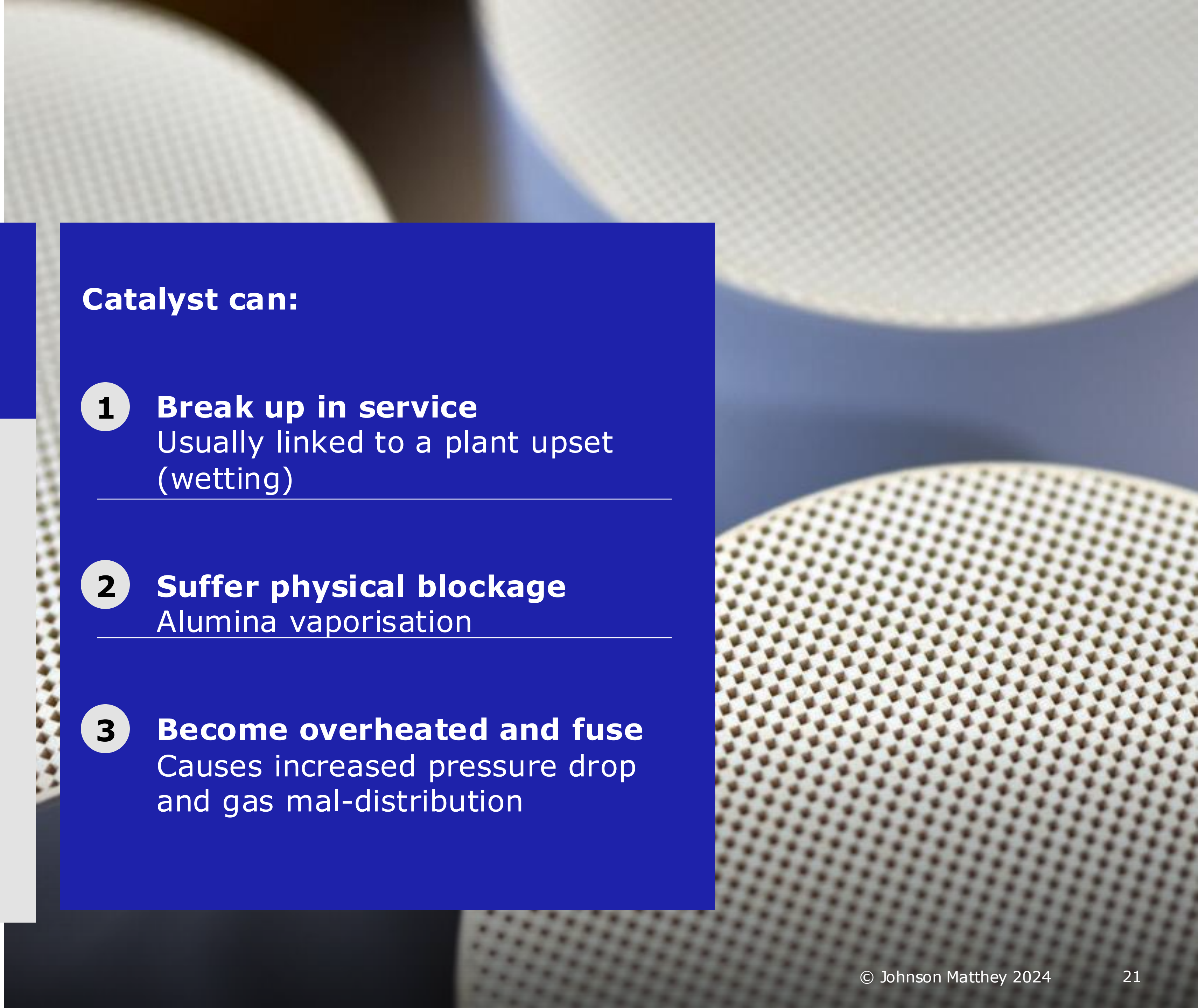
Diffusion through gas film – **slow**

Catalyst Deactivation and Breakage

Catalyst is exposed to very high temperatures

Nickel sintering is the main deactivation mechanism of the catalyst

Most poisons pass straight through the catalyst bed



Catalyst can:

1. **Break up in service**
   Usually linked to a plant upset (wetting)
2. **Suffer physical blockage**
   Alumina vaporisation
3. **Become overheated and fuse**
   Causes increased pressure drop and gas mal-distribution

Johnson Matthey Secondary Reforming catalysts/inert material

Catalyst solutions

KATALCO 54-series
Catalyst of choice for sec. reformers

KATALCO 23-series
Catalyst of choice for ATRs

KATALCO 28-series
Higher activity catalyst

KATALCO 89-series
Advanced protection catalyst

Hold-down and supports

KATALCO 90-series
Hold-down alumina lumps

KATALCO 23-8EQ
Active hold down

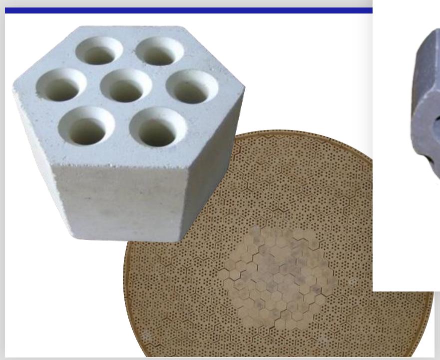
KATALCO 92-series
High purity alumina support balls

KATALCO 94-series
Alumina and zirconia tiles

QUADRALOBE catalysts

Provide the best combination of

1. Activity (maximum GSA)
2. Thermal stability
3. Mechanical strength/ Low PD



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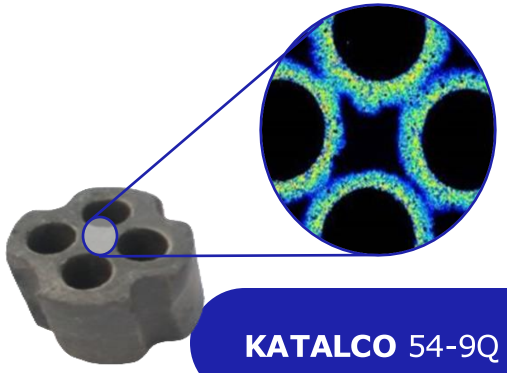
Superior Performance with **KATALCO** 54-9Q



An innovation in Secondary Reforming catalysts

The high temperatures in ATR and secondary reformers means that the reaction happens in a concentrated diffusion film.

Johnson Matthey are the only catalyst supplier with an egg-shell Secondary Reforming catalyst. The patented technology allows 20-25% higher activity over conventional catalyst due to improved metal distribution and active site accessibility.

Ammonia plant secondary reformer performance after 6 years on line		
	100% **KATALCO** 54-8Q	50% **KATALCO** 54-8Q 50% **KATALCO** 54-9Q
Bed volume (m^3)	12.0	12.0
Outlet T (°C)	979	978
CH4 slip (mol%)	0.36	0.34
ATE (°C)	2.7	2.0
dP (bars)	0.13	0.13

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Johnson Matthey experience and innovations

JM's ATR technology is well proven

>40yrs experience with ATRs

Rugged/reliable designs with low maintenance input

Experience with **23 operating ATRs**

Experience with **12 O_2 fired units**

- Only ATR where air and O_2 firing use the same design

JM's ATR catalyst is well proven and world leading

Avoids alumina vaporisation and condensation

Long term thermal and mechanical stability

8 year lives with little pressure drop build up

Developed the design in late 1960s

Uses a **unique design**

Developed **in house**

Used on **all ICI plants for >30 years**

Gives **almost perfect mixing**

Exceptional operability record

Very little maintenance required

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