Structured catalyst for steam reforming

A catalyst system for steam methane reforming for improved heat transfer, pressure drop and catalyst effectiveness

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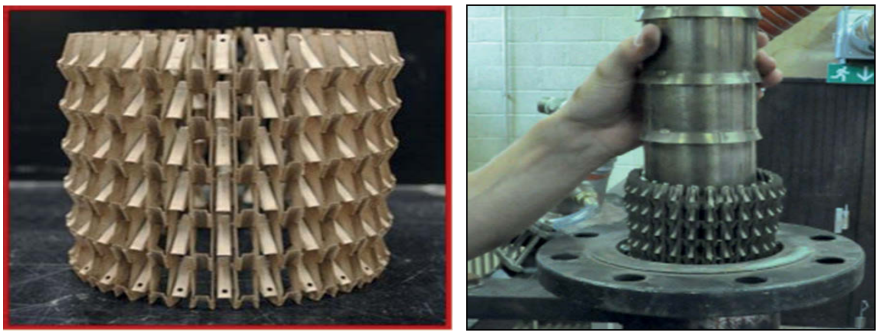

Figure 1 ZF Reactor's typical casing and assembly

The predominant technology for hydrogen-syngas generation over the years has been steam reforming of light hydrocarbons, mainly natural gas, commonly called steam methane reforming (SMR). This mature technology, however, has seen only incremental improvements in its catalyst design and its performance in conjunction with superior tube metallurgy and reformer design with the aim of better efficiency and reliability.

ZoneFlow Reactor Technologies (ZFRT) has developed proprietary structured catalyst solutions for steam reforming, pre-reforming and recuperative reforming. ZoneFlow (ZF) Reactors provide higher heat transfer, lower pressure drop, higher geometric surface area (GSA), more uniform flow and heat distribution, and long term structural integrity compared to pellet catalyst. Use of ZF Reactors enables significant capital and operating cost reduction in steam reforming for new plants as well as revamps.

Current best technology

Conventional pellet steam reforming catalysts suffer from inherent limitations and/or operational deficiencies. These mainly relate to: uneven random packing voidage leading to undesired flow and temperature maldistribution; catalyst attrition and breakage from thermal cycling leading to increasing pressure drop and related capacity limitations; and pore diffusion limited reaction path leading to curtailed intrinsic activity and lower resistance to carbon formation.

With the steam reformer as the heart of a syngas plant, carrying out the reactions involves heat, mass and momentum transfer and the reforming catalyst plays a critically important role in thermal design, performance, reliability and cost effectiveness.

Past attempts to develop structured steam reforming catalysts to overcome some of these limitations have suffered from innate problems around differential expansion gaps leading to feed bypassing and disturbed boundary layer endotherm, as well as from the reactions being mostly realised away from the tube wall, with heat transfer limitations leading to insufficient conversion and/or hotter tubes.

Nested modules

ZF Reactor technology overcomes these deficiencies but also offers a combination of higher heat transfer with substantially lower pressure drop. The reactor's structure also imparts a high degree of proximal flexibility which eliminates the differential thermal expansion gaps while carrying high physical strength against breakage over its lifetime.

Its nested modules provide more geometric surface than pellets and remove diffusion-limited access to the layered catalyst, resulting in much higher catalyst effectiveness factors and increased resistance to carbon formation compared to pellets.

ZF Reactors vs pellet catalyst

ZF Reactors are advanced catalyst systems based on an 'annular' foil casing structure (see **Figure 1**) offering two primary advantages over conventional pellet steam reforming catalysts:

- Lower pressure drop (dP): the ZF uses dP mainly to enhance turbulence near the tube wall, largely avoiding 'unutilised' dP
- Superior heat transfer: ZF's annular structure directs the gas flow towards and away from the tube wall to impinge on the hot surface of the tube wall which significantly enhances heat transfer, lowering tube skin temperatures, or allows higher heat flux for the same tube design temperature.

Additionally, ZF Reactors offer advantages compared to pellets for revamping as well as new steam reformers:

- Much higher catalyst effectiveness resulting from the use of thin catalyst layers
- Uniform heat transfer and fluid flow in all the tubes against the inherent maldistribution of flow per tube with pellets (typically +/-2-5%) and

thus tube temperature non-uniformity on the same plane across the tubes, thereby also eliminating hot tubes that can restrict full load operation while also risking shorter tube life and coke formation

- Long term structural integrity, including mechanical features to accommodate thermal cycling, thus avoiding pressure drop build-up over time related to progressive deterioration of pellets.

Development and validation

Various computational fluid dynamics (CFD) and finite element analysis (FEA) studies have confirmed these properties and enabled deeper insights into ZF's performance and design, helping to optimise the balance between these performance parameters (see **Figure 2**). The reactors can be tailored for an optimum combination of higher heat transfer coefficient and lower dP compared to pellet catalysts (see **Figure 3**).

ZFRT has achieved various development and validation milestones in recent years: bench scale validation at the University of California's Davis HyPaul labs; independent CFD reactor modelling for optimisation of heat and mass transfer and pressure drop; and FEA to establish mechanical robustness and long term durability. The designs have been further tested and demonstrated in a commercial SMR with ZF inserted in two tubes (out of more than 200), allowing direct comparative assessment of conventional pellet catalyst under the same operating conditions, apart from verification of loading/unloading into commercial scale tubes. The results achieved near two-fold higher heat transfer reflected in a tube skin temperature lower by up to 60°C with more than 25% lower pressure drop compared to the adjacent tubes operating with pellet catalysts. The reactor designs can be optimised and customised for required balance between heat transfer and pressure drop for specific applications, and can also be made to fit any commercial SMR tube size.

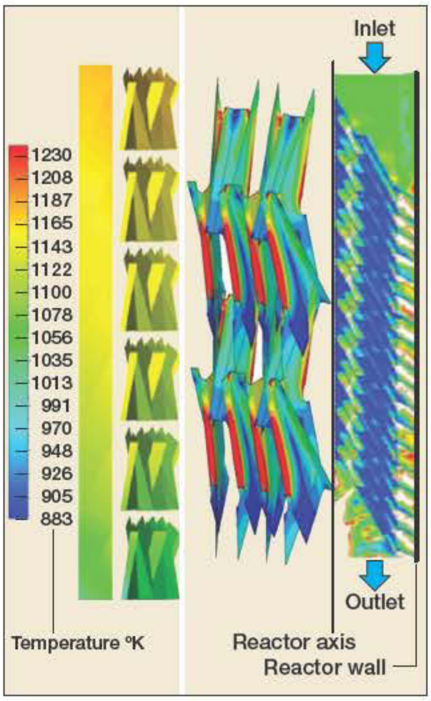

Figure 2 CFD modeling (upflow) and FE analysis (downflow)

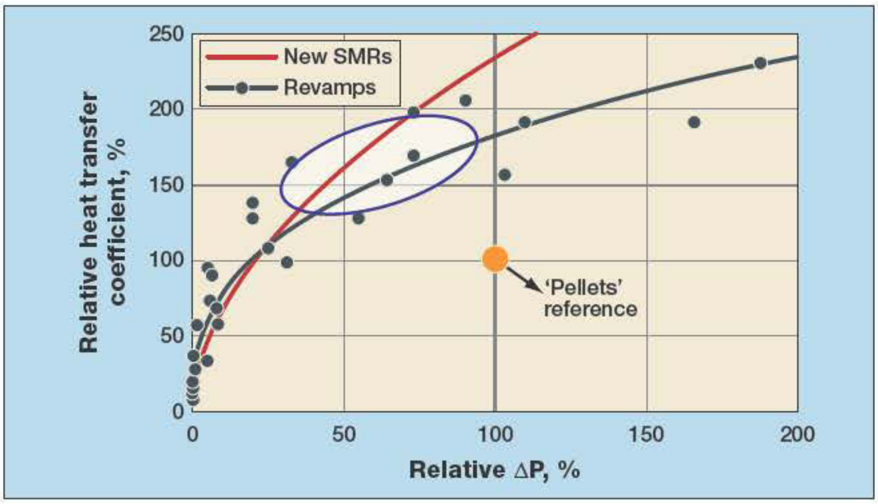

Figure 3 ZF Reactors exhibit higher heat transfer coefficient and lower dP

Pilot plant

ZFRT's pilot plant is nearing completion at the Université Catholique de Louvain, Belgium (UCL). It is a fully equipped and instrumented pilot plant with a microalloy tube suspended in an electric furnace. This installation will enable an extensive set of planned tests to further validate the performance and physical integrity of ZF Reactor designs under a wide range of conditions. It is expected to commence operation in mid-2018.

Various ZF performance and integrity tests will be conducted over a range of operating conditions covering commercial levels and beyond in terms of S/C ratios, pressures and temperatures. The severity levels cover S/C down to 1.7 and exit temperatures up to 900°C with pressures up to 30 barg. Both ZF-single pass as well as ZF-Bayonet for recuperative reforming will be tested.

The UCL pilot plant consists of methane feed pretreatment and compression as needed, water demineralisation, boiler feed water pump, start-up boiler, syngas boiler and steam superheater, supply of support gases (argon, nitrogen and hydrogen), steam reforming unit with electrical multi-element heated and controlled full bore tube (>6 m long), and a syngas cooling section followed by a back pressure regulator and condensate separation for safe flaring of syngas.

The plant is instrumented with state-of-the-art mass flow controllers, pressure, temperature and level controllers, as well as high integrity thermocouples with monitoring clusters for the process gas and tube skin temperature measurements. Excess steam produced is vented. The reformed gas composition is measured by on-line gas chromatography.

ZF Reactor designs can be optimised and customised for the required balance between heat transfer and pressure drop for specific applications, and can also be made to fit any commercial SMR tube size.

Solutions for advanced SMRs

The following case analyses cover ZF applications in a SMR:

ZF-Single pass

- Destressing and debottlenecking SMRs
- Higher flux, cost effective and more reliable SMRs.

ZF-Convective pre-reforming

- In situ retrofit for additional capacity in existing SMRs without major modifications
- Efficient and cost effective applications in new SMRs.

ZF-Bayonet

- Applicable to recuperative reforming, overcoming current barriers.

In these case analyses, the common underlying advantages of ZF's lower dP and higher heat transfer coefficient include: higher outlet temperature without increasing maximum tube skin temperature (TSM); higher heat flux and/or higher outlet temperature without increasing bridge wall temperature, or related SMR firing duty; and lower approach to equilibrium.

Case 1: Destressing or debottlenecking of existing SMRs

- Additional ~5% capacity while retaining or safely utilising typical design margins
- Higher average heat flux without exceeding tube design temperature
- Improved temperature uniformity
- Extended tube life and improved reliability
- Better catalyst performance and 'life cycle' costs
- Optimised operation and enhanced reliability.

For a highlighted comparative analysis, see **Table 1**.

Case 2: Convective pre-reforming (ZF-CPR)

ZFRT has also designed and engineered an ultra low pressure drop structured catalytic reactor with high surface area/low cross-section for non-adiabatic low temperature convective pre-reforming (CPR, see **Figure 4**). It offers the benefits highlighted in **Table 2**.

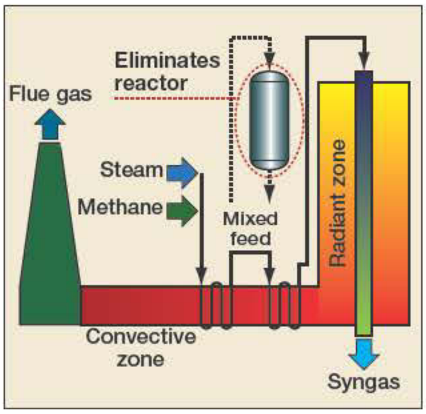

Figure 4 ZF-Convective pre-reforming versus Adiabatic pre-reforming

Case 3: ZF-Bayonet (ZF-B) for recuperative reforming

ZF Reactors are inherently suited to 'bayonet' (tube in tube) recuperative reforming based on their annular casing design. The reformed process gas flows out through the centre (core) tube providing part of the high grade heat recovery for steam reforming, thus lowering the fired duty as well as size of the reformer by 15-20%, apart from even larger reduction in the size of the steam system. The ZF-Bayonet application can be incorporated in any SMR firing configuration, whether top-fired, side-fired or (upflow) bottom-fired (see **Figure 5**).

Economic benefits and applications

ZF Reactor's advantages can translate into benefits ranging from relieving 'stressed' reformers, extending reformer tube life and capacity revamps, to lowering SMR-related opex and capex. It covers the capacity span from large hydrogen generation plants for the refining sector (whether new or revamp of existing plants) to advanced solutions for small scale distributed hydrogen for a future energy landscape. Its advantages also cover hydrogen production for methanol and GTL plants, including modularised units for remote gas monetisation as well as flare gas reduction.

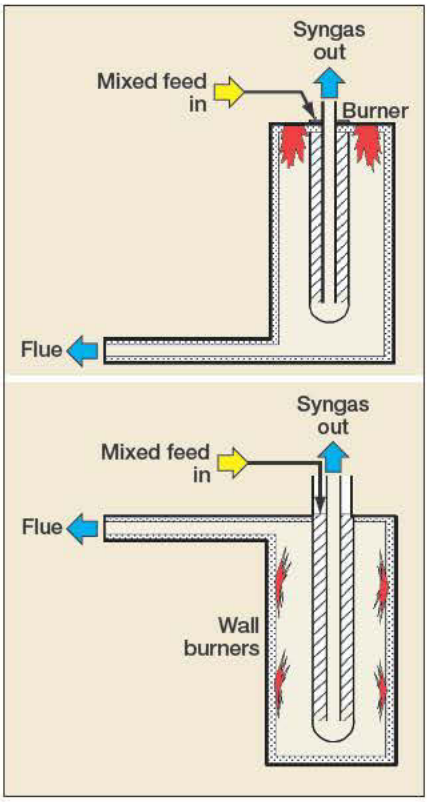

Figure 5 ZF-Bayonet applications in different SMR configurations

ZF-SP application assessment

	Reference	ZF-SP
Relative capacity, %	95/100	100/105
Capacity limitations	dP, TSM	Removed
S/C ratio	3.0	2.8
Outlet temp., °C	865	874
Approach to equilibrium, °C	-10	-7
CH_4 slip, dry vol%	5.5	5.6
Radiant pressure drop (dP), bar	2.8	2.5
Relative radiant duty, %	100	104
Avg. heat flux, kW/m²	75	78
Bridge wall temp, °C	1008	1004
Max. tube skin temp., °C	940	938

Table 1

Summary of ZF-CPR revamp analysis

	Reference	ZF + CPR
Relative capacity, %	100	115
S/C ratio	3.0	2.8
SMR inlet temp., °C	550	550/575*
SMR outlet temp., °C	870	870/878*
Approach to equilibrium, °C	-10	-7
CH_4 slip, dry vol%	4.8	5.4/5.0
Radiant pressure drop (dP), bar	2.5	2.3
Avg. heat flux, kW/m²	80	80-82
Relative radiant duty, %	100	100/103
Bridge wall temp, °C	1020	1009/1018
Max. tube skin temp., °C	950	938/948

*Exploiting existing design margins

Table 2

Conclusion

ZFRT developed innovative structured catalyst technologies for steam reforming with demonstrated improvement in heat transfer, pressure drop and catalyst effectiveness. The company's portfolio also includes pre-reforming and recuperative reforming.

Based on a paper presented to the AFPM Annual Meeting, 11-13 March 2018, New Orleans.

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