Johnson Matthey Inspiring science, enhancing life

Americas Hydrogen and Syngas technical training seminar

Autothermal and secondary reforming

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Autothermal reforming

The secondary reformer in the ammonia plant plays an important role in further converting methane from the primary reformer and introducing nitrogen into the process by the addition of air



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

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

Autothermal reformer purpose

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

Reduce methane slip to very low levels ~0.3-0.5% mol dry Helps down-size the primary reformer

For ammonia plants provide nitrogen

Generate heat for HP steam in waste heat boiler



Autothermal reforming reactions

	$2H_2 + O_2 \rightarrow 2H_2O$
Combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Steam	
reforming	

 $CH_4 + H_2O \rightleftharpoons 3H_2 + CO$

Water gas shift

 $CO + H_2O \Rightarrow CO_2 + H_2$

> Exothermic

Endothermic

 \rightarrow

 \rightarrow



Typical reforming configuration





Feedstock types

Natural gas	Preformed natural gas	Reformed gas exit SMR (secondary reforming)	Mixed natural gas and reformed gas exit SMR	
Coke oven gas	Coal gasifier syngas	Methanol loop purge gas		



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 if used
- 3. Main bed of standard catalyst

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Reformer burners for ATRs

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
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Key components: burner gun

Burner alloys must handle the heat, and oxidant drives the mixing. Both are more challenging for pure oxygen feed Good mixing is absolutely essential

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

Root cause can be checked with CFD



Alumina vaporization can occur from maldistribution

Alumina reacts
with steam $AI_2O_3(s) + 3H_2O(g) \Rightarrow 2AI(OH)3(g)$ 1 \rightarrow As hot gas flows
through target
tiles and top
catalystForward reaction occurs $AI_2O_3(s) + 3H_2O(g) \rightarrow 2AI(OH)3(g)$ AIumina removed from top of catalyst bedAIumina removed from top of catalyst bedGas becomes saturated with aluminium hydroxide

As gas cools in the catalyst bed Reverse reaction occurs

 $2AI(OH)_3(g) \rightarrow AI_2O_3(s) + 3H_2O(g)$

Alumina crystallises out on colder catalyst surfaces

Leads to an increase in pressure drop and maldistribution of the process gas, impacting efficienty and production rate.

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Effect of alumina condensation



Difficulty in discharging catalyst



Target tiles



Vaporized tiles and large catalyst



Severe fouling of main bed



Rubies













Value of good performance

Poor performance with 20-50°C ATE



 CH_4 slip up by ~0.1–0.3%

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 CH₄ slip by 0.1% on a 2000tpd ammonia plant

With H₂ recovery - approx. 14tpd ammonia

Without H_2 recovery - can be >30tpd ammonia

Cost of ATR catalyst bed skim

For a 3500tpd methanol plant (260MMSCD syngas), an ATR outage every 2 years to skim the top of the bed and replace with fresh catalyst to mitigate pressure drop rise may result in

30 hrs to shutdown, 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

(best case assumption wrt minimum downtime)

For a **\$100 gross margin** on a **\$350/te** selling price

Lost revenue = 145tph*142hr*\$100/te = \$2.06MM per event



Johnson Matthey secondary reforming catalysts/inert material

Catalyst solutions

KATALCO 89-series (PGM / Ceramic)
Precious metal advanced protection
KATALCO 54-series
Catalyst of choice for sec. ref.

KATALCO 23-series Catalyst of choice for ATRS

KATALCO 28-series For high temperature duties

Hold-down and support material

KATALCO 90-series Hold-down alumina lumps

KATALCO 23-8EQ Active hold down

KATALCO 92-series High purity alumina support balls

Quadralobe catalysts

Provide the best combination of

Activity (maximum GSA)

Thermal stability



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Mechanical strength/ Low PD

Advanced protection with **KATALCO** 94-series and 89-series products



Catalyst

Fixed bed with multi-hole pellets



Maximise surface area/ unit volume

Standard Quadralobe reforming shape

Expected **4 year lives**

Majority of bed OK using Ni on Al_2O_3

Top of bed in ATR/O₂ fired units runs hot

Some risk of Ni/Al_2O_3 vaporization

Utilise PGM on specialized ceramic support

JM experience



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 O₂ 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

Johnson Matthey's autothermal reformer

Developed the design in late 1960s





JM ATR Burner Design

Completes combustion away from the catalyst bed

Combusts as it mixes

Combustion affects mixing rates must be taken into account

Mixing driven by **oxidant momentum and classic jet theory**

01

Oxidant jet expands entraining gas

02

Gas mixes rapidly into oxidant jet

03

Oxidant jet attaches to wall preventing gas bypass





01

Flame core limited radius

02 Combustion

complete in short distance

An ATR with exceptional performance and reliability



Innovative "long neck" design
Gives Perfect Mixing / Distribution
Protects catalyst and
maximizes production and uptime

A simple ATR burner with exceptional performance and reliability

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



Autothermal reformer

CLEANPACETM Hydrogen and Methanol Substitution of the SMR with GHR/ATR

All the high grade process heat is recycled to provide energy for reforming

JM's **LCH™** technology provides lowest carbon intensity

Feed gas ➤ Syngas (CO, CO₂, H₂) Interchanger Oxygen Gas heated reformer Autothermal reformer

GHR-ATR technology for optimised heat recovery

 Low cost of hydrogen production derived from lowest capex and highest feedstock efficiency
 CO₂ released in a single stream at high pressure – facilitates very high rates of carbon capture (> 95%)
 Carbon intensity below the low carbon hydrogen standards – ensuring long term viability of the asset

Confidence in technology deployment: technology proven at scale

Project execution and deployment: partnering for EPC execution & distribution. Design once, build many approach

