

# JM

# Steam reforming catalysts

Natural gas, associated gas and LPG

**KATALCO 23-series, KATALCO 25-series  
and KATALCO 57-series**

**Johnson Matthey**  
Inspiring science, enhancing life



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# Introduction

**Steam reforming is the key process in the formation of synthesis gas (syngas) for ammonia, methanol, hydrogen and hydrogen/carbon monoxide (HyCO) production.** The reformer is the largest and most expensive piece of equipment on these plants, and efficient and reliable operation is key to the performance of the whole plant

The choice of steam reforming catalyst is extremely important and has a significant effect on the reformer and performance. Choosing the correct catalyst has a direct impact on plant rate, tube life, methane slip and the formation of carbon, which can have a significant and detrimental impact on the reformer performance and operation.

Johnson Matthey (JM) is the world leader in steam reforming catalysts with **KATALCO™** and **KATALCO PERFORMANCE** products.

Our expertise is the result of our fundamental understanding of the steam methane reforming process. This has allowed us to develop market leading steam reforming catalysts that give flexibility and longevity in operation, along with recovery from plant upset conditions. Installing **KATALCO** catalyst allows operators to process a wide range of feedstocks, extend turnaround cycles and prolong reformer tube lives.

At the same time operators have the reassurance that the product can recover from both poisoning and carbon formation incidents due to its resistance to steaming. **KATALCO** catalysts are the product of choice for plants with highly stressed, uprated operating plants. Our product range also allows us to offer tailored solutions and customised loadings.

JM's customers recognise that having the right catalyst installed is only part of what makes plant operations successful and value our exceptional support, which is delivered through our global network of technical experts. These experts, along with our Research, Development and Engineering functions based in the UK, are able to deliver an unparalleled range of reformer based services.

In successfully developing **KATALCO** catalysts and services, we have also focused our knowledge to meet specific customer operational needs for all types of steam reformer from top fired to terraced, side fired, compact and gas heated reformers.

# KATALCO catalyst selector

JM manufactures three main catalysts for use in steam reformers using lighter hydrocarbon feedstocks ranging from refinery off gas, natural gas to lighter LPG.

## KATALCO 23-series

This catalyst is nickel oxide on an alpha alumina support.

## KATALCO 57-series

This catalyst is nickel oxide on a calcium aluminate support.

## KATALCO 25-series

This catalyst is a lightly alkalisied nickel oxide catalyst on a calcium aluminate support.

These catalysts are made in a range of sizes allowing optimum reformer loading for each individual plant.

Selecting the right catalyst for your application is essential for good steam reformer performance. JM will make detailed recommendations based upon your individual operating conditions. However, some generic guidelines are given below.

Typical catalyst loadings depend on the product being produced and the reformer type; however, some generalisations can be made to allow the operator to determine the optimal catalyst loading for a reformer. In general, it is necessary to use **KATALCO 25-series** catalyst in the inlet 40 - 50 % of the steam reformer tube where conditions are more difficult. This can be where the steam to carbon ratio is low, heat flux is high or there is a higher content of C<sub>2</sub>+ hydrocarbons. In these cases, the **KATALCO 25-series** catalyst will be loaded with either **KATALCO 23** or **KATALCO 57-series** catalyst in the remainder of the steam reformer tubes. At less severe conditions, these catalysts will be used throughout the steam reformer tube.

## Ammonia plants

Feedstock type	KATALCO PERFORMANCE catalyst recommendation
High methane content gas, design plant rates	57 or 23-series
Feedstock with significant levels of higher hydrocarbons	A combination of 25-series with 57/23-series
Low steam to carbon ratio, high methane content gas	A combination of 25-series with 57/23-series
<b>Plant limitation</b>	<b>Recommendation</b>
High pressure drop (high plant rates)	XQ, GQ and Q size combination
High tube wall temperatures	MQ and Q size combination
High methane slip	MQ and Q size combination

## Methanol plants

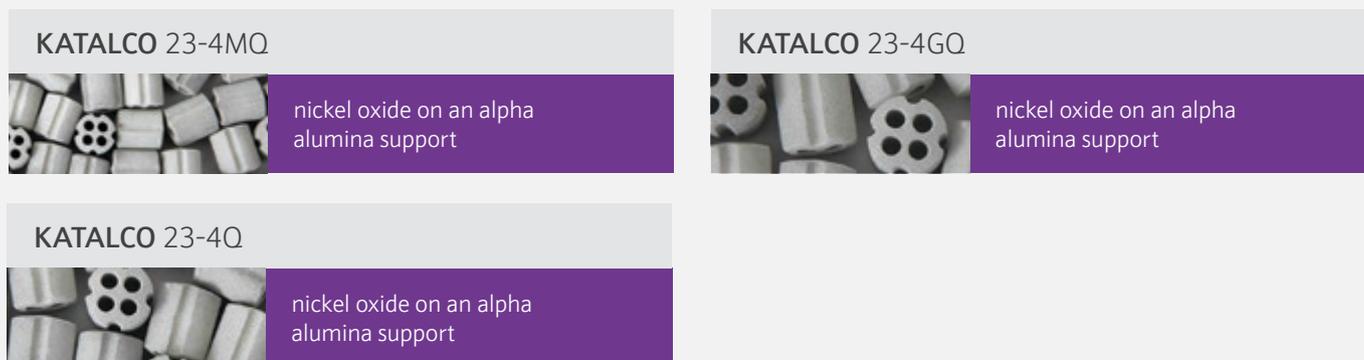
Feedstock type	KATALCO PERFORMANCE catalyst recommendation
High methane content gas, design plant rates	A combination of 25-series with 57/23-series
Feedstock with significant levels of higher hydrocarbons	A combination of 25-series with 57/23-series
Low steam to carbon ratio, high methane content gas	A combination of 25-series with 57/23-series
<b>Plant limitation</b>	<b>Recommendation</b>
High pressure drop (high plant rates)	XQ, GQ and Q size combination
High tube wall temperatures	MQ and Q size combination

## Hydrogen and HyCO plants

Feedstock type	KATALCO PERFORMANCE catalyst recommendation
Refinery off gas and high methane content gas, design plant rates	57 or 23-series
Natural gas with significant levels of higher hydrocarbons	A combination of 25-series with 57/23-series
Pre-reformed feedstock	57 or 23-series, optionally with 25-series for additional operability
LPG feedstock with high C <sub>3</sub> content and/or high steam to carbon ratio	A combination of 25-series with 57/23-series
HyCO production from natural gas or pre-reformed feedstock	A combination of 25-series with 57/23-series
<b>Plant limitation</b>	<b>Recommendation</b>
High pressure drop (high plant rates)	XQ, GQ and Q size combination
High tube wall temperatures	MQ and Q size combination

# Catalyst characteristics

## KATALCO 23-series



### Composition

Nickel oxide dispersed on an alpha alumina ceramic support, typically containing 17% NiO, 01. % SiO<sub>2</sub> and 0.05% SO<sub>3</sub>.

### Physical properties (typical)

Catalyst	23-4Q	23-4MQ	23-4GQ
Form (QUADRALOBE)	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges
Length (mm)	17	13	20
Outer diameter (mm)	13	10.5	16
Inner diameter (mm)	3.5	2.7	4.4
Typical loaded density (kg/m <sup>3</sup> / lb/ft <sup>3</sup> )	1090 / 69	1140 / 73	1050 / 67

### Important note

The loaded density values are typical values. Depending on reformer type, loading technique etc, actual achieved density may be different from these values. Also, if alternative shapes are provided by special arrangement, the density values may differ significantly and should be confirmed.

# Catalyst characteristics

## KATALCO 57-series



### Composition

Nickel oxide dispersed on a calcium aluminate ceramic support, typically containing 16% NiO, 01. 5% SiO<sub>3</sub> and 0.05% SO<sub>3</sub>.

### Physical properties (typical)

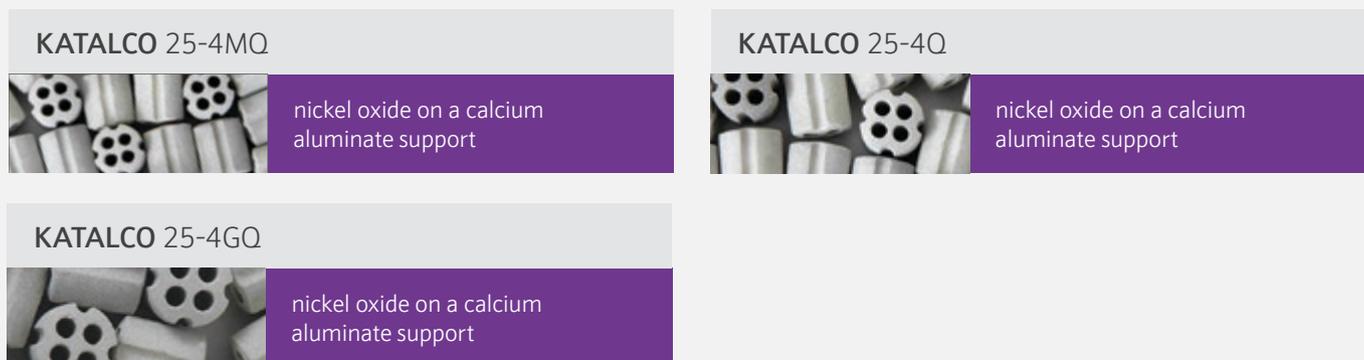
Catalyst	57-4Q	57-4MQ	57-4GQ	57-4XQ
Form (QUADRALOBE)	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges
Length (mm)	17	13	20	20
Outer diameter (mm)	13	10.5	16	19.7
Inner diameter (mm)	3.5	2.7	4.4	5.5
Typical loaded density (kg/m <sup>3</sup> / lb/ft <sup>3</sup> )	880 / 55	900 / 57	780 / 49	780 / 49

### Important note

The loaded density values are typical values. Depending on reformer type, loading technique etc., actual achieved density may be different from these values. Also, if alternative shapes are provided by special arrangement, the density values may differ significantly and should be confirmed.

# Catalyst characteristics

## KATALCO 25-series



### Composition

Nickel oxide dispersed on an alpha alumina ceramic support, typically including 18% NiO, 1.8% K<sub>2</sub>O, 0.15% SiO<sub>2</sub> and 0.05% SO<sub>3</sub>.

### Physical properties (typical)

Catalyst	25-4Q	25-4MQ	25-4GQ
Form (QUADRALOBE)	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges	4-hole cylinders with 4 flutes and domed edges
Length (mm)	17	13	20
Outer diameter (mm)	13	10.5	16
Inner diameter (mm)	3.5	2.7	4.4
Typical loaded density (kg/m <sup>3</sup> / lb/ft <sup>3</sup> )	870 / 55	950 / 60	790 / 50

### Important note

The loaded density values are typical values. Depending on reformer type, loading technique etc., actual achieved density may be different from these values. Also, if alternative shapes are provided by special arrangement, the density values may differ significantly and should be confirmed.

# Advantages of choosing KATALCO

## Catalyst selection for plant optimisation

Although many plants may have the same design conditions, the operation of each plant is unique, and depends on a variety of factors including the gas feed, the plant rate, steam to carbon ratio and operating pressure and temperature. These differences in plant performance are critical when it comes to the selection of a steam reforming catalyst.

**KATALCO 23-series** and **KATALCO 57-series** catalysts are non-alkalised high activity steam reforming catalysts suitable for light hydrocarbon feeds. **KATALCO 25-series** are lightly alkalised steam reforming catalysts, widely used to achieve longer life in problem plants with feedstocks containing higher hydrocarbons or operating under severe conditions. **KATALCO 25-series** are typically used in combination with non-alkalised catalysts for steam reforming natural gas.



JM is the world leader in steam reforming for the production of ammonia, methanol, hydrogen and HyCO for a very good reason. Not only is **KATALCO** the best commercially available range of steam reforming catalysts, but **KATALCO PERFORMANCE** is tailored for each plant on an individual basis in order to meet the operator's specific requirements. Our world-class reformer simulation programme, REFORM, allows us to accurately predict the exact performance of any given catalyst combination. Whether we recommend a combination of alkalised and non-alkalised catalysts or a variety of catalyst sizes you can have confidence in your plant performance.

## Reliability

The **KATALCO** steam reforming catalyst ranges have the well-earned reputation for delivering the world's most reliable reformer operation. They are physically strong to withstand plant upsets. The high activity of **QUADRALOBE™**, plus the tailored use of potash delivers carbon free operation in the most highly loaded plants. If carbon is formed the ability to remove it is greatly enhanced by the resistance of **KATALCO QUADRALOBE** catalysts to steaming and the acceleration of carbon removal by the potash promotion.

## Feedstock versatility

JM steam reforming catalysts operate with every normal feedstock processed using steam reforming technology. These include refinery off-gas containing hydrogen, natural gas, associated gas, LPG and naphtha. Feedstocks may also include recycled carbon dioxide.

**KATALCO 23-series** and **KATALCO 57-series** catalysts are designed for use on natural gas or hydrogen rich feeds. For more severe duties such as high reforming heat flux, low steam to carbon ratio, or heavier hydrocarbons feeds, catalysts must be selected with a higher resistance to carbon laydown. In these situations, the alkalised **KATALCO 25-series** catalysts are used in the upper part of the steam reformer tubes in conjunction with **KATALCO 23-series** or **KATALCO 57-series** unless the hydrocarbon feedstock is butane or heavier in which case alternative catalysts from the JM range are required.

### Long catalyst lives

**KATALCO QUADRALOBE** catalysts have delivered lives in excess of eight to ten years. Long catalyst lives are achieved through formulations that deliver high stable activity and the ability to recover from plant upsets. High activity is required at the top of the tubes to prevent carbon formation and at the bottom of the tubes (along with high heat transfer) to keep tube wall temperatures within acceptable limits. **KATALCO 25-series**, **KATALCO 23-series** and **KATALCO 57-series** catalysts are designed to maintain a high activity in steam reforming applications. Catalyst activity is unaffected by periods of prolonged steaming during plant upsets or frequent start-up or shutdown procedures. Low temperature activity is stable and ensures maximum reaction at the top of the tubes to minimise tube wall temperature in top-fired furnaces.

The alkali in **KATALCO 25-series** increases the margin against carbon formation and accelerates its removal during operation and steaming.

The **QUADRALOBE** shape further enhances activity and assists in reducing tube wall temperatures when compared with other commercially available shapes.

### Long tube lives

The major cost in running a reformer is tube replacement. Tube replacement costs are typically double the catalyst cost on an annualised basis. Tube lives can be halved by a 20°C (36°F) increase in temperature so catalyst activity and heat transfer are critically important. The high stable activity of JM steam reforming catalysts keeps tube temperatures low throughout their length. The **QUADRALOBE** shapes also achieve the highest heat transfer from the tube wall to the process gas. This is particularly important towards the tube exit since in most plants this is where the maximum tube wall temperature occurs.

### High plant rates

The high activity and low pressure drop of the **QUADRALOBE** shape enables plant rate increases with little or no penalty on tube wall temperature or methane slip. The JM REFORM program accurately simulates all standard reformer types and enables selection of the best catalyst formulation and size combination to achieve the desired operating conditions.

### Low pressure drop

Pressure drop across steam reformers is becoming increasingly important and is directly related to plant rate for many operators. **KATALCO 23-series**, **KATALCO 57-series** and **KATALCO 25-series** catalysts are available in a range of different sizes. Combined with their excellent activity, this allows optimised reformer loadings to minimise pressure drop.

The high strength of **KATALCO** steam reforming catalysts minimises the pressure drop increase during the catalysts life.

The introduction of **KATALCO 57-4XQ** offers the lowest pressure drop available.

### Strength

**KATALCO 25-series**, **KATALCO 23-series** and **KATALCO 57-series** catalysts have high stable strength during operation and retain more than 80% of initial strength after five years of operation.

### Low silica

In order to avoid all problems associated with silica migration, **KATALCO 25-series**, **KATALCO 23-series** and **KATALCO 57-series** catalysts contain the lowest possible levels of silica.

### Size range

All **KATALCO QUADRALOBE** catalysts are available in a range of sizes to suit individual requirements. All steam reformers are different, therefore the catalyst requirements vary from plant to plant.

MQ, Q and GQ sizes of **QUADRALOBE** have been optimised to give the same pressure drop as our previous 4-hole product, resulting in higher activity catalysts. The XQ size has been optimised to give the same activity and thus even lower pressure drop when compared to our 4-hole G size product. Hence, the **QUADRALOBE** catalyst range offers products with the highest activity and lowest pressure drop commercially available.

Using JM's expertise in steam reforming operations and detailed modelling capability, it is possible to optimise the performance of a given steam reformer by selecting the correct size range to give the required activity, heat transfer, and pressure drop.

## Ease of reduction

**KATALCO** 25-series, **KATALCO** 23-series and **KATALCO** 57-series catalysts are supplied with the nickel in the oxide form and so need reducing to become active. These catalysts are easily reduced in the plant using well-established procedures, advice on which is given in the appropriate JM operating manual.

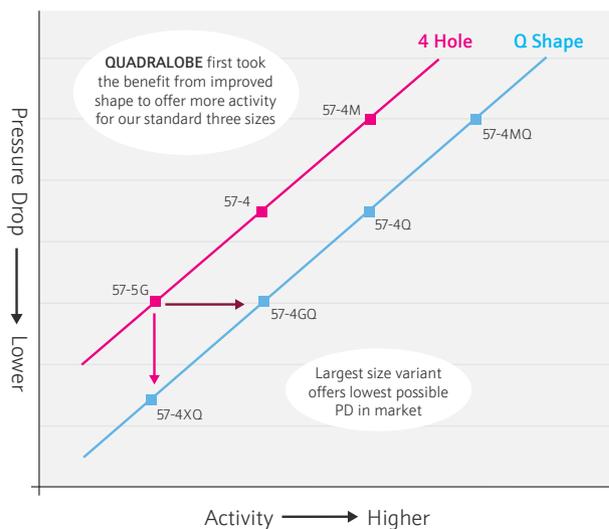
In rare cases where low reformer inlet temperature makes full reduction of the catalyst at the tube inlet difficult, catalysts can be supplied in the pre-reduced form.

The pre-reduced material is only required in the inlet 1-2m (3-6ft) of the reformer tube where the operating temperature is lowest.

## Stability

All **KATALCO** steam reforming catalysts will withstand typical plant problems, e.g.,

- short exposure to temperature in excess of 1000°C (1830°F)
- prolonged steaming at operating temperatures
- steaming to remove carbon deposited on the catalyst or to remove sulphur poisoning
- the effects of condensing steam



# Additional capability with **KATALCO Performance**

There are a variety of factors that determine what is most important to plant operators when it comes to optimising their plant performance. From feedstock costs to market dynamics and local legislation, each operating site is unique.

At JM we understand this, and we offer a range of services specifically designed to help you improve your plant operations, be it through higher efficiency, reliability or throughput. Our background in plant operations, together with our catalyst know-how, has made us the number one supplier of steam reforming catalysts and services world-wide.

We offer a unique range of services directly related to steam reformer operation, all of which are designed to improve your plant performance. JM will recommend the relevant products from the **KATALCO PERFORMANCE** portfolio to address the specific issues on your plant.



## **Reformer surveys and operational audits**

The optimal temperature to operate the reformer is a balance between maximising both methane conversion and the lifespan of the equipment.

JM's reformer surveys provide accurate tube wall temperature measurement – often a key performance indicator for the reformer - using the latest measurement techniques. This data is used in conjunction with detailed kinetic modelling of the reformer catalyst to check current performance versus expectations and generate future performance predictions. It can also be used to identify current or potential operational issues and provide a baseline for plant uprate studies.

JM offers several different types of reformer surveys from a quick health check of the reformer to a significantly more detailed assessment. Depending on their scope, these surveys use a JM optical pyrometer together with a gold cup contact thermocouple and/or a reformer imager (an unrivalled, portable, thermal imaging camera using near infrared temperature measurement technology).

The scope of the reformer survey is tailored to meet individual client situations and can be extended to include the convection section heat recovery and synthesis gas cooling train. If a reformer survey concludes that more detailed investigation is needed to solve a particular problem, JM has access to a wide variety of additional techniques that can also be employed. The combination of techniques selected is tailored to the specific problems to enable a targeted and comprehensive analysis of the issues.

## Steam reformer modelling - REFORM

Accurate modelling of steam reformers is critical for predicting reformer operation and determining the correct catalyst selection for any given plant. REFORM, the JM reformer simulation model, looks at all aspects of the steam reformer.

It models the flue gas side from the flame heat release, radiation from the flame, radiation from the gas, radiation from the wall of the furnace and radiation from the coffins. As well as receiving the radiation on the tubes it considers which direction the radiation is coming from and hence the temperature distribution both axially along the tube and radially around the tube circumference.

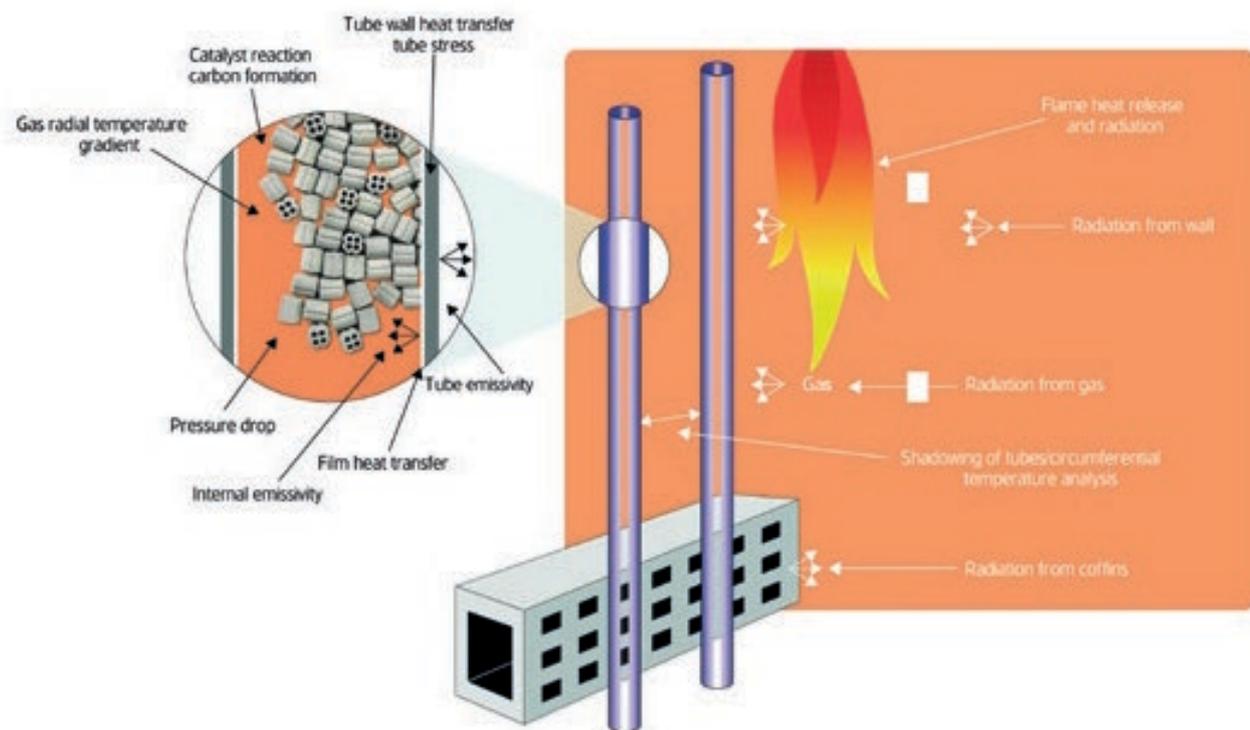
The inside of the tube is modelled by considering the heat transfer between the tube inside wall and the gas phase, the catalyst and the catalyst reactions in both an axial and a radial direction. This is then used to work out the tubes stresses very precisely. Carbon formation and detailed pressure drop through the catalyst are also calculated.

With a model of this detail we are able to precisely predict how different catalyst combinations are going to work under any given set of conditions. This allows us to recommend the optimum catalyst solution for any type of steam reformer. JM also uses this program in troubleshooting problems on steam reformers as part of our steam reforming optimisation studies.

## Advanced reactor thermometry technology

Accurate temperature measurement within a catalyst bed can be crucial for understanding the performance of the catalyst, diagnosing operational upsets and determining remaining life. JM has formed a partnership with Daily Thermetrics to offer catalyst users the most advanced temperature tracking technology currently available – the CatTracker™.

The CatTracker employs advanced technology and offers catalyst users the most rugged yet flexible temperature probes designed to be in direct contact with the process. Optimised for use in steam reformers, each CatTracker probe is installed using a patented JM loading technique. The temperature sensors give temperature readings at different points in the reformer tube, giving continuous on-line monitoring of the tube temperature profile, with the profile available in real time through the plant DCS system.



## Reformer consultancy

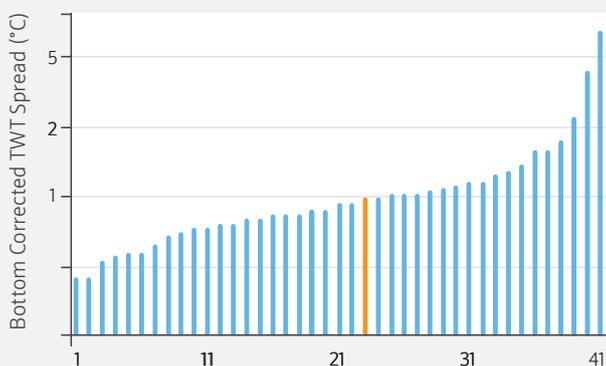
Experienced JM engineers can assist in identifying operational problems, whether related to process operation or mechanical equipment, and in developing appropriate solutions.

Practical JM experience gained on a range of different steam reformers and other furnaces can be applied to customers with similar designed steam reformers to give them a benchmark of how they are operating against similar designs and assistance in how to improve their furnace operation.

## Reformer process and mechanical design consultancy and engineering services

Through our operational experience in running large steam reformers, JM has developed design skills and knowledge that can be shared for the benefit of our catalyst customers. This includes advice on options for taking advantage of new materials for reformer tubes, reconfiguring tube support systems or replacing collection and transfer headers.

## Benchmarking reformer operation (vs Ammonia top-fired only)



## Managing the life cycle of reformer catalyst tubes

For effective operation, reformer catalyst tubes operate at temperatures high enough to cause material creep, and hence they are designed for a finite life. The determination of the actual rate of creep damage and the prediction of likely future life before failure involves careful consideration of inspection data together with plant operating history and the ability to accurately simulate reformer temperatures at proposed future conditions. Johnson Matthey is able to combine skills in all these areas to help determine appropriate operating conditions and timing for future changes.

JM and Quest Integrity offer a highly accurate, rapid (two to three minutes per tube) inspection process to measure the tube diameter and hence give detailed information on creep damage. This information can then be used to determine the remnant life of each reformer tube.

We offer two techniques for measuring creep in steam reformer tubes. The choice of technique depends on whether the catalyst is being removed during the shutdown or not. LOTIS™ is an internal tube measurement that can be carried out alongside catalyst loading / unloading with no additional time required on the shutdown schedule.

An external tube inspection, MANTIS™ inspection can be conducted at any shutdown as this takes place with the catalyst still in situ in the reformer tubes.

Further details on these and other services capabilities are available from JM.

# Case studies

## Case study 1: unique reformer insights using JM's reformer imager

A number of alternative techniques are available for measuring tube wall temperatures in steam reformers. Whilst each has its individual merits, the reformer imager, available from JM, provides unprecedented insight into previously inaccessible parts of the reformer during operation. A combination of a fish eye lens and long light tube ensure that all tubes within the reformer, along with the reformer coffins, can be assessed whilst the reformer is on line.

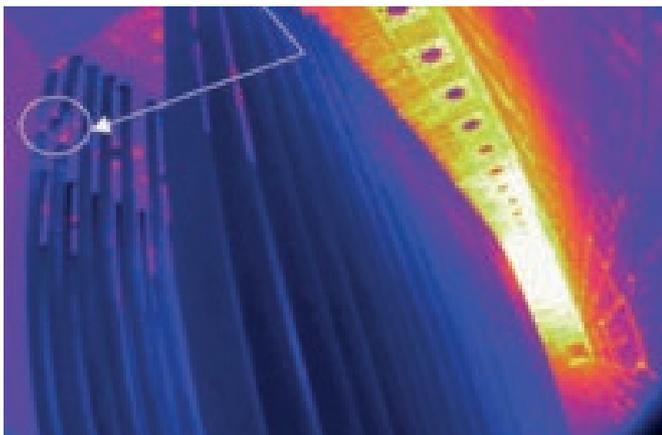
One example of this is a study completed on the top fired reformer on a methanol plant in Asia. The plant, which had a competitor steam reforming catalyst installed, suffered from both hot spots and hot bands on the tubes within three years of operation on its first charge. Within a few months of operation of its second charge, two tubes had ruptured and additional hot tubes and hot spots developed after every plant trip. In order to manage the furnace, the plant trimmed the fuel to the burners in the areas of the reformer where the problems were evident.

It was not possible to determine the temperature of all of the tubes using conventional temperature measuring devices such as an optical pyrometer, and personnel were unable to diagnose if the problems were caused by poor catalyst packing, carbon formation or poisoning. At this point the team sought help from JM in order to diagnose the root cause of the issue.

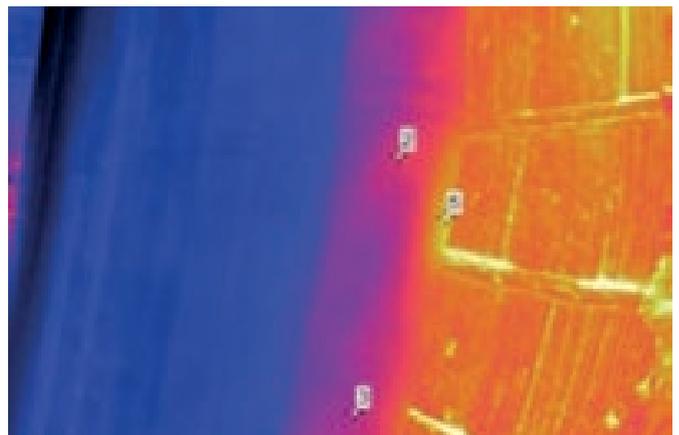
A team of experienced JM engineers conducted a complete reformer survey for the customer. Temperature measurements were taken quickly and easily for all parts of the reformer. The imager was able to identify hotspots on the tubes that were hidden from the peephole view and identify hot spots that were previously invisible due to flame interference. Hot spots on already hot tubes also became apparent.

With thousands of data points available from the reformer imager, the exact location of the hotter tubes and hot spots could be pinpointed exactly. The data was used to diagnose the problem, which was proven to be carbon formation. Hot tubes were consistently found at the end of rows, suggesting additional heat reflection from the refractory walls.

JM's engineers made both short and long term recommendations to the plant including a review of and recommendations on the operator start-up procedures. A robust combination of catalysts, tailored to suit the plant operation from the survey findings, was recommended and installed during the next planned shutdown. This has overcome the start-up problems in the reformer, which is now giving excellent performance.



Hotspots on the first few tubes hidden from peephole view



First tube in the row was found to be hot

## Case study 2: **KATALCO PERFORMANCE** improves plant reliability

JM offers a full range of catalyst products for steam reforming hydrocarbon feeds, for light feeds such as natural gas or refinery off gas up to heavy feeds such as naphtha. Appropriate combinations of catalysts are recommended to best operate in differing circumstances. For refinery hydrogen plants which operate on a combination of hydrocarbon feeds up to light LPG, the catalyst combination usually recommended is **KATALCO 25-series** in the top (inlet) 50% and **KATALCO 57-series** in the bottom (exit) 50% of the tube.

A refinery hydrogen plant in Western Europe experienced various problems with competitive catalyst offerings. The plant uses LPG feedstock usually in combination with refinery off gas in a top-fired reformer. The problems included difficulties with steaming the catalyst, which proved susceptible to carbon laydown due to exposure to hydrocarbon during plant trips. This led to both hot bands and also pressure drop problems. Ultimately, the plant experienced short lives from these catalyst charges. A further problem was the inability to hold the competitive catalyst under steam only for more than a short period in a hot stand-by mode.

The plant operator switched to a charge of **KATALCO 25-4** series and **KATALCO 57-4** series products. This catalyst combination can be steamed if needed and is not sensitive to trace levels of hydrocarbon during shutdown routines. The first charge of these **KATALCO** catalysts ran for seven years without any major issue, which far exceeded what had previously been achieved. The operator was also able to hold the reformer on hot stand-by with steam in order to complete mechanical repairs. This avoided a costly full shutdown which would have been necessary with the steam intolerant catalyst type used previously.

The operator opted to install **KATALCO** catalysts again, and continues to enjoy significant cost benefits from reduced catalyst purchases and additional time on line.

## Case study 3: Low pressure drop catalyst benefits with KATALCO 57-4XQ

Each steam reformer is unique, with a variety of factors affecting the catalyst choice. Some plants require the lowest possible pressure drop through their reformer and, where appropriate, we recommend the installation of **KATALCO 57-4XQ**.

In this particular case study we will look at a European ammonia plant operating at 2,000 mtpd (2,205 stpd). The plant management wanted to improve the plant efficiency by saving energy on their syngas compression. This would be possible if the suction pressure was increased as a result of a lower pressure drop through the front end of the plant, mainly through the steam reformer.

The plant was already using **KATALCO** catalysts and had previously achieved a ten year catalyst life using **KATALCO 57-4G**. The catalyst had delivered a very stable performance and the pellets were still in excellent condition when discharged at their end of life.

Following a detailed assessment and consideration of the benefit possible in terms of pressure drop saving, **KATALCO 57-4XQ** catalyst was developed as the optimum catalyst for the next charge. This product offers a higher activity, increased strength and lower pressure drop compared to the previous generation of products. As a result of these features the catalyst was installed safe in the knowledge that there would be no increase in tube wall temperature and no increased risk of carbon formation.

Installing **KATALCO 57-4XQ** resulted in a pressure drop decrease across the steam reformer, going from 2.3bar to 1.8 bar (33.4 to 26.1psl). After the catalyst was installed, we also carried out a survey of the reformer including detailed temperature measurements using both optical and gold cup pyrometry. The results of this survey confirmed that the tubes were in good condition and the tube wall temperatures, methane slip and 20% reduction in pressure drop were all as predicted by JM's proprietary models.

The charge continues to operate well, giving predictable, trouble free operation for the plant..



Discharged **KATALCO 57-4G** after ten years of service



Image showing **KATALCO 57-4G** and **KATALCO 57-4XQ**, which is currently installed in the reformer and giving excellent performance after ten years in service

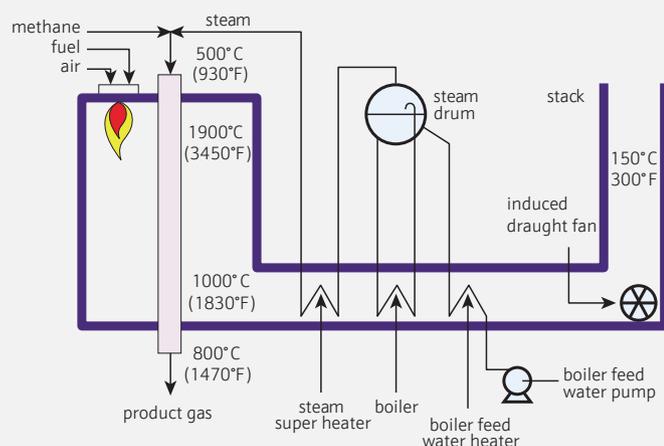
# Appendix 1: The steam reforming process

Steam reforming is the process by which hydrocarbon fuels ranging from natural gas to naphtha are converted to hydrogen and carbon oxides. The reaction is catalysed by a number of different metals, including ruthenium, nickel, cobalt, rhodium, iridium, palladium and platinum. Nickel is normally used for industrial catalysts due to economics. The overall process is strongly endothermic.

Purified feedstock is pre-heated with steam and passed through a nickel catalyst bed packed into vertical, narrow tubes mounted in a furnace or other heat exchange device. The reforming process is endothermic and, in a standard box furnace steam reformer, the reformer tubes are heated by burners together with radiant heat from the furnace walls.

Furnace design is complex and an appropriate gas temperature must be maintained inside the tubes to give design conversion without overheating the external tube surface. Small tube diameters increase the area available for heat transfer and improve gas mixing in the catalyst bed. Process conditions have, therefore, been optimised as better alloys enable small bore thin walled tubes to be used for long periods with no physical deterioration. Reformers usually operate at high pressure and temperature, balancing factors such as tube design life, front end product compression costs and the relatively unfavourable thermodynamics.

## Typical reforming furnace arrangement

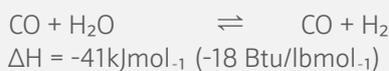


Design criteria for furnaces require that catalysts used for steam reforming have a number of carefully defined properties. The current **KATALCO** range of impregnated nickel catalysts is based on strong refractory materials with stable activity and carefully optimised shapes. Supports must be strong to avoid disintegration during use which would cause high pressure drop and hot spots inside tubes. The support must also be formulated to prevent carbon formation when certain feedstocks are used. Promoted catalysts are often required to ensure economic operation under the most severe operating conditions.

## Steam reforming reaction

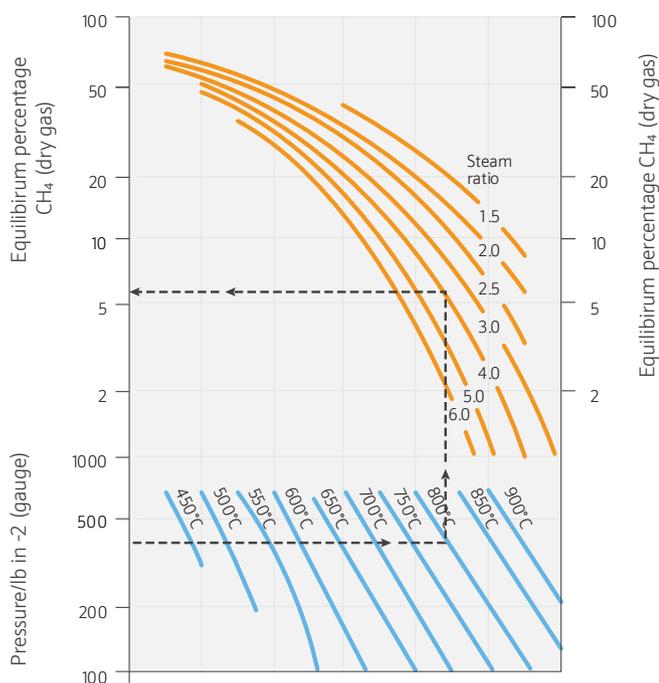
Steam reforming produces hydrogen and carbon oxides by the reaction of hydrocarbon and steam. Feedstocks vary from light feeds such as refinery off-gas and methane rich natural gas to naphthas boiling at 225°C (435°F) and containing up to 25% of aromatic compounds.

The reforming of natural gas is based on two simple reversible reactions:



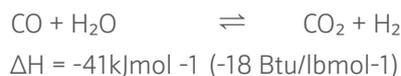
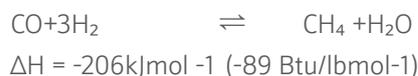
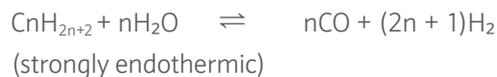
Methane conversion is favoured by low pressure, high temperature and a high steam to carbon ratio. Carbon monoxide conversion to carbon dioxide is favoured by low temperature and a high steam to carbon ratio.

An excess of steam is required to suppress carbon formation and promote the reforming reaction, so that the steam ratio is normally in the range 2.5-5.0 although lower ratios may be employed in particular circumstances. Also, despite the thermodynamics of the process, reformers operate at high pressure to optimise the overall economics of the process. More and more plant operators are also reducing the steam to carbon ratio in order to reduce operating costs and increase the throughput of existing plants. The equilibrium concentration of methane as a function of temperature pressure and steam to carbon ratio for methane reforming can be calculated, and shown opposite.



As process gas progresses through the reforming tubes, the position of equilibrium is constantly changing due to the changing gas composition and temperature. At the top of the tubes the reaction rate is slow due to the low temperature. There is a high heat flux due to the position of the flames and the effect of radiant heat transfer and the large temperature differential between flue gas and process gas. This corresponds to a wide approach to equilibrium (ATE) at the top of the tubes. Further down the tubes there is a fast reaction rate due to the high process gas temperature. Towards the end of the tube the heat flux is lower and the rate at which the equilibrium position is changing decreases. It should be noted that at this point in the tube, there is a small temperature differential between the flue gas and process gas and at this point the reaction rate is controlled by the rate of heat transfer and equilibrium. Therefore it is possible to achieve a narrow ATE at the bottom of the tubes. It is never possible to achieve a zero approach to equilibrium, although very close approaches are possible.

The reforming of saturated hydrocarbons is based on three reactions:



Despite the exothermic methanation and water gas shift reactions, the overall reaction is endothermic with all hydrocarbon feeds. When reforming higher molecular weight hydrocarbons it is even more important to ensure an excess of steam to promote reaction as there is a greater tendency to form carbon. The hydrocarbon decomposition/reforming reactions can be regarded as irreversible at normal operating conditions. Intermediates will then come to equilibrium by the methanation and shift reactions. The equilibrium concentration of methane as a function of temperature, pressure and steam to carbon ratio for heavier hydrocarbon feeds can be calculated assuming that carbon forming reactions are suppressed and that carbon is removed from the catalyst surface by choice of a suitable catalyst.

The ATE at any point along the catalyst bed is the difference between the actual gas temperature and the equilibrium temperature corresponding to the gas composition. The ATE can be used as a good measure of the performance of the catalyst when the operating parameters such as pressure and temperature of the reactor is held constant, and when the reaction is equilibrium limited, such as with primary reforming.

Equilibrium calculations for the steam methane reforming reaction can be completed using the Johnson Matthey ACE app, available online by visiting [www.jmprotech.com/ACE](http://www.jmprotech.com/ACE).



## Carbon formation and prevention

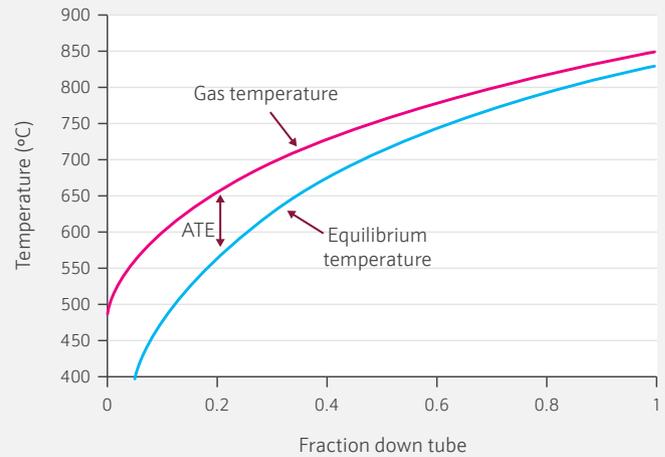
Carbon is an unwanted by-product that is formed in all steam reformers and may occur for a number of different reasons, for example:

- Steam to carbon ratio is too low
- Catalyst is not active enough
- Higher hydrocarbons are present
- Tube walls are too hot (high heat flux)
- Catalyst has poor heat transfer characteristics
- Low flow due to poor loading

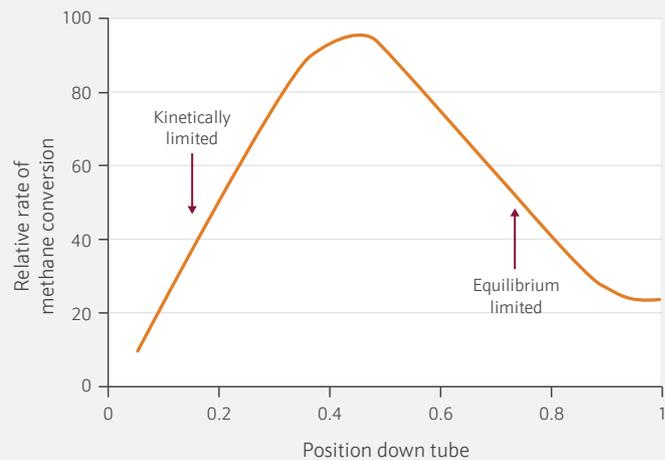
There are several effects of carbon formation in reformer tubes. There can be physical poisoning as carbon covers the surface of the catalyst blocking the active nickel sites. The pressure drop can increase as carbon fills the voids between the catalyst in the tubes, and carbon formed inside the catalyst pores weakens or breaks the catalyst. This normally only occurs in severe situations. Finally there can be hot tubes as carbon lay down on the inside of the catalyst tubes and the reduced catalyst activity affect the heat transfer and result in higher tube wall temperatures.

By suitable catalyst selection, net carbon deposition can be avoided in the upper part of the reformer tubes allowing excellent activity for long periods of operation without the occurrence of hot bands.

## Reformer tube - gas and equilibrium temperatures



## Reformer tube - reaction rate



## Carbon formation mechanism

All hydrocarbons will decompose spontaneously at reforming temperatures in the absence of steam to form carbon and hydrogen.



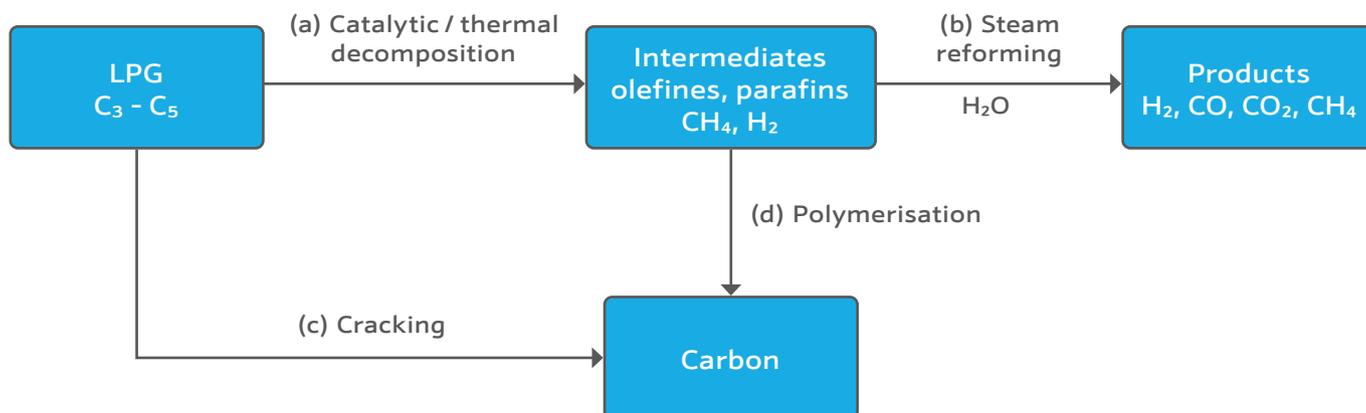
During normal operation in the presence of steam, methane cracking is still on the carbon forming side of the equilibrium along part of a methane reformer tube but, fortunately, the rate of carbon formation is slow and the carbon monoxide disproportionation and reduction reactions favour carbon removal through carbon gasification by reaction with steam and carbon dioxide.



Decomposition of heavier hydrocarbons to form carbon is more complex than the decomposition of methane. Carbon can form either by direct thermal cracking, or during reaction by polymerisation of the intermediates formed by pyrolysis. The main objectives during operation are, therefore, to minimise the concentration of intermediates on the catalyst surface and to inhibit carbon forming reactions.

## Predicting carbon formation

It is extremely important to be able to predict the likelihood of carbon formation in a steam reformer. Johnson Matthey do this using our world class steam reformer simulation program. As well as heat and mass transfer calculations this program accurately predicts the risk of carbon formation. The risk of carbon formation is dependent on a number of factors including feedstock and operating conditions and will vary for each plant. Our highly trained engineers use this information together with their experience and knowledge so that we can determine the correct catalyst loading for each customer plant.



## Preventing carbon formation

Carbon formed by methane cracking should always be removed by reaction with steam or carbon dioxide provided that the rate of carbon removal is faster than the rate of formation. This is normally true at temperatures below about 650°C (1200°F) provided an active catalyst is being used. Above 650°C (1200°F) sufficient hydrogen will have been formed for the methane cracking reaction to be on the carbon removing side of the equilibrium.

Therefore natural gas reforming catalysts should always have high, stable activity particularly when operating at low tube inlet temperatures. This ensures rapid feedstock conversion which produces sufficient hydrogen to repress methane cracking.

For gas containing heavier hydrocarbons the main objective during operation is to minimise the formation of intermediates (olefins and paraffins).

High reforming activity to remove intermediates can only be maintained if carbon deposition is slow and by completely removing any carbon which does form by reaction with steam. This makes it virtually impossible to produce a catalyst based solely on supported nickel which combines both the high reforming and carbon removal activities needed for operation at economic steam ratios.

In the 1970s our scientists found that the addition of alkali to a nickel catalyst could decrease support acidity and provide potash to remove any carbon forming on the active surface by reaction with steam. These catalysts were the precursor to today's **KATALCO 25-Q** series catalysts, which have the potassium incorporated into the catalyst in ceramic phase reservoirs with a precise stability to regulate the optimum release onto the surface. This leads to the right level of potassium and hydroxide species on the surface to ensure gasification of carbon from all Ni-sites throughout the catalyst's lifetime.

Carbon formation can therefore be prevented in a number of different ways, depending on the gas feedstock.

- **More active catalyst**

A more active catalyst generates hydrogen closer to the top of the tube stopping cracking earlier. It also reduces the process and tube temperatures delaying the onset of cracking and reforms more of the higher hydrocarbons most likely to form carbon. The overall effect is to move the process gas away from the carbon forming region.

- **Better heat transfer**

By using optimally shaped catalyst the resistance to heat transfer on the inside of the tube wall can be minimised. This improved heat transfer reduces the overall driving force required for heat flux into the process gas. It results in a lower tube wall temperature and helps to keep the inside of the tubes cool, thereby reducing the possibility of carbon formation.

- **Good packing**

How a catalyst packs in a tube is critical to the overall performance of the reformer. Poor packing with large voids and spaces will result in uneven pressure drop across the reformer tubes and hot bands or patches as no reforming will occur in these parts of the reformer tubes.

- **Reduce levels of higher hydrocarbons**

A gas feed with lower levels of higher hydrocarbons will also have a lower level of intermediate compounds and olefins in the process gas. This has a direct effect on the possibility of carbon formation.

- **Increase the steam ratio**

Operating with higher steam to carbon ratios moves the equilibrium position of the CO reduction reaction and encourages carbon removal. It also affects the steam reforming reaction, encouraging more reforming by changing the equilibrium position.

- **Potash doped catalyst (KATALCO 25-series)**

The addition of potash to the catalyst support reduces carbon formation by increasing the basicity of the support and by promoting carbon gasification (aids adsorption of water). Potash is mobile on the catalyst surface allowing it to migrate to the tube wall where it can be effective at preventing carbon build up.

The level of potash required for a reformer depends on feed and heat flux. Increasing the content of alkali (potash) allows higher heat flux for light feeds, heavier hydrocarbons in feed, lower steam to carbon ratios and faster carbon removal during steaming.

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