A STEP CHANGE IN CATALYST DEVELOPMENT

Mark Stuckey, UNICAT Catalyst Technologies LLC, discusses the emergence of next generation spherical catalysts and their impact on yield increases and reduced carbon dioxide (CO_2) emissions in tubular reformers.

Designs of tubular steam methane reformers (SMRs) have, wherever possible, been optimised around the limitations of key component capabilities, i.e. dimensions and high temperature creep of tubes, together with the pressure drop and activity of the conventional catalysts within the tube. Over the years, tube and catalyst manufacturers have improved their respective products, but limitations of conventional catalyst carrier manufacturing processes have slowed any significant developments over the last 20 years.

The next generation of catalyst required a step change in carrier manufacturing processes. It is generally known that spherical shapes pack better in tubes than alternate cylindrical types, but it has been difficult to manufacture spheres in volume, so all conventional carriers have been non-spherical. However, 12 years ago, UNICAT, knowing the packing benefits, introduced the first spherical catalyst into a tubular steam reformer.

This article will detail two industrial cases which demonstrate the effect of catalyst shape optimisation – moving to spheres from non-spheres. The first case will be UNICAT's plain spheres, with 12 years of operation in a 450 Tube DRI reformer. The second is a US refinery installed with UNICAT's Magcat Textured Sphere technology.

Background

The overarching efficiency of a reformer is derived from the efficiency of heat transfer through and into the tube. This heat energy, combined with the catalyst, promotes the reaction between the process gas (steam and methane) to produce hydrogen.

The effectiveness of getting heat into the tube and facilitating the efficiency of the reforming process is highly dependent on the flow of the process gas through the tube. The aim is to facilitate the lowest amount of process gas flow restriction whilst allowing for sufficient time for the reforming reaction to take place.

The catalyst shape and how the thousands of individual catalysts pack impact the flow dynamics of the process gas. Conventional catalysts pack chaotically due to their non-spherical shape, and this leads to uneven flow, flow bottlenecks, and sub-optimal heat transfer.

Conventional catalysts are produced using either extrusion or hydraulic pressing. As a result of these manufacturing techniques, only mono-directional shapes are able to be manufactured. Holes are added to try and reduce the shape pressure drop issues and to introduce mathematically-calculated geometric surface area.

However, this has a limited benefit. Firstly, the mono-directional shape and alignment of holes within that shape will not pack within a tube with the holes aligned to the process gas flow. Secondly, process gas will always look to follow the easiest path through a restricted tube. The majority of the flow will preferentially look to find the voids between the shapes, and these voids in a tube packed with conventional catalysts are chaotic.

Spheres pack uniformly, naturally resulting in the voids being the same shape and size, meaning even distribution of the process gas across and through the tube. The benefit of this even distribution effect with spheres is that the process gas restriction (pressure drop) is lower, allowing for significantly more flow through the tube. Additionally, because the process gas evenly reaches every individual catalyst sphere within the tube, all of the active surface area is available and involved in the reforming.

UNICAT's plain spheres (see Figure 1) have a low geometric surface area (GSA) relative to their volume, and so deliver the pressure drop benefits but are not optimised for active surface area. The Magcat technology added golf ball-like surface texturing, maintaining all of the process flow distribution benefits of spheres whilst optimising the active surface area.

Tubular SMRs are used extensively in the production of hydrogen, generating 96% of hydrogen produced worldwide.[1] On average, 65% of global refinery hydrogen demand is satisfied by reforming and cracking processes, and 32% is provided by on-purpose units.[2]

Sphere catalyst technology

Generation 1.0 technology is based on plain four-holed spheres, under the brand MYD-S (see Figure 1). The sphere was introduced to facilitate uniform packing and flow. The holes were added for customer visual acceptance rather than any process benefits. The sphere manufacturing technology is economically-viable for the larger > 20 mm spheres, and as such was only offered to the Direct Reduction of Iron (DRI) market in July 2012.

27 mm four-holed spheres were supplied into a 450 x 11 in. dia. tube DRI SMR in the Americas. Tubes were loaded with the same-sized 28 mm MYD-S sphere containing between 8 – 11 wt% nickel. They replaced a previous charge of ribbed cylinder-shaped catalysts.

The customer referenced the following differences in performance in March 2018:

- The overall reformer pressure drop had fallen by 60% as compared to the previous charge.
- Reformer gas quality remained equal.
- Approximately 15% energy savings were achieved.
- An increase in total plant capacity to 210 tph from 190 tph.
- No intermediate plant shutdown was required over the five years for dust removal.

The customer could have increased plant capacity further, however they were limited due to the compressor capacity. The change from cylinders to spheres delivered other physical benefits which will be explained in the following sections.

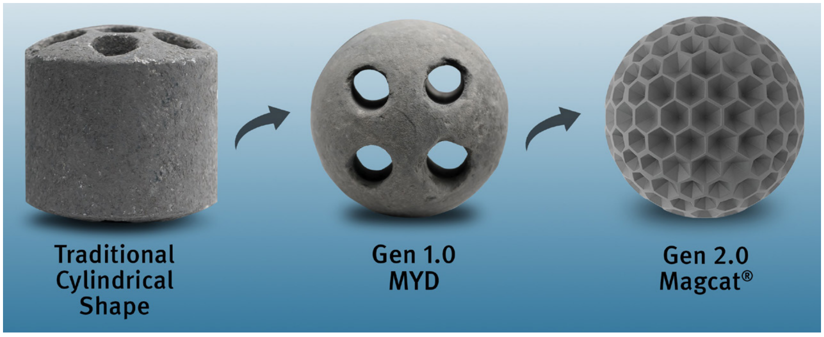

Figure 1. Examples of SMR catalysts in traditional cylindrical shapes, UNICAT's Gen 1.0 plain spheres and Gen 2.0 textured sphere (left to right conventional cylinders, MYD-S plain spheres, Magcat® textured sphere).

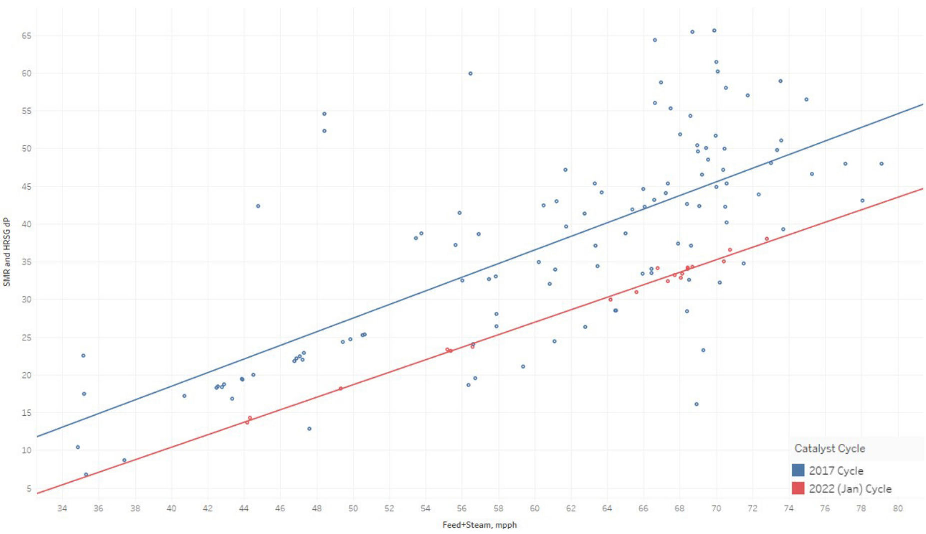

Figure 2. Operating data from a top five US refiner comparing throughput to unit pressure drop with different SMR catalysts.

Next generation SMR sphere catalyst technology

Magcat Textured Spheres' manufacturing processes and shapes were designed to optimise the compromises of plain spheres. Essentially, the manufacturing process was developed to enable the mass production of any sized spheres with surface textures.

Magcat is compatible with all tubular steam reformers (primary reformers) used for SMR, and is now installed in over 27 hydrogen plants worldwide.

Generation 1.0 spheres and Generation 2.0 Magcat have been shown to increase hydrogen production and reduce carbon dioxide (CO_2) emissions by 10 – 20% in ways that are easily implemented, and which avoid equipment investment costs. Spheres demonstrate lower pressure drop than previous charges, which in turn allows for higher process gas flows. Traditionally, SMR pressure drop is reduced by moving to larger catalyst pellet sizes. Larger pellets provide more voids, which translates to lower pressure drop. However, the trade-off of larger size pellets is lower total bed surface area, which results in higher methane slip, particularly late in cycles. The use of spheres and, more recently, externally-textured spheres, decouples concerns with surface area and pressure drop.

This premise is supported by SMR operating data (see Figure 2) for a site that installed Magcat in early 2022. The data demonstrates that, for fixed conditions, this technology generates 10 psi (0.7 bar) lower pressure drop at all corresponding feed rates, compared to previous installations of conventional, cylindrical SMR catalyst. Counterintuitively, Magcat of smaller size than the previous catalyst was loaded into this reformer to prove the advantage of spherical shaped catalyst in promoting uniform flow. To make use of this benefit, total feed to the reformer (feed gas plus steam, at constant or lower steam-to-carbon ratio) can be increased 10% at constant pressure drop or observed hydraulic limit. Operating at constant feed rate, this pressure drop benefit significantly offloads feed gas compressor duty at fixed reformer outlet pressure, reducing unit power consumption. Magcat and MYD-S spherical shapes have no straight edges, reducing excessive pressure drag associated with cylindrical pellets. Plain spheres have a drag coefficient of 0.47, textured spheres 0.27, and cylinders between 0.82 – 1.15.[3] The lower the drag coefficient, the lower the pressure drop. Additionally, a regular surface flow over the sphere is maintained (see Figure 3/4), adding symmetrical spheres into a

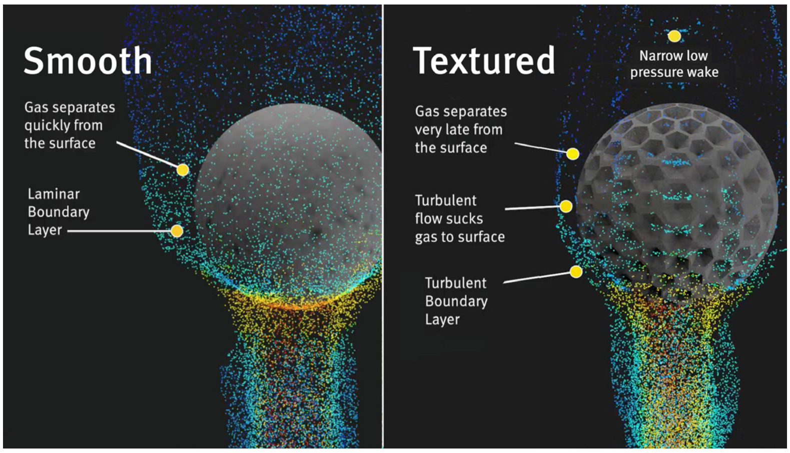

Figure 3. Flow simulation comparison of gas passing over a smooth spherical catalyst next to Magcat® textured spherical catalyst (gas moving from bottom to top).

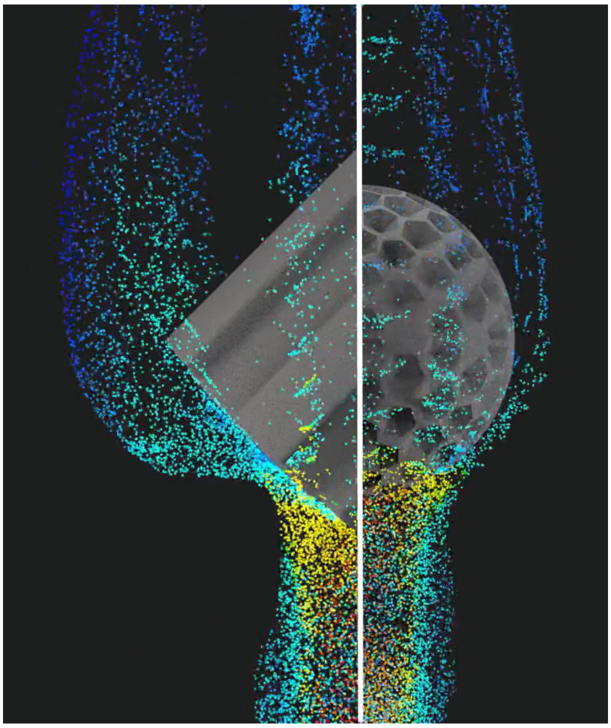

Figure 4. Flow simulation of gas passing over a half, static Magcat® textured spherical catalyst (gas moving from bottom to top) and a half ribbed cylinder showing the flow differences.

tube naturally generates repeatable and predictable packing patterns not otherwise associated with random loadings of cylindrical pellets.

Effects on fluid flow from uniform packing vs chaotic packing are profound. Gases entering tubes filled with spheres divide evenly to flow around full hemispheres of each sphere. Uniformity of spherical packing creates unbiased and equal flow paths for the entire cross-section. Upon exiting the initial layer of spheres, via regular and homogeneous void apertures between adjacent spheres, reactant gas flow immediately encounters the next layer of uniformly-packed spheres, over which it will again divide and reconnect with contiguous flow paths. This 'snaking' fluid flow across spheres encourages excellent mixing and intimate gas-to-surface contact. More crucially, lateral movement promotes heat collection from the tube wall and transportation of heat energy to the core of the tube to satisfy endothermic reforming reactions and equilibrium conditions favouring conversion to hydrogen at high temperatures.

In comparison, tubes packed randomly with cylinders induce high pressure drag over bluff bodies in most aspects, and generate chaotic fluid flow paths, resulting in dead spots; back-eddies; bypassing; and hosing through catalyst holes when vertically orientated, thus diminishing lateral movement that is critical for effective radial heat transfer.[4] Spherical catalysts generate numerous, predictable pellet-wall contacts disturbing convectional boundary layer thickness along the wall and redirecting heated flows laterally into the bed (see Figure 5).

Magcat's SMR catalyst does not incorporate holes. Literature lists the advantages of multiple holes in cylindrical pellets as: increased voids (associated with lower pressure drop in conventional loadings), and increased active surface area. Magcat is not limited in either, due to expanses of surface area from external texturing and internal porosity, and substantial and regular voids between particles when packing solid spheres.[5]

Another benefit is lower inherent pressure drop imparted by spheres in comparison to other common SMR catalyst shapes. Further, observed void increases during bed movement of textured sphere packing during heat up, which allows smaller Magcat sizes to be selected than would be traditionally expected for an application.[3] Smaller spheres further increase surface area, wall contact points, and promotion of radial flow without compromising overall system pressure drop compared to a loading of larger cylinders.

Disadvantages for holes that are listed in literature are particle weakness and reduced radial flow. Additionally, holes will not offer the gains proposed unless available to flow by being orientated vertically or near-vertically. Random packing results in proportions of pellets not oriented in ways that are beneficial. Without strength, surface area or pressure drop concerns, Generation 2.0 Magcat spheres exclude holes to maximise radial heat transfer, which benefits steam reformers the most.

Radial heat transfer is key for efficient hydrogen production in SMR. Energy movement from externally-heated tube surfaces to the inner bed core replenishes energy debts generated by net endothermic reforming reactions. UNICAT's Generation 1.0 and Generation 2.0 Magcat applications observe much lower tube wall temperatures (TWT), typically decreasing tube failure due to creep by at least 40%. Further, hot spots and red bands are less likely in spherical catalyst loadings as uniform packing minimises bridging. This means further increased tube lifetimes and the avoidance of common points of failure.

The same industrial user observed that, after switching to Magcat, the same methane slip could be achieved at significantly lower combustion outlet temperature under other constant conditions as a result of the heat transfer improvements discussed (see Figure 6). It is this unlocking of

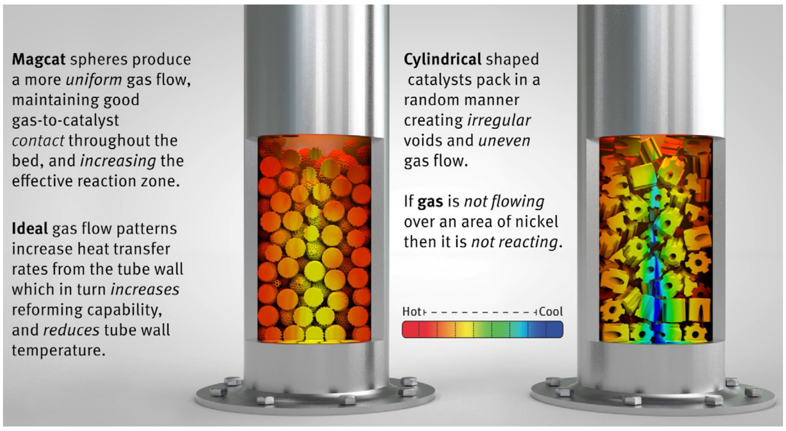

Figure 5. Simulation of gas flow in packed tubes with Magcat® (left) and cylindrical catalyst (right), emphasising preferential flow path differences.

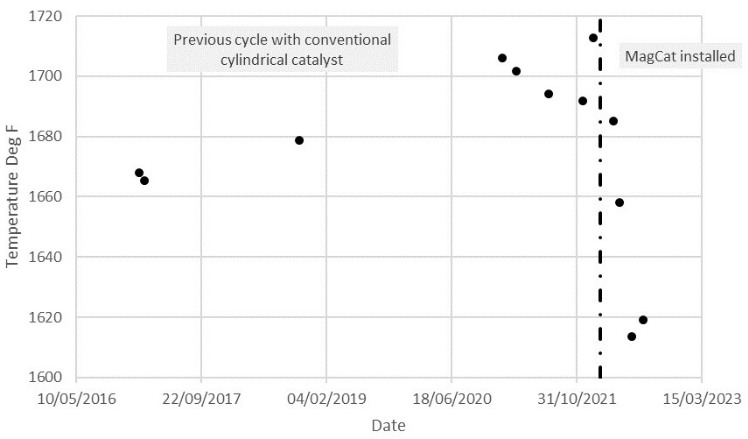

Figure 6. Increases in reformer outlet temperature through operating cycle using conventional SMR catalyst compared to low outlet temperature with Magcat® installed.

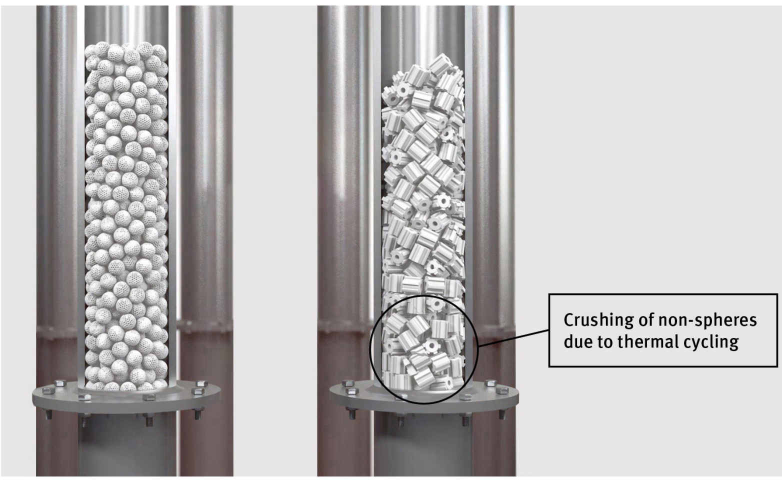

Figure 7. Cut through tube view of spherical catalyst (left) showing even and supported fill, and conventional catalyst (right) showing crushing impact of tube thermal cycling due to lack of support facilitating catalyst dropping and crushing.

constraints, particularly the most challenging and most limiting factor of improved radial heat transfer, that allows MYD-S and Magcat users to increase hydrogen production above nameplate capacity and historical maximums via increased throughput.

A further advantage of spherical catalysts can be seen in Figure 7. As the tube cycles from hot to cold for any number of reasons, it exerts radial pressure on the catalysts packed in the tube. The sphere packing, due to its uniform nature, provides support for all of the spheres. This limits the voids between the pellets to less than half the diameter of an individual sphere, and creates a relaxing effect with subsequent hot/cold/hot tube movements. As there is nowhere for the spheres to go, the radial pressure pushes the spheres closer to each other on cooling, and opens up the voids slightly during heating – stopping the catalysts from crushing each other. The opposite happens with a conventional cylinder packed system, i.e. on heating, holes are opened up between catalysts, allowing corners or edges to drop into gaps that have opened up; and on cooling the tube diameter closes, crushing catalysts against each other.

Conclusion

UNICAT's MYD-S and Magcat spheres are demonstrating excellent performance in tubular SMR reformers, as shown in one such example operated by a top five refiner in the US, and as referenced by a global steel company operating a DRI reformer. These benefits can be clearly understood from underlying effects on fluid dynamics, thermodynamics, and heat transfer of spheres vs conventional shapes. Energy efficiency, lower CO_2 emissions, increased hydrogen production, and extended tube life are some of the advantages of next generation spherical catalysts. HE

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