Structured catalysts for steam reformers

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A foil based catalyst aims to avoid the limitations of ceramic pellet substrates in steam reforming

Steam reforming catalyst design is a balance between many competing requirements such as strength, heat transfer, activity, pressure drop and the avoidance of carbon formation. Catacel CATACEL® JM SSR is a coated foil based alternative to metal-impregnated ceramic pellet media. A foil based structure enables CATACEL® SSR to avoid many of the limitations imposed by the use of ceramic pellets. It exhibits higher activity, improved heat transfer, lower pressure drop and improved carbon resistance all at the same time.

Depending on the plant design, CATACEL® SSR can be used to decrease tube temperatures, reduce natural gas fuel consumption or increase throughput of the reformer. New reformers can typically be designed with lower capital cost of the radiant box. This technology has been demonstrated in two commercial hydrogen plants since May 2012.

Catalyst coated foil

The principle of the technology is the ability to coat catalyst materials onto the surface of thin metal foils. The coating process ensures that the catalyst remains attached to the surface of the foil during the catalyst’s lifetime.

Alloy strip is formed into engineered foil supports called fans (see Figure 1). The fans are coated with a nickel based steam reforming catalyst. The fans are quite ‘springy’ and can easily be pulled or pushed into different diameters or shapes.

They are stacked one upon another, separated by thin metal washers (see Figure 2) in groups up to one metre long over a support structure that sits within the central space of the fans. This central structure aids in the speed and accuracy of catalyst installation.

Figure 1 CATACEL® SSR fan

Figure 2 CATACEL® SSR stack

Figure 3 Gas forced out of triangular ducts

Figure 4 Gas flowing over the edges

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by avoiding the need to install the fans individually. The stacked fans deliver superior heat transfer by impinging gas on the internal surface of the reforming tube, rather than relying on convective heat transfer mechanisms. This results in about 20–30% more heat transfer for the same (or lower) pressure drop when compared to traditional catalyst pellets. In addition, the fans offer 1.5 to 2.0 times more geometric surface area than conventional pellets.

**How CATACEL JM SSR works**

The stacked fans and impingement mechanism work as follows. Gas flowing down the tube encounters the first fan structure. It cannot move through the fan as the bottom of the fan is closed and the central hole is blocked by the support structure. The gas is therefore forced out of the triangular ducts, impinging directly on the internal surface of the reformer tube, where it gathers heat (see Figure 3). Having nowhere else to go, the gas flows around the edges of the fan and back into the triangular duct on the underside side of the fan (see Figure 4). The washers that separate the fans from one another facilitate this flow back into the fan. Once inside the fan, the gas is free to move to the next fan in the stack and repeat the process.

The gas moving in and out of the fans continuously flows over all of the catalyst-coated surfaces of the fans, where the reforming reaction takes place.

The impingement heat transfer mechanism results in a significant performance benefit when compared to pellets. Results from tests are shown in Figures 5

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**Figure 5** Pressure drop vs flow

**Figure 6** Heat transfer vs flow

**Figure 7** Relative performance of various steam reforming catalysts

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and 6. A CATACEL JM SSR design was selected that gave a pressure drop very similar to that of KATALCOJM.GQ size QUADRALOBESM reforming catalyst pellets (see Figure 5). The improved heat transfer achieved by the CATACEL JM SSR design is shown in Figure 6, which illustrates an improvement of approximately 30%.

The key performance indicators for the CATACEL JM SSR catalyst set on a timeline of the various Johnson Matthey steam reforming catalysts is shown in Figure 7. This shows how the activity, heat transfer and pressure drop of steam reforming catalysts have developed over the past three decades.

Set against this, the performance improvements of the CATACEL JM SSR catalyst are substantially larger than those that can be obtained by further development of ceramic based pellets and are larger than any previous improvements seen.

Any of the improvements in performance taken on their own would generate substantial benefits for operators of steam reformers. However, as the activity and heat transfer can both be markedly improved whilst at the same time reducing the pressure drop, it generates the potential for noticeable improvements in steam reformer operation. The CATACEL JM SSR catalyst will generate reductions in tube wall temperature, increasing the heat transfer efficiency of the furnace. It will reduce the approach to equilibrium and methane slip, decrease operating pressure and the risk of carbon formation, increasing both catalyst and tube lives. In a new reformer, considerable capital can be saved. These benefits will be described in more detail in the case studies presented below.

**Initial installation: Turkey**

In August 2008, an early version of CATACEL JM SSR was installed in a small can reformer in a hydrogen plant in Turkey. The plant ran well for four years in spite of numerous upsetsun related to the catalyst. Even though it was still performing well, that catalyst was removed in January 2013 at a scheduled turnaround and replaced with the current version of CATACEL JM SSR. The removal and reinstallation process was accomplished without major incident. The coated foils removed maintained their original integrity in spite of the process upsets and significant contamination from boiler feed water, indicating that coated foil materials can survive and thrive in a reforming environment. The new charge started up well and has operated without issue since installation.

**Second installation: Mexico**

In May 2012, CATACEL JM SSR was installed in a small can reformer in a hydrogen plant in Mexico. This user sought to obtain natural gas savings by reducing fuel consumption, while having
the option to increase throughput beyond the name plate capacity, and attain a longer operational lifetime for both the catalysts and reforming tubes. The reformer configuration in the plant consisted of reformer tubes of varying ages, several of which had been recharged with ceramic pellet catalyst as recently as January 2012. After thorough study and analysis, the plant’s managers decided to replace the ceramic catalyst media in all reformer tubes with CATACEL JM SSR catalysts. The change-out was completed with minimal downtime in May 2012 by plant staff under supervision.

After installation, the hydrogen plant restarted without incident, and immediately demonstrated a 13.5% reduction in burner make-up fuel consumption. Over the following weeks, the plant’s operating conditions were optimised to take advantage of CATACEL JM SSR. Figures 8 and 9 show furnace temperature reduction (40-60°C) and fuel savings (25-30%) realised at various plant rates with the optimised plant.

The plant continues to perform at optimum levels and the estimated payback time for the entire charge is two years based only on fuel savings alone. This does not account for savings to be realised over years to come by eliminating catalyst and tube changes.

Case studies

The development path for CATACEL JM SSR catalyst has demonstrated its performance in two small can reformers. However, the majority of operators in the syngas industry use either top fired or side fired reformers. A series of case studies based on plant performance modelling follows, demonstrating several scenarios in which the technology can improve steam reforming operations for typical top fired and side fired reformers.

Hydrogen plant uprate

In the first case study, a small hydrogen plant was initially designed to operate on naphtha feedstock which was later changed to natural gas. The heat exchange duty in much of the plant was reduced because the steam ratio was reduced, which also decreased the combustion air flow requirement, resulting in excess capacity in the combustion air fans. However, the reformer is now operating close to the tube wall temperature limit. In an attempt to moderate the peak tube wall temperature at the top of the tubes, excess fan capacity is currently being used to provide high excess combustion air.

Whilst the rest of the plant is capable of operating at this higher capacity, the
tube wall temperatures are the limiting factor. The option chosen to release the available capacity in the rest of the plant is to change to CATACEL\textsubscript{JM} SSR catalyst in the steam reformer. The higher heat transfer and higher activity of the catalyst can reduce the tube wall temperature significantly, allowing higher throughput and firing for the same reformer pressure drop. Table 1 shows the reforming parameters for the hydrogen plant based on the KATALCO\textsubscript{JM} QUADRALOBE and CATACEL\textsubscript{JM} SSR catalysts.

The base case defines the maximum operating point of the plant based on the current limit of tube wall temperature and pressure drop.

Case 1 shows the impact of installing CATACEL\textsubscript{JM} SSR catalyst in the reformer at the current throughput. There is a significant improvement in both the pressure drop and the maximum tube wall temperature, so that these conditions no longer limit the reformer.

**Installing CATACEL\textsubscript{JM} SSR catalyst can provide a simpler and more cost effective way of achieving the increased throughput required**

Case 2 shows that a 15\% increase in throughput can be achieved within the existing constraints of tube wall temperature and pressure drop. The fuel required rises by 12.5\% and the combustion air rises by 5\%. This reduces excess air making the furnace more efficient, with the result that the flue gas temperature increases by just 15 °C.

**Impact of CATACEL\textsubscript{JM} SSR catalyst on a new terrace wall reformer**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>QUADRALOBE</th>
<th>CATACEL\textsubscript{JM} SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number tubes</td>
<td>352</td>
<td>322</td>
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<td>Number tubes/row</td>
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<td>Tube ID, mm</td>
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<tr>
<td>Tube OD, mm</td>
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<tr>
<td>Tube wall thickness, mm</td>
<td>12.0</td>
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<tr>
<td>Tube heated length, m</td>
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<td>14.00</td>
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<tr>
<td>Furnace length, m</td>
<td>36.03</td>
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<tr>
<td>Furnace width, m</td>
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<td>200</td>
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<tr>
<td>Heat load, MW</td>
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</tr>
<tr>
<td>Catalyst pressure drop, bar</td>
<td>3.31</td>
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<tr>
<td>Minimum tube wall margin, °C</td>
<td>34</td>
<td>34</td>
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<tr>
<td>Relative cost, %</td>
<td>100.0</td>
<td>90.2</td>
</tr>
</tbody>
</table>

**Table 3**

**Impact of CATACEL\textsubscript{JM} SSR catalyst on a new top fired reformer**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>QUADRALOBE</th>
<th>CATACEL\textsubscript{JM} SSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number tubes</td>
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<td>Number tube rows</td>
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<td>Number tubes/row</td>
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<td>53</td>
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<td>Tube ID, mm</td>
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<td>Tube OD, mm</td>
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<tr>
<td>Tube wall thickness, mm</td>
<td>9.70</td>
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<tr>
<td>Tube heated length, m</td>
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<tr>
<td>Furnace length, m</td>
<td>14.96</td>
<td>15.22</td>
</tr>
<tr>
<td>Furnace width, m</td>
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<td>27.94</td>
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<tr>
<td>Heat load, MW</td>
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<tr>
<td>Catalyst pressure drop, bar</td>
<td>2.83</td>
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<td>Minimum tube wall margin, °C</td>
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<td>79</td>
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<tr>
<td>Relative cost, %</td>
<td>100.0</td>
<td>92.0</td>
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</tbody>
</table>

**Table 4**

Installing CATACEL\textsubscript{JM} SSR catalyst in this plant can provide a simpler and more cost effective way of achieving the increased throughput required. The operator in this case is installing CATACEL\textsubscript{JM} SSR catalyst during 2015 to support the plant uprate.

**Hydrogen plant reduced steam ratio**

There is a trend in hydrogen plant designs to seek operation at a lower steam to carbon ratio to improve the economics of the overall hydrogen process. CATACEL\textsubscript{JM} SSR catalyst, with its significant increase in activity, reforms the hydrocarbons more quickly. This increases the hydrogen content, thus reducing the rate of carbon formation and increasing the rate of carbon removal. Additionally, the improved heat transfer of the catalyst results in a lower tube wall temperature at all points along the tube and, as carbon typically forms at the tube wall, this will also reduce the propensity for carbon formation. Therefore, the benefits of the catalyst can be taken as a reduced steam ratio to bring the plant to the same margin from carbon formation as with the pelleted catalyst at a higher steam ratio.
An assessment of the benefits of a reduction in steam ratio from 2.9 to 2.7 with CATACELJM SSR catalyst for a hydrogen plant is shown in Table 2.

The base case gives the key parameters for the reformer with KATALCOJM QUADRALOBE pelleted catalysts, indicating that the tube wall temperatures are 39°C from the carbon formation temperature.

Case 1 shows the predictions for operation with the CATACELJM SSR catalyst at the same hydrogen production rate as the base case at the original steam ratio. There is a 50% increase in the margin between carbon formation and the inside tube wall temperature.

Case 2 shows the predictions for operation with the CATACELJM SSR catalyst at the lower steam ratio. The hydrogen production rate remains the same by increasing the feed rate to compensate for the increased methane slip. Overall, the reformer’s efficiency is increased as the total natural gas feed plus fuel flow is lower than Case 1 and there is less heat transferred into the flue gas or process gas.

New reformers designed for CATACELJM SSR technology

In recent years, there has been a trend towards reformer designs with larger diameter, longer tubes to take advantage of the improved catalysts and reformer tube materials available. Such designs result in a smaller number of tubes, which reduces the costs of the reformer.

The adoption of CATACELJM SSR catalyst can have a significant impact on the design of new reformers due to its higher heat transfer, higher activity and lower pressure drop. The reduced tube wall temperature allows the use of thinner wall tubes, reducing the tube cost. The reduced pressure drop allows the use of a smaller number of longer tubes for the same overall pressure drop, creating additional cost savings.

Several reformer designs have been investigated, with a redesign based on CATACELJM SSR catalyst. Cost comparisons have been made between the reformer designs to show the savings that are available. The reformer designs have been made on identical process duties and the same design tube wall temperature design margin.

Tables 3 and 4 show the results for two different reformer configurations and duties, where the design based on KATALCOJM QUADRALOBE has been modified for CATACELJM SSR catalyst. The key dimensions of the furnace are given along with the key process parameters. The final row in each table gives an estimate of the relative cost of the radiant box for both pelleted catalyst and CATACELJM SSR catalyst.

The data show a capital cost saving of the order of 8-10% for each of the designs listed. Additional studies over a wider range of reformer duties have shown that this is repeatable for most reformers, with the smallest savings no less than 5% and some redesigns showing a cost saving of 15%.

Conclusions

Structured CATACELJM SSR technology delivers a significant improvement in performance compared to traditional pelleted catalysts. The catalysts have been demonstrated to be mechanically and chemically robust during operation over typical reforming catalyst lives in commercial steam reformers. Their adoption in a steam reformer results in significantly cooler tubes with lower methane slip and lower pressure drop.

This can result in the easing of these operating limits on the reformer, which can allow significant increases in throughput to be achieved. Substantial savings can also be made in the size and capital cost of new reformers designed on the basis of the technology.

KATALCO, QUADRALOBE, CATACEL and CATACEL SSR are trademarks of the Johnson Matthey Group of Companies.

William A Whittenberger is Site and Technology Director with Johnson Matthey Process Technologies, Inc, which acquired the assets of Catacel Corp, Ohio, in September 2014. He co-founded Catacel in 2001 to develop and commercialise catalyst materials and systems using metal foil substrates. He holds a bachelor’s degree in mechanical engineering from Ohio State University, a MBA from Pepperdine University and 50 patents covering foil based catalyst design.

Peter Farnell is Reforming Technology Manager with Johnson Matthey Process Technologies. He holds a master’s degree in chemical engineering from Loughborough University of Technology, UK.