Optimising hydrogen production

Stephen B. Harrison, Nexant Energy & Chemicals Advisory, Germany, looks at methods to optimise refinery hydrogen production on steam methane reformers.

The use of steam methane reformers (SMR) is the most common large-scale hydrogen production technique in use on refineries. In fact, the majority of the world's installed base of SMRs is linked to refinery operations, with the balance being associated with syngas and methanol production in the chemicals industry and ammonia production for nitrogen-based fertilizers.

Hydrogen consumption on refineries has increased significantly in recent decades to produce clean burning low sulfur fuels, process heavy feedstocks to produce the desired product mix, and in the production of biofuels. The most recent uptick in demand has been driven by the IMO2020 regulations which increased the demand for low sulfur marine fuels. With CAPEX always under scrutiny in the refining sector, anything that could be done to squeeze a few percent more hydrogen out of an existing SMR has been desirable.

Strategies that SMR operators have been using to increase hydrogen output have included upgrading to more modern catalysts with lower pressure drop or higher conversion yields and maximising the catalyst performance with timely replacement. Minimising hydrogen losses through optimising the PSA hydrogen purification cycle and other SMR debottlenecking activities have also contributed to the optimisation initiatives.

Routine preventative maintenance and turn-around upgrades have also ensured that equipment remains functional to maximise up-time of the SMR. Furthermore, installation of additional reformer tubes within the SMR to increase the catalyst volume and plant capacity or the addition of a pre-reformer or post-reformer have also been possible for some operators. Low-cost changes, including process control improvements, such as adjusting the steam to carbon ratio in the feed to the SMR and the use of better gas analysis instrumentation, have also made a difference.

Focus can yield better results

For many refinery SMR operators, some of the optimisation ideas above may theoretically be achievable but might be a distraction from processing crude oil to produce a profitable palette of refined products. In recognition of the

Figure 1. Aerial view of a hydrogen plant at a refinery.

Figure 2. Lima SMR (image courtesy of Matheson).

principle that focus adds value, producers of industrial gases have developed expertise in SMR operations over many decades and have taken on the operation of 'captive' refinery SMRs, converting them to 'over the fence' (OTF) or pipeline hydrogen supply schemes.

Speaking for Taiyo Nippon Sanso's US subsidiary Matheson, Dr. Marco A. Márquez, Director of Business Development – Refining says that "through our hydrogen OTF supply service we often get involved in supporting refiners. Such was the case recently in North America where a refinery SMR was convert it to an OTF supply. Using our technical and operational expertise, we identified and resolved major issues affecting the plant capacity and efficiency. After the first stage retrofit was completed, the plant capacity was increased, and the efficiency was improved. The operating cost savings were significant, being in the order of several millions of [dollars] per year".

Economies of scale have tremendous advantages for industrial gases hydrogen producers. Márquez again: "We own and operate SMRs worldwide. We have cases where customers over time have come back to us for a second or third SMR in one location, for example in our Ohio Cluster. This clustering has some advantages: improve the overall reliability and ensure optimal performance of each SMR. Customers hooked up to clusters or pipelines have the security of a backup supply if one of the SMRs needs to be taken out of service for maintenance or catalyst replacement.

"Furthermore, to leverage Taiyo Nippon Sanso's international presence the SMRs are digitally connected to our Remote Operations Centre (ROC) in Texas, from where we can monitor and operate them. Our tools allow us to continually observe and control what is happening. Panel operators can run specialised simulations to visualise what should be happening, or get support from our experts at headquarters. This means they can intervene before minor issues escalate to become major problems. It adds up to better safety, improved reliability and enhanced energy efficiency, thus maximising hydrogen availability for all our customers".

Process control secures environmental benefits and profitable operations

Whether the panel operators are local to the SMR or in a remote location, the fundamentals of SMR operational economics are universal: maximise the hydrogen production and minimise hydrocarbon consumption. However, optimising the process to achieve these goals is not quite so simple. If it was possible to see inside the box, parameters could be adjusted based on what is observed, but that is easier said than done. The SMR is heated to 1000°C and thick metal tubes obscure the view. So, instrumentation is used to measure temperature, pressure and analyse gas compositions. A picture of the process emerges through these key parameters. In this respect, gas analysis instrumentation has a critical role to play.

Some of the most fundamental gas analysis requirements on an SMR are measurement of the energy calorific value (Btu/scf) of the incoming feedstock; monitoring methane slip through the SMR; controlling the steam to carbon ratio in the SMR and measurement of the final hydrogen product purity. For these diverse requirements, a wide range of gas analysers will be required. Steve Gibbons, Head of Product Management for the continuous gas analyser product range within ABB's Measurement & Analytics business line, says that "a key factor in selecting the right analyser is to decide what the most essential functionality is. Perhaps the priority is continuous and instantaneous measurement of a specified molecule. Or, the critical issue may be simultaneous measurement of a diverse mix of gases, for which a small delay in receiving the signal may be acceptable. For example, the Btu/scf value of the natural gas coming into the SMR is best measured using a rapid response process GC-TCD such as the PGC1000 which is optimised for natural gas BTU analysis. This instrument can analyse and characterise a gas mixture sample every two minutes".

From a precise analysis of the gas composition, it is possible to calculate its BTU value using formulae described in ISO 6976:1995 Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition.

Figure 3. Aerial view of an SMR at a refinery.

Diversity of composition vs direct response

In the case of BTU value determination, a process gas chromatograph (GC) is required to analyse the mixed composition of the natural gas stream, which can contain a variety of light hydrocarbons such as ethane and propane in addition to the base of methane. Or, in some instances, the SMR is fed with refinery gas, which can contain a highly diverse mix of fuel gases. Direct read techniques are good for looking at individual components, but do not have the flexibility of a GC which is able to see across a broad range of species. However, the advantage of direct read gas analysers is that they provide continuous information. There are no blind spots in the intervals between samples. Every tiny change in the process can be observed and reacted to within seconds to ensure continuous optimisation.

Gibbons again: "Methane slip from the SMR is a perfect case for a direct read gas analyser. Methane is IR active and can be detected with high accuracy using a non-dispersive infrared (NDIR) analyser such as the Uras26. Methane should be reacted to CO_2, carbon monoxide (CO) and hydrogen in the SMR and if excessive amounts of methane slip through the process it is a clear sign that something is sub-optimal. For example, it could indicate that the catalyst needs replacement, or it could be caused by low temperatures in the SMR which can be corrected by increasing the amount of fuel gas supplied to the burners. Some of these changes, such as catalyst performance, are longer term. Others, such as temperature changes, can happen quickly, and a direct read instrument will help to fix the issue with minimal delays meaning that the operation returns to its optimum as soon as possible."

NDIR analysers are also ideal for measurement of the final hydrogen purity. Gibbons points out an irony here: "to measure hydrogen, a TCD analyser such as our Caldos27 is often used. Hydrogen is not IR active and is not detected on an NDIR. So, why do refinery hydrogen producers choose an NDIR instrument to measure the final gas purity? It's generally taken for granted that the gas coming off the SMR will be hydrogen but what really matters is the absence of CO and CO2. These two gases are poisons to the hydro-treating catalysts in the subsequent processes on the refinery. Typically, the final hydrogen product specification will have a maximum total combined CO and CO_2 content of 10 ppm by volume (VPM). Simultaneous measurement of these two components is right in the sweet spot for the Uras26".

New generation of steam reforming catalysts

To ensure optimal hydrogen production and energy efficiency, reforming catalysts should provide high activity and stability, as well as minimise the pressure drop in the SMR. Until now, the specialty chemicals company, Clariant, has met these requirements with its ReforMax® LDP series catalysts. Operating in over 100 syngas facilities globally, these catalysts have achieved consistently high efficiency under diverse operating conditions. In a recent innovation, Clariant has introduced its ReforMax LDP Plus catalysts. The 'Plus' series combines the excellent activity of its predecessor with an extremely low pressure drop, which is enabled by its eight-hole, flower-like shape. This allows higher hydrogen production throughput and/or energy savings. Furthermore, the larger holes in the catalyst improve the heat transfer inside the SMR tubes, thus enhancing the chemical reactions.

These performance benefits have been demonstrated at commercial scale in the ammonia plant of OCI Nitrogen in Geleen, the Netherlands. ReforMax LDP Plus has reduced pressure drop in the reformer tubes, thus providing OCI Nitrogen with significant energy savings. Christian Librera, Head of Business Segment Syngas BU Catalysts at Clariant Catalysts, confirms that "since its installation, ReforMax LDP Plus has delivered the improvements we expected. The SMR has benefitted from a 20% reduction in pressure drop, leading to a significant increase in energy efficiency. Whilst this case study is related to an SMR in the fertilizer sector, similar benefits can be achieved on SMRs producing refinery hydrogen".

Beyond offering catalysts, Clariant also provides thermal imaging technology to accurately monitor tube wall temperatures and evaluate catalyst performance. The service identifies any malfunctions or uneven heat distribution inside the furnace. This enables safer plant operation and helps to prevent plant shutdowns.

Conclusion

Optimisation of refinery hydrogen production can yield economic and environmental benefits. An armoury of measures from low cost process control or instrumentation improvements to more fundamental engineering changes or catalyst replacement can yield impactful results. Or, outsourcing the hydrogen production to a focused industrial gases producer is an alternative approach.