JM

Getting most $ value from your Ni

Improved profitability and reduced emissions from sustainable reforming catalysts

Thomas Ithell – Johnson Matthey

Reprint from Nitrogen & Syngas Conference, Berlin 2022

Johnson Matthey
Inspiring science, enhancing life

Efficient reformer operations depend on a reliable catalyst that has been optimised to provide sufficient activity over its life to ensure the tube wall temperature is as low as possible while maintaining a low and stable operating pressure drop. Selecting the correct combination of catalysts for a reformer will increase efficiency and reduce operating costs and carbon emissions. However, making a poor selection can lead to carbon formation reducing the catalyst lifetime and causing reformer tube overheating, incurring greater long-term costs which can outweigh any possible up-front savings.

Steam reforming catalyst has been developed over decades to synergise with improvements in refomrer design to deliver better process efficiencies. This has culminated in Johnson Matthey's **QUADRALOBE™** range of pellet designs which offer the optimum balance between pressure drop, heat transfer and activity. While these remain the optimum solution at the millimetre scale, the latest understanding from Johnson Matthey at the nanometre scale has led to solutions involving placing nickel where it is most needed in customised catalyst designs. These developments provide the benefit of lower pressure drop, longer catalyst life and reduced operating costs through the better management of tube wall temperature.

This paper will describe the reduced operating costs available through modern steam reformer catalyst design which is tailored in shape, size and nickel loading.

1. Introduction

Steam reforming is an important operation in the generation of syngas. The steam reforming process converts hydrocarbon feedstocks to hydrogen and carbon oxides. Note that the reforming of methane is an equilibrium reaction. An increase in the conversion of methane at equilibrium is promoted by higher temperature, lower pressure and increased steam concentration:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = +206\ kJ.mol^{-1}$$

$$CxHy + xH_2O \rightarrow xCO + (x+y/2)\ H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -41\ kJ.mol^{-1}$$

A purified hydrocarbon feed is mixed with steam and heated to the reformer inlet temperature. In the reformer, the feed mixture is introduced to the catalyst. Commercial steam reforming catalysts consist of an alumina-based support, impregnated with nickel and potentially other promoters. In order to deliver the pressure drops and activities required to meet the operating cost, lifetime and operability requirements of plants the support shape and nickel and promoter loading can be tuned.

2. Reformer design

Since the steam reformer is typically the largest and most expensive item in the flowsheet, efficient design and operation of the unit is important in the economics of running the plant.

To provide the process heat and heat of reaction a reformer is designed to hold the catalyst within tubes in a furnace. The lifetime of the tube is sensitive to the peak tube wall temperature, so it is important that the reformer and catalyst design is optimised to minimise the peak temperature and maximise the tube life.

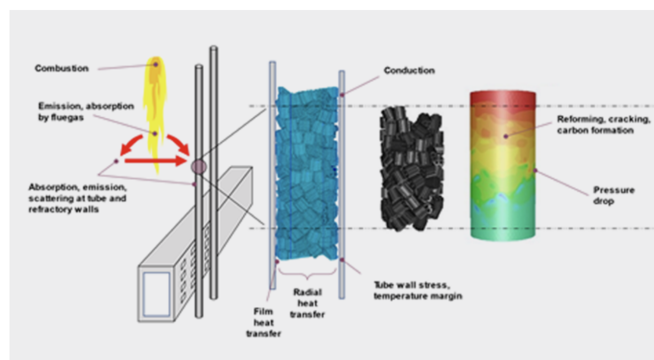

Fig. 1: Illustration of reformer tube and heat transfer contributions and factors

Good reformer design relies on creating the optimal combination of catalyst activity with the heat transfer achieved at each location in the reformer tube to make the most efficient use of the energy provided to drive the conversion of methane (Fig. 1). A poor choice of catalyst and operating conditions will promote hydrocarbon cracking and carbon formation rather than reforming and will reduce the lifetime of the reformer due to overheating (Fig. 2).

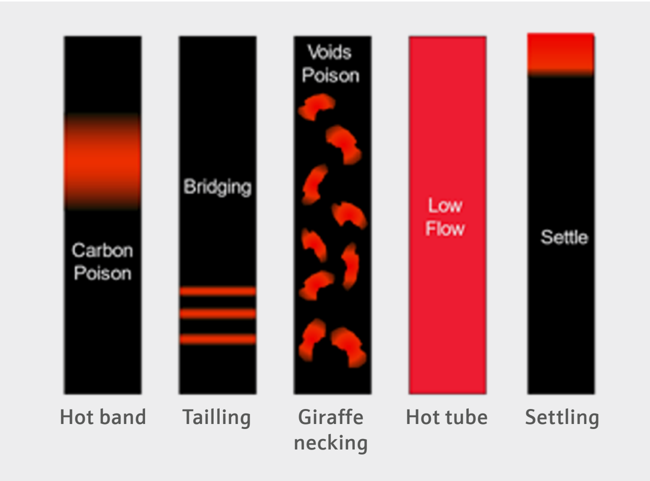

Fig. 2: Tube appearances during operating issues resulting from installation of inadequate catalyst

3. Steam reformer modelling

Johnson Matthey has used the knowledge built through 60 years of experience to develop the **KATALCO**™ **REFORM**™ simulation which models the steam reformer including the flue gas and flames with the heat transfer to the reformer tubes as well as the process gas and the reforming reactions. As well as the progression of the steam reforming reactions, which is common in many basic reformer models, **REFORM** also calculates the pressure drop through the catalyst and precise tube wall stresses, as well as accurately calculating the risk of carbon formation along the tube.

The modelling is based on detailed testing of the range of catalysts available in the market as well as Johnson Matthey development products and is continually validated through support and interaction with the customer data from the field. This ensures a high level of trust in the model outputs, with high confidence in results that help the ability to plan and reliably hit scheduled shutdowns with confidence, reducing the risk of unplanned costs and organisational strain for an operator.

When it comes to optimising individual reformers, **REFORM** allows Johnson Matthey to develop catalyst offerings tailored to specific duties. Through collaboration with operators JM can target the catalyst design which offers the maximum value from your investment.

4. Reformer monitoring

Though **REFORM** gives Johnson Matthey unparalleled insight into reformer design and operation via modelling, monitoring of the reformer is considered as important, both in terms of continual validation of the models and identifying non-ideal operation. Inspection of the reformer using visual and infrared techniques is essential to diagnosing issues such as flame impingement and poor furnace balancing.

Designing optimal reformer catalyst loadings requires a detailed understanding of the configuration and operation of the reformer. By taking measurements of reformer parameters, the temperature, heat flux and carbon formation potential profiles along the tubes can be generated and a catalyst offer tailored to make the most efficient and beneficial use of the nickel on the catalyst. Johnson Matthey's unique manufacturing processes enable the active metal to be more accessible on the catalyst pellet, which can thus reduce the level of nickel required in the catalyst charge.

Johnson Matthey can offer a range of reformer surveys with varying scope for investigation which, when coupled with Johnson Matthey's **REFORM** and plant analysis tools, can be used to inform decisions about reformer operation, catalyst performance and future catalyst offers.These can include a range of measurement techniques including optical pyrometers, contact thermocouples and reformer thermal imagers. The information gained from these measurements, along with the **REFORM** modelling tools can inform the optimisation of the reformer operation, considering pressure drop, heat flux, carbon formation and fuel consumption. Continuous measurements of the reformer conditions can also offer insight to the operation and optimisation of the reformer.

5. Steam reforming catalysts

The design of the steam reforming catalyst is important to efficient reformer operation and can have a significant effect on the performance of the plant. There are many factors that are important to the design of steam reforming catalysts.

Assuming the chemical factors to be constant the changes relating to the pellet geometry that can made to optimise the performance are increasing the geometric surface area, increasing the packed bed heat transfer coefficient and decreasing the pressure drop.

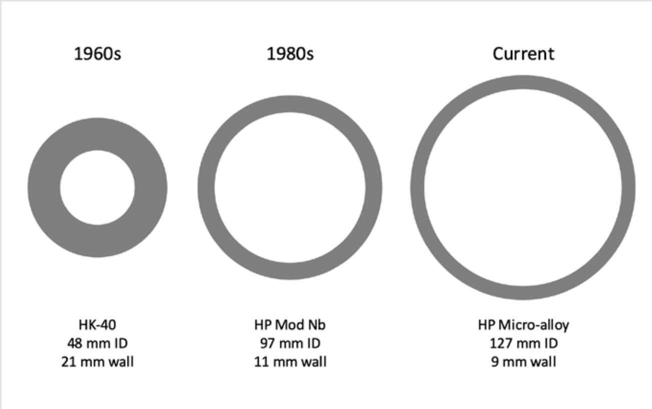

Fig. 3: Reformer tube diameters and wall thicknesses over time

Much of the development of steam reforming catalysts to date has focused on the design of the shape of the pellet to improve the activity for a given pressure drop. Ring catalyst pellets were improved by the designing pellets with multiple channels, and a further step change in performance was achieved in the development of the **KATALCO QUADRALOBE** shape which offers the highest available activity for the lowest pressure drop while retaining catalyst strength.

Over the past 60 year there have also been developments in the design of primary reformer tubes as alloys have developed. Tube diameters today are over double that of the 1960s with thinner walls (Fig. 3), which makes the design of catalyst loadings even more critical to limit the maximum tube wall temperature. These larger diameter tubes have allowed for developments of bigger pellets to achieve lower pressure drop. However, it is essential that large pellets retain suitable activity, breakage and heat transfer characteristics.

5.1 Activity

The catalyst should have a high activity to reduce the volume of catalyst required and provide protection against carbon formation. It is important to appreciate that the overall catalyst activity is a combination of chemical factors (e.g. nickel crystallite size and distribution, interactions between nickel and the support and the use of promoters) as well as physical factors (e.g. pore size, catalyst geometry).

Assuming the chemical factors to be constant, changes can be made to the pellet geometry that have the effect of increasing the geometric surface area and increasing the packed bed heat transfer coefficient while decreasing the catalyst bed pressure drop. However, changing the properties to achieve these benefits must not adversely affect the strength of the pellet, the breakage pattern of the catalyst, or the packing properties of the shape within the reformer tube. Clearly optimising this design is complex, and it is important to have a thorough understanding of the relative benefits of each of these properties to a reformer design.

Catalyst pellets promote heat transfer via the breakup of the laminar gas film at the tube wall. Larger pellets result in a thicker film at the wall than smaller pellets (Fig. 4), and therefore a greater inherent activity is required in larger pellets to compensate for the poorer heat transfer performance in the reformer heat balance. A large pellet with insufficient activity will not protect against carbon formation, tube overheating and failure and a resulting loss of production.

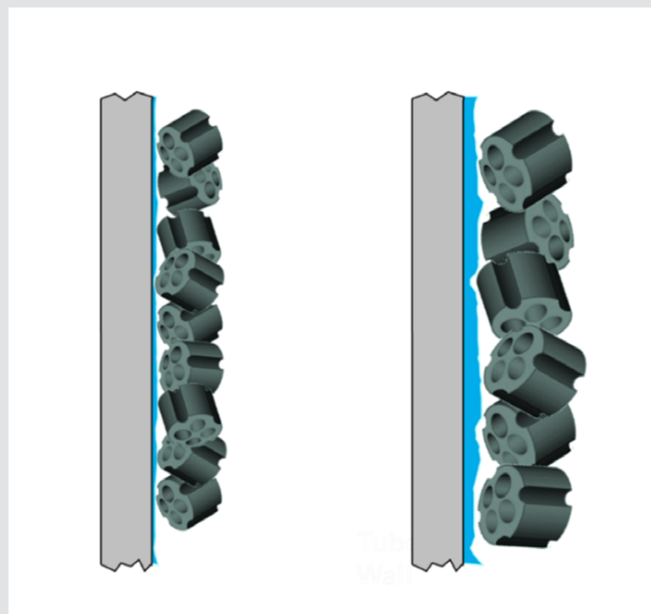

Fig. 4: Illustration of relative size of gas film at the wall for small pellets (left) and large pellets (right)

Under the conditions at which a reformer operates, the reaction is often limited by the mass transfer effects from the gas to the catalytically active sites. Therefore, the surface area of the catalyst is an important factor in its activity. Since the geometric surface area of a pellet is related to its size, and the pressure drop of a catalyst bed is a function of the size of the pellet an optimal balance needs to be struck between the pressure drop and activity. This is achieved through sophisticated modelling which includes calculation of the risk of carbon formation over a desired life.

5.2 Pressure drop

As with all operations within the syngas generation train, reforming catalyst should offer a low pressure drop to minimise the operating costs of the plant and maximise the plant rate. The pressure drop is a function of the catalyst size and voidage in the catalyst bed. For tailored pressure drop options Johnson Matthey pellets in a range of sizes from small **KATALCO** MQ **QUADRALOBE** pellets to large **KATALCO** XQ **QUADRALOBE** pellets which gives the lowest pressure drop available in the market and therefore offers the greatest increase in production or energy saving (Fig. 5).

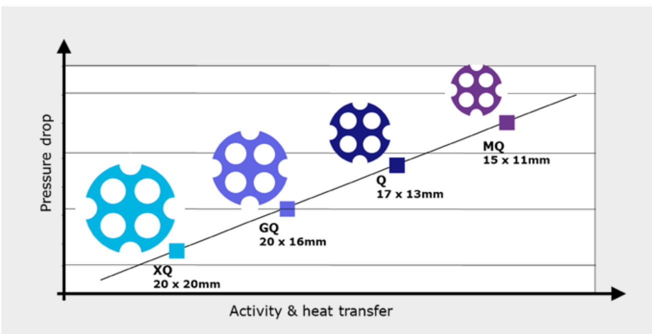

Fig. 5: Relative pressure drop and activity for range of sizes of Q shape pellets

While the initial size is a factor in the pressure drop, the pellet strength and breakage characteristics are important in the development of the pressure drop throughout the life of the catalyst. During the expansion and contraction of the tubes through operating cycles the catalyst will also be exposed to crushing stresses which will cause breakage. **KATALCO QUADRALOBE** catalysts have been designed such that the fracture pattern creates large fragments which themselves retain strength and thus limit the increase in pressure drop and resulting increased operating costs. This means it is much less likely that the catalyst pressure drop will be the limiting factor that dictates the need for a shutdown and replacement, and more likely that the catalyst will be able to last for two turnaround cycles typically saving 300k-400k USD in catalyst replacement and handling costs.

Longer life case study

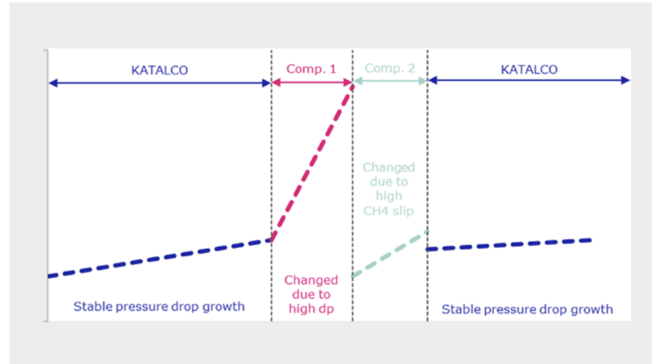

Fig. 6: Normalised pressure drop trends over the lives of KATALCO and competitor materials

A large North American reformer initially loaded **KATALCO** catalysts and the material was changed at the end of an 8-year life with little increase in pressure drop. Subsequently two different competitor materials were loaded, which each lasted less than three years. The first competitor charge was changed due to the development of excessive pressure drop, and while the second competitor charge was changed due to high methane slip, it also demonstrated a faster increase in pressure drop than the **KATALCO** charge. The customer returned to a **KATALCO** solution, which demonstrated excellent pressure drop performance for over five years.

The financial impact of a shortened catalyst life due to intolerable conditions or operating costs is expected to be between 300k-500k EUR for typical ammonia plants considering only the cost of replacing reformer catalysts. Additional costs will also be incurred due to increased creep aging wear to the reformer tubes from high temperatures, with reformer tube replacement typically costing 5,000-10,000k EUR depending on the size of the plant.

5.3 Potash doping

In duties with particularly high potential to form carbon in the high temperature section of the tube it is possible to add extra protection against carbon formation via the addition of potash to the catalyst using **KATALCO** 24-5Q series. Potash acts to promote the gasification of carbon, and therefore shifts the equilibrium away from deposition of carbon on the catalyst and the tubes.

Potash is precisely added so that islands of potassium form and are incorporated into alumina support structure. This means that enough potash is provided within the support to offer the protection against carbon over the entire catalyst life. The association of the potash with the alumina support and its precise stability is such that the rate of dissociation is optimised. The dissociation is slow enough to allow for a continual release of potassium to the surface over the life of the catalyst, while the potash is mobile enough to drive the gasification of carbon from the catalyst surface

In order to protect the tube walls as well as the catalyst, it is essential that potash is mobile within the reformer. If the potash is bound too well to the catalyst it will not offer protection against carbon build-up at the tube wall, and the associated development of hot zones in the tube, which would reduce the tube life. Johnson Matthey has been developing alkali promoted nickel catalysts for 50 years, and the design of modern-day catalysts is built on that historic knowledge. The potassium is incorporated within pellet structure with a precise stability which allows for the optimum release to the surface. The level of potash required depends on the reforming conditions, most specifically the feed and the heat flux. **REFORM** modelling allows Johnson Matthey to investigate the carbon formation potential of a range of feeds across a range of firing conditions and to target the loading of potash in the tube to locations where it will offer the most value.

5.4 Nickel loading

While benefits can be realised in shape development at the millimetre scale, there is also the opportunity to realise sustainability benefits at the nanometre scale with the tailoring of nickel loading in the pellet. Due to the diffusion limitation of the steam reforming reactions under the operating conditions in a reformer, there may be no reaction deep in the catalyst pores. Therefore, any nickel loaded onto the pellet below the surface does not confer any benefit to the process. Johnson Matthey's patented manufacturing techniques can create a **KATALCO** 57-6Q series pellet with a thin layer of nickel concentrated at the surface (Fig. 7). The **KATALCO** 57-6Q series catalysts can demonstrate the same performance as a pellet with twice the amount of nickel, so making more sustainable use of nickel resources. Sustainable use and purchasing of nickel will be important in a future in which increased requirements for nickel in battery technologies will drive a much stronger demand across the market for nickel.

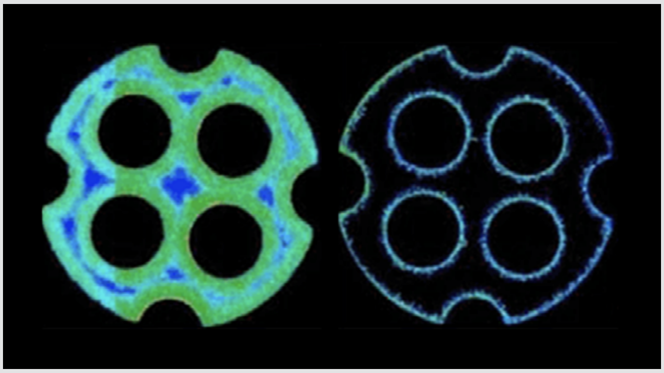

Fig. 7: Nickel loading on conventional pellet (left) and eggshell pellet (right).

The high temperatures in the lower section of the reformer tube and the associated diffusion limitation of the rate, and the equilibrium limitation on the potential extent of reactions means that **KATALCO** 57-6XQ is well suited to this region. The XQ shape offers the lowest pressure drop, with the **QUADRALOBE** shape retaining good activity for its size, and the eggshell loading of nickel ensures that the required activity is achieved with the most efficient use of nickel.

Using the same technology to target the application of intensified nickel at the pellet surface, Johnson Matthey can also deliver lifetime extension benefits by offering increased nickel loading catalyst in the top of the tube. Over the course of a reformer's life, this can translate to fewer shutdowns and fewer catalyst charges. **KATALCO** HXQ catalysts can offer enhanced activity due to the increased level of nickel, and Johnson Matthey's expertise in reformer modelling and catalysis can identify the cases where this high metal loading confers value. The high nickel loading brings an added robustness to the catalyst since the additional nickel can act as contingency if there is a poisoning event in the top of the reformer.

At a mid-point along the tube, the heat flux is highest. In this high heat flux region, there is potential for carbon formation, often manifesting as hot bands in the tube. The temperature is increased from the inlet meaning that diffusion starts to limit the reaction. In this region, **KATALCO** 25-4HXQ catalyst used in conjunction with **KATALCO** 57-6XQ delivers both the benefits of increased activity and targeted nickel loading in the region of peak heat flux where there is the highest carbon risk. By using a nickel profile within the pellet it is possible to offer the lowest pressure drops, and therefore lowest financial and environmental costs of compression required in plants running at high rates while retaining the activity necessary to prevent carbon deposition (Fig. 8).

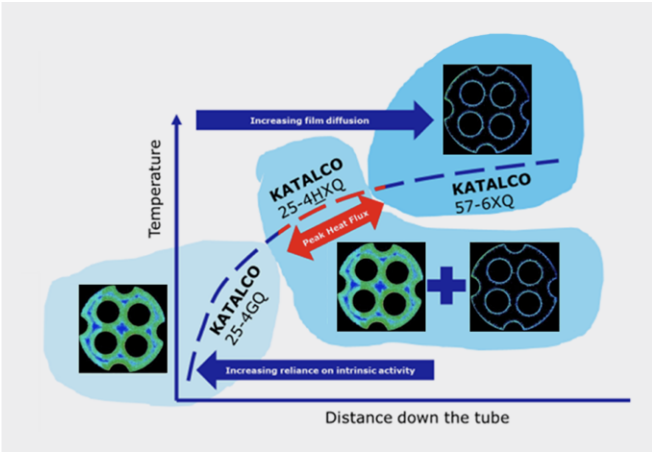

Fig. 8: Illustration of loading using KATALCO 25-4HXQ in peak heat flux region of tube to offer low pressure drop, high activity and potash to protect against carbon formation, extend tube life and reduce operating costs.

Low tube wall temperature case study

A highly stressed reformer installed **KATALCO** 25-4Q series catalyst at the top of the tubes to use the increased activity as protection against high tube wall temperatures. Where the reformer had previously seen hot banding, the use of higher nickel loading catalyst **KATALCO** 25-4HQ series reduced the evidence of hot banding, and imaging of the reformer indicated that the peak tube wall temperature had been reduced by 65 °C.

The major cost in running a reformer is tube replacement, and tube lives can be halved by a 20°C increase in peak wall temperatures. Thus this reduction in temperature can be worth an additional tube life of 9 years. Retubing a reformer of this size would be expected to incur costs estimated at 8,000 k EUR, but the use of high nickel **KATALCO** 25-4HQ series prolongs the tube life meaning both the costs of retubing and any associated disruption costs are incurred less frequently.

Conclusion

The efficiency of steam reforming operations is a key factor in the production rate and sustainability of syngas generation processes. Maximising the efficiency of a steam reformer relies on selection of the optimal catalyst combination for the operating conditions to balance the effects of pressure drop, heat transfer and activity. A poor choice of catalyst will result in carbon formation, hot tubes and a reduced catalyst lifetime and increased operating costs, negating any initial potential savings in catalyst cost.

Historical development of Johnson Matthey's **QUADRALOBE** pellets has created catalysts that offer the best activity for a given pressure drop in the market. Not only does the **QUADRALOBE** shape offer low pressure drop at start of life, but the design of the shape and optimised fracture patterns ensure that pressure drop growth over time is low, delivering low operating costs throughout service. Johnson Matthey's expertise in targeted nickel loading has led to the development of the **KATALCO** 57-6XQ catalyst which offers the same activity as a pellet with twice the amount of nickel, ideally suited to the high temperature regions of reformer tubes. Similar targeted nickel loading has been used to develop higher nickel loaded **KATALCO 25**-4HXQ catalyst which can demonstrate longer life and improved performance in high heat flux regions of the tube as well a driving purchasing sustainability and reducing consumption of raw materials.

Johnson Matthey's unique experience in reformer modelling and monitoring allows the benefits of larger pellets and targeted nickel loading to be precisely evaluated, meaning that reformers which use **KATALCO** catalysts can operate with lower pressure drop, longer catalyst life, and reduced operating costs.

Designed and produced by www.houseoftype.co.uk

For further information on Johnson Matthey, please contact your local sales representative or visit our website. KATALCO, QUADRALOBE and REFORM are trademarks of the Johnson Matthey group of companies.

Billingham, UK
Tel +44 (0) 1642 553601
www.matthey.com

Johnson Matthey
Inspiring science, enhancing life

1871JM/0822/0/CT