Structured catalyst reactor system for steam methane reforming

Results from pilot plant test programme confirm significant advantages and value creation

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Steam methane reforming is the predominant and most widely used process for syngas and hydrogen production. The catalyst-induced reforming reaction is highly endothermic, thus calling for multiple tubes filled with catalyst and suspended in a furnace known in the industry as a steam methane reformer (SMR). The design, efficiency, tube life, and operational reliability of a SMR are governed to a large extent by its catalyst.

Although a matured technology, it has seen only incremental improvements in its catalyst design in conjunction with superior tube metallurgy over the years. The size and shape of current state-of-the-art pellet catalysts reflect the various developments aimed at improving heat transfer, pressure drop, and catalyst effectiveness. However, SMR performance with pellets catalyst remains inherently limited by heat transfer between the inner tube wall and the process gas, pore diffusion limitations, and heat transfer improvement at the cost of a higher pressure drop.

ZoneFlow Reactor Technologies LLC (ZFRT) developed the proprietary ZoneFlow structured catalytic reactor system (hereafter called 'ZF reactor') for steam methane reforming as a technological advancement (see **Figure 1**). It has been shown to provide numerous benefits over conventional pellet catalyst in terms of heat transfer, pressure drop, and catalyst effectiveness properties.[1,3]

ZF reactor modules have an annular and structured flexible casing, designed to double heat transfer compared to pellets without increasing pressure drop.[3] The development journey of ZF reactors included catalyst selection for coating based on kinetic testing and modelling,[2] optimisation of the reactor design, and cost-effectiveness based on heat transfer-pressure drop testing,[3] as well as computational fluid dynamics (CFD) modelling.[4,5]

Past work and referred publications reported the results of detailed CFD modelling and comparative measurements of the pressure drop and heat transfer of commercial pellets vs ZF reactors. ZF reactors showed a heat transfer enhancement to the extent of 2.2-2.4 times that of the conventional pellet catalyst without any pressure drop increase at commercial flow regimes (mass flux of 9-12 kg/sec-m^2).[3,4,5]

Subsequently, a rigorous pilot plant test programme for performance validation of the ZF reactors on near-commercial conditions was successfully conducted and completed by November 2022 in a joint effort based on the Joint Development Agreement between Honeywell UOP and ZFRT ('Pilot Plant Test Program'). Details and results of the pilot plant test programme are described further in this article.

Table 1 summarises the main differentiators of ZF reactors over state-of-the-art pellets based on the results of the pilot plant test programme. Apart from the main advantages of enhanced heat transfer (2.2-2.4 times that of pellets without pressure drop penalty) and lower pressure drop (40-50% lower vs pellets at the same flow rate), ZF reactors are stacked as modules in uniform loading in all the tubes. This results in uniform flow distribution over each tube compared to the randomly packed pellets causing inherent non-uniformity of flow even with the best pellet loading methods.

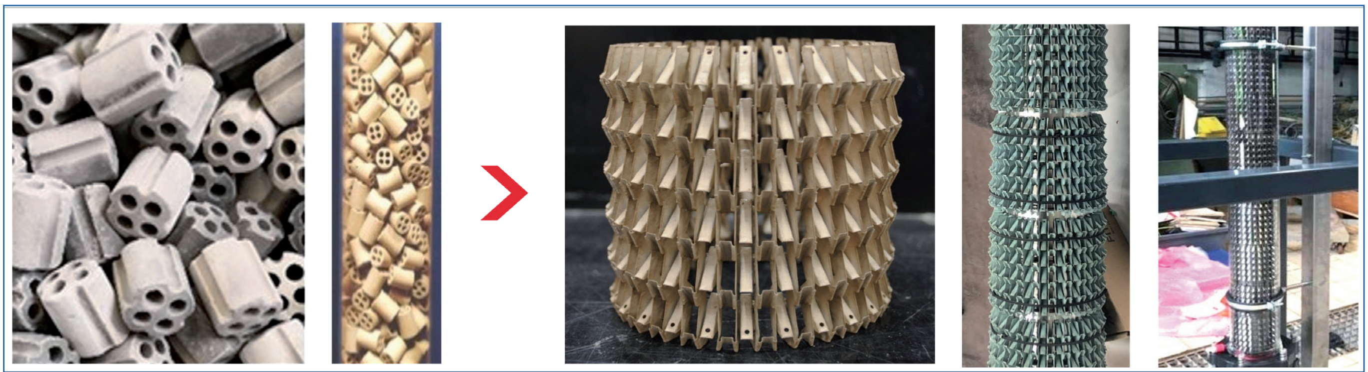

Figure 1 ZoneFlow structured catalytic reactors to replace pellets in steam methane reforming. Left, conventional pellet SMR catalyst. Right, ZoneFlow reactor structured catalyst system

ZF reactor differentiators over state-of-the-art pellets

Characteristic	Pellets – status quo	Zoneflow – a breakthrough
Substrate	Ceramic – cement	Engineered metallic foil
Geometry	Pellets in various shapes	Structured annular casing
Loaded pattern	Random, non-uniform	Aligned stack, fully uniform
Strength and voidage	Mutually limiting	Robust, higher voidage, flexible
Flow/temp maldistribution	Inherent – rising over time	None or minimised – entire life
Thermal cycling effects	Attrition and setting; dP >>	No attrition and setting stable dP
Geometric surface – active sites access	Inherent diffusion limitation, partial utilisation	Open-acess' catalytic surface, minimised diffusion limitation
Catalyst – tube wall proximity and temperature gradient	Sporadic wall contact irregular gaps; larger gradient	Full peripheral contact – in cold AND hot condition, lower gradient
Catalyst effectiveness	**Low (inherent)**	**Higher (by multi-fold times)**
Pressure drop	**Base, increasing over life**	**~ Half; same over entire life**
Heat transfer	**Base, stagnant inner film**	**~ Double; near-wall turbulence**

Table 1

Based on industry best practices and modern methods for loading pellets, at best, the target can achieve as low as +/-3-4% variation in pressure drop over the multiple tubes in the SMR (measured using a preset air flow in each tube during loading), leading to inherent flow variation. In contrast, since ZF reactors are in a uniformly stacked identical metallic structure assembly in all the tubes, the non-uniformity of pressure drop and related flow rate per tube is deemed to be negligible (as confirmed by 3-D CFD modelling[4,5]). The uniformity of feed flow per tube minimises the variations in heat pick-up across the multiple tubes (based on a homogeneous stirred firebox). It thus minimises temperature spread and maldistribution in terms of tube skin temperatures as well as the outlet gas temperature from each tube, thereby requiring lower design margins for the outlet system.

The results and findings of the pilot plant test programme alidated the uniformity and robustness of the metallic foil substrate and stacked module design assembly. It also thereby prevents settling, crushing, and breakage. These are typical problems with pellets, causing increasing pressure drop over their operating life and thus worsening the maldistribution of flow and related tube temperatures.

The reactor's design capabilities were demonstrated and verified in all the test campaigns based on the measured methane slip being very close to that simulated from the operating conditions (and expected approach-to-methane equilibrium). If there were any feed bypassing along the tube wall due to gaps between the ZF assembly and tube wall under hot/operating conditions, the methane slip in the reformed gas (and the approach to methane equilibrium) would have been far higher than observed.

Pilot plant description

The ZFRT pilot plant has been built for extensive testing and performance evaluation of different steam reforming catalysts. It is a world-class unit in terms of capacity, reformer geometry, boundary conditions, instrumented provisions, and operational safety.

The driving force and underlying objective to realise such an ambitious venture was to have an unconstrained and dedicated capability for testing and demonstrating the performance of ZF reactors compared to conventional state-of-the-art pellet catalysts under the same operating conditions covering (near-) commercial levels in terms of operating conditions, heat flux, and feed conversion.

Referring to the diagram of the ZFRT pilot plant in **Figure 2**, the main individual functioning units (IFUs) are desulphurisation and compression of the supplied natural gas, feed

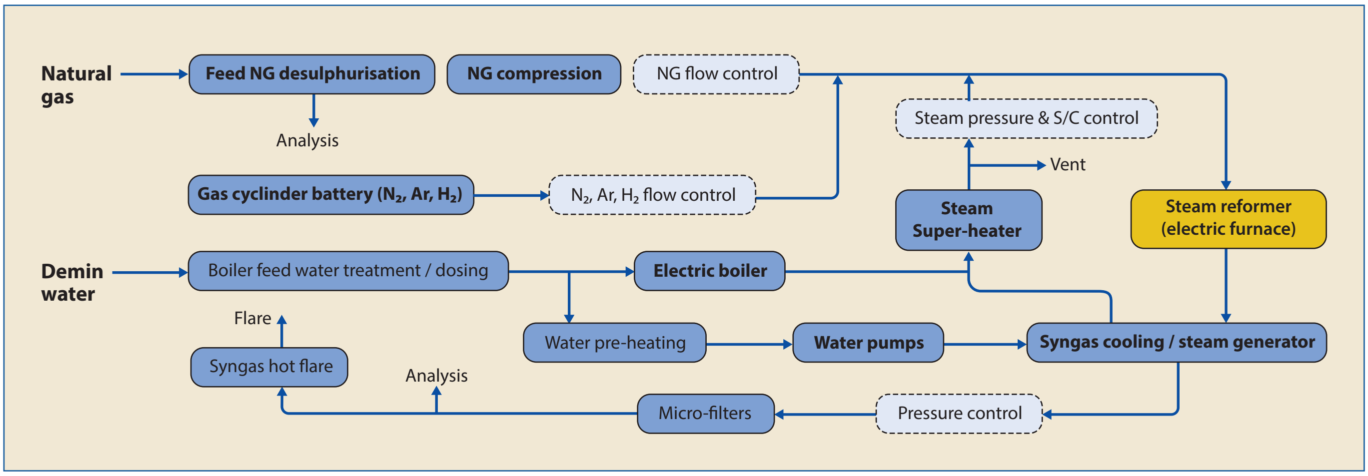

Figure 2 Pilot plant block flow diagram

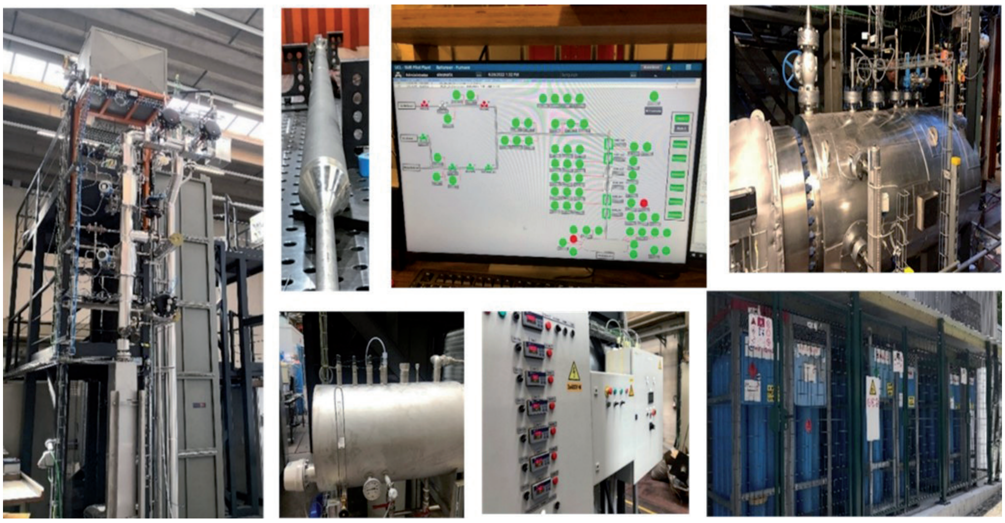

Figure 3 The ZFRT pilot plant at UCLouvain, Belgium

section for other gases (N_2, Ar, H_2), water pretreatment, an electric steam boiler, an electrical SMR furnace for steam reforming, an outlet expansion interconnecting piece, a syngas steam generator, a steam superheater and flow and pressure control system, and back pressure regulation for flaring the generated syngas.

The feed natural gas is drawn from the local low-pressure supply net. It is almost fully desulphurised in a two-layer catalytic adsorption reactor before compression in a compact multi-stage compressor. Other gases like N_2, Ar, and H_2 are fed from gas cylinder batteries. Boiler feed water is pretreated (softener, RO unit, degassing, dosing) and fed to an electrical start-up/make-up boiler and to the syngas steam generator, which is used to cool the syngas exiting the reactor. The steam is superheated before being mixed under the imposed S/C-ratio control with natural gas and other gases. The reactor pressure is controlled through a back pressure regulator, and the pressure in the steam supply system through an independent back pressure regulator via which excess steam is vented. Mass flow controllers are used to control all flow rates. A syngas sample line for gas analysis is installed in the syngas exit line to the flare.

The pilot plant is equipped with more than 300 instruments and I/Os, plus more than 120 valves and SPMs. Multiple thermocouples are employed to measure the tube skin temperatures and process gas temperature along the reformer tube length, with each temperature measurement de-doubled or tripled. The sulphur slip in the desulphurised natural gas is monitored online with a detection limit of 100 ppb. A few pictures of the pilot plant sections are shown in **Figure 3**.

The ZFRT pilot plant has been designed with special attention to safety requirements and health and environment considerations, given its location within the university campus. The plant engineering also involved an extended cause-and-effect analysis and related DCS and PLC programming for various modes of operation and upset conditions. This was based on the operating philosophy/logic and related operating procedures covering start-up, normal operation, and routine and emergency shutdowns. The pilot plant is equipped with multiple observation cameras and gas monitors/detectors, also used for automated actions.

Apart from ensuring full compliance and accreditation with the various applicable tiers of codes and standards covering international, EU, and local regulations and statutory requirements, the pilot plant design and provisions underwent an exhaustive safety and operability review. This involved an external independent and accredited safety organisation conducting an extensive Hazard & Operability (HAZOP) study and stringent layers of protection analysis (LOPA) to match or even exceed the industrial safety standards.

Test campaigns

As part of the pilot plant test programme, four test campaigns, each extending over three to four weeks, were concluded successfully from July to October 2022. These safely covered near-commercial design and operating conditions in terms of space velocities, S/C ratios, temperatures, and heat fluxes (space velocity of 3,000-3,500/h, S/C of 2.5-3.0, outlet temp of ~860°C, avg. heat flux of ~75 kW/m²). One of the campaigns was carried out with state-of-the-art pellets for establishing the benchmark, and three with ZF reactors coated with different catalysts formulations from the leading steam reforming catalyst suppliers for comparative analysis.

The natural gas flow rate varied up to 30 Nm³/h, and the furnace power was regulated to maintain the maximum tube skin temperatures within range. The operating pressure was set to 8 barg and the S/C ratio to 3. Some additional tests at a lower S/C ratio of 2.5 were carried out with all ZF reactors to verify the resistance to coke formation of the different catalysts.

The extensive operating data of all the test cases were continuously collected and stored as DCS/PLC parametric data, including detailed composition analysis of the produced syngas (both dry and wet) using an online gas chromatograph and mass spectrometer. The gas chromatograph analysis data were collected at minimised intervals based on the time needed for the analysis. The feed natural gas composition was also analysed periodically to confirm its stability using another in-line GC-MS. The vast amount of collected data covering all flow rates, axial profiles of the tube skin, process gas temperatures, and dry and wet gas composition were also used. This then helped to further develop and validate a simulation model for the prediction of commercial plant reactor performance and optimisation in conjunction with the SMR design.

The analytical apparatuses were regularly and independently re-calibrated and had a good cross-check alignment between the GC and the MS for desired accuracy and

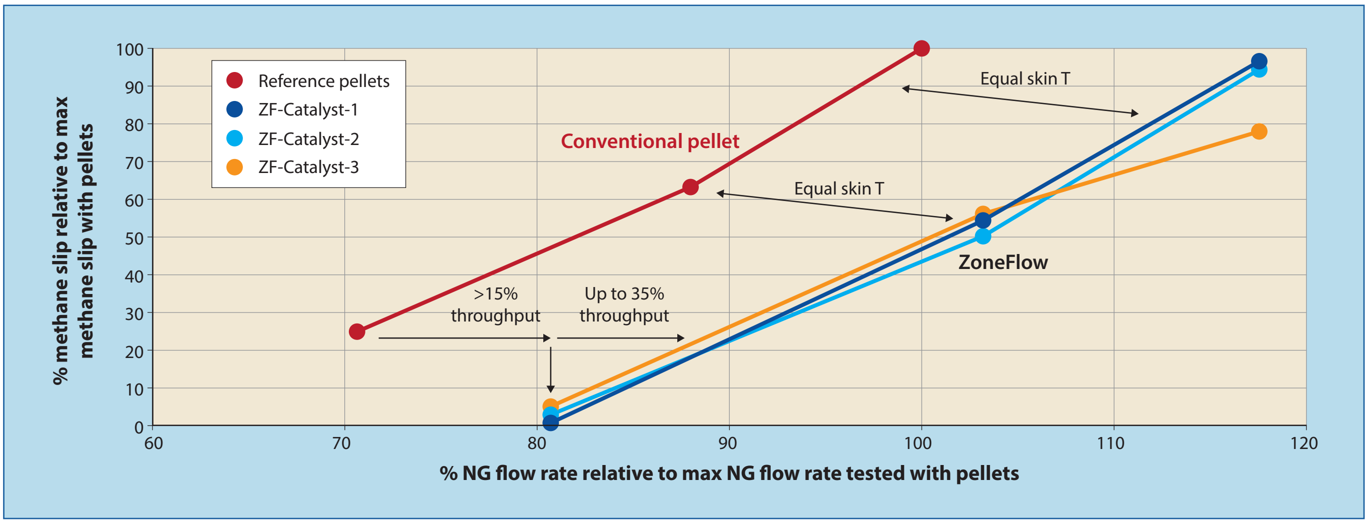

Figure 4 Comparative performance of the ZoneFlow reactors with three different catalysts and of state-of-the-art pellets as observed in the pilot plant test campaigns

confirmation. Boiler feed water quality analysis was done at the RO unit exit, along with chemical dosing under make-up water control and continuous conductivity measurement in the syngas boiler.

Results and conclusions

The pilot plant test programme was aimed at:

❶ Testing at equal capacity for lower methane slip at lower tube skin temperature than for the pellets reference case

❷ Testing for at least a 15% increase in capacity compared to conventional pellets with no higher methane slip, maximum tube skin temperature, or pressure drop. Appropriate repetitive testing was also included in the test programme.

As shown in **Figure 4**, all three ZF reactor campaigns conducted as part of the pilot plant test programme validated increased reforming capacity by at least 15% in terms of feed flow compared to the pellets, with no higher methane slip and without increasing the maximum tube skin temperature and pressure drop. For these campaigns, an additional test case at a lower S/C ratio (of 2.5 vs 3.0) was conducted to observe any susceptibility of the catalyst to carbon formation (or alternatively to ensure an adequate approach to C-equilibrium). No declines in performance – as measured by the % methane slip – were observed.

The X-axis in **Figure 4** shows the % NG flow rate relative to the maximum NG flow rate tested with the pellets. It should be noted that the NG compressor could be operated at 115% of its rated capacity. The y-axis in **Figure 4** shows the % methane slip relative to the maximum methane slip observed with the pellets as 5% vol dry at 100% relative NG flow rate.

For the pellet reference condition and all three ZF reactors, the pilot plant test programme reported superior performance beyond the test target of a 15% increase in capacity at a lower methane slip and up to a 35% increase in capacity at the same methane slip with certain catalysts.

The test results of the pilot plant test programme campaigns also supported the derivation of correlations for the ZF reactor interfacial mass and heat transfer coefficients; that is, for mass/heat transfer between the process gas and the catalyst surface. This allows a high level of confidence in establishing the simulation models for scaling up to any commercial SMRs and using those models to analyse the value creation in ZF reactor deployment to commercial SMRs.

Importantly, the results of the testing campaigns allowed us to confirm several advantageous characteristics of ZF reactors that contribute to their improved performance vs conventional SMR pellet catalysts:

- The heat transfer coefficient is increased to such an extent that the otherwise heat-transfer-limited steam reforming with pellets becomes instead catalyst-activity constrained
- There is no bypassing of gas along the reactor tube wall, reflecting close contact of the ZF reactor with the tube wall
- Catalyst coatings on the ZF reactor can provide more than sufficient intrinsic catalyst activity compared to state-of-the-art catalyst pellets
- The ZF reactor structure promotes about a 5% radiative heat transfer contribution from tube wall to catalyst surfaces
- The temperature curve from the tube wall to the inner portion of the reactor is flattened significantly.

Value creation and NPV analysis

Based on the verified results and findings of the pilot plant test programme,[9] a detailed analysis of ZF reactor applications was conducted with the following benefits assessment:

ZF reactor retrofit in existing SMRs

Considering the two modes of retrofit application, the following are the main benefits:

❶ SMR catalyst replacement
- Overcoming capacity limitations from 'stressed' reformers
- Energy (heat and power) savings
- Prolonged tube life and enhanced reliability.

❷ Capacity upgrading
- 15% reforming capacity increase without increasing pressure drop, maximum tube skin temperature, and methane slip
- Related product capacity increase with only minor (case-specific) modifications

ZF reactor-based SMR retrofit case analyses

Parameter	SMR de-stressing	SMR upgrading
Maximum current capacity (nameplate 100), %	95	100
Post-ZF retrofit capacity, %	100	115
S/C Ratio (molal)	3.1	2.8
Outlet temperature, °C	860	878*
Approach to equilibrium (end-of-run), °C	-10	-10
CH_4 slip, vol%, dry	5.5	5.4
Catalyst pressure drop (design 2.8 bar), bar	2.8	2.8
Average heat flux, kW/m	75	84
Bridge-wall temperature, °C	1,003	1,014
Max. tube skin temperature (design 940 C), °C	912	912**

* Within existing outlet system design temp based on minimised temp non-uniformity and related margin

** Based on enhanced heat transfer and flattened radial temp gradient

Table 2

• Improved energy efficiency by improved heat transfer efficiency and the potential to operate at a lower S/C ratio
• Enhanced SMR reliability by the possibility to operate at lower tube skin temperatures for a given capacity compared to pellets, by avoiding catalyst crushing and by the flexibility of the ZF reactor structure ensuring close contact with the wall during its lifetime.

Table 2 provides an overview of the SMR performance for the following ZF retrofits case analyses:

❶ De-stressing of existing SMRs which cannot achieve design capacity constrained by excessive pressure drop, leading to flow limitation and overheating of tubes due to pellet breakage causing throughput limitation together with increased maldistribution, poor heat transfer and/or lower catalyst effectiveness, just by replacing the pellets with ZF reactors

❷ Capacity upgrading of 15% based on utilising the ZF reactor merits of higher heat transfer without pressure drop penalty even with increased throughput and also exploiting the reduced non-uniformity or temperature spread. This was achieved without exceeding the maximum tube skin temperatures while maintaining the conversion of the increased feed flow in terms of methane slip.

Further, ZF's high level of reforming capacity increase provides the following additional benefits against the best alternative technology (BAT) of integrating a post-reformer based on recuperative reforming with the existing SMR for obtaining such a step capacity increase:

• Involves replacing only the pellets catalyst with ZF catalytic reactors and some minor case-specific modifications executable during a typical plant turnaround, compared to the capital intensity and major revamp with post-reforming and related extended project schedule and downtime
• No energy efficiency penalty as in the case of post-reforming due to lower feed conversion based on the temperature approach between the heating fluid at the bottom and the post-reformer tube exit temperature
• No concerns over minimum per cent make-up fuel or curtailed steam balance
• Higher reliability and cost-effectiveness in terms of avoiding the major risk of metal-dusting and the high cost of protection against it as a catastrophic corrosion characterised by pitting and surface erosion in high-temperature alloys applied in the post-reformer. It is mainly caused by Boudouard carbon equilibrium in the temperature range of 500-750°C, through which the reformed gas must pass based on heat recuperation for post-reforming duty. This is not the case with the conventional process gas boiler, which involves low alloy materials and quick cooling of reformed gas to below the range.

Result of detailed techno-economic analysis

	15% capacity upgrade retrofit (ZF reactor vs BAT)
15-yr NPV	$28 million

Table 3

Table 3 provides the result of detailed techno-economic analysis (TEA) for an 80 mmscfd hydrogen plant by employing ZF reactors in place of state-of-the-art pellets for a 15% capacity upgrade retrofit and its net present value (NPV) over the typical 15-year period. The analysis is based on Honeywell UOP-developed simulation models, the UniSim simulation model, the standard PDD tool, and optimisation. Key variables include stream composition, utility price set, price of H_2 of $1685/ton, natural gas feed price of $327/ton, fuel price (HHV) of 6.5/MMBTU) and HP steam export credit of $28/ton, cost of capital 12%, 350 days per year on-stream, and 2022 US Gulf Coast basis.

Deploying ZF reactors in a new hydrogen plant SMR offers the unconstrained potential for design optimisation in terms of S/C ratio, outlet temperature, and average heat flux for SMR size reduction and better process efficiency, resulting in Capex and Opex gains, as well as enhanced reliability compared to conventional pellets. The NPV for the deployment of ZF reactor technology in new SMRs will depend considerably upon the plant flowsheet and its design optimisation based on various project-specific factors.

End-to-end SMR optimisation and revamp solutions

In short, the results and findings from our recently conducted pilot plant test programme conducted in our world-class pilot plant have validated our target merits in terms of achieving increased reforming capacity of at least 15% without any increase in methane slip, maximum tube skin temperature or pressure drop compared to the pellets under the same operating conditions. The pilot plant test programme final report was released by ZFRT-UCL in February 2023, delivering the results and conclusions based on detailed simulation and reconciliation of the collected data from all the test campaigns, which was fully ratified by Honeywell UOP, as presented in this article.

Acknowledgement

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