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Novel Approach to Ammonia Plant Revamps with ZoneFlow™ Reactor Technology

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Global growth for nitrogen fertilizers is projected to be more than 2% per annum over the coming years, mainly led by urea demand and lower-cost natural gas. A good portion of such growth is expected to be realized through incremental capacity from existing facilities via revamping and expansion, driven by several favourable factors in comparison to new facilities.

For most of these opportunities, expansion of the ammonia plant capacity is the key requisite; and this is usually constrained by syngas availability from the existing plant. Most often, the primary reformer acts as the crucial bottleneck for increasing reforming and thus syngas capacity, mainly in terms of excessive pressure drop, additional reformer firing and higher tube wall temperatures.

These limitations are typically attributable to the inherent deficiencies of the conventional "pellet" steam reforming catalyst. These include most significantly limited heat transfer, increased pressure drop, and flow / temperature non-uniformity due to random packing and catalyst attrition / breakage from thermal cycling, with the latter further adding to pressure drop with consequent reduced flow and higher tube temperatures.

ZFRT has developed and also demonstrated its innovative and proprietary ***structured catalyst*** *design called the* ***ZoneFlow™ Reactor (ZF) catalyst system*** *as a breakthrough technology overcoming the above-mentioned deficiencies. ZF offer the unmatched advantage of enhanced heat transfer combined with step reduction in pressure drop compared to pellets. They also have the inherent properties for effecting more stable and hence sustained activity as well as physical flexibility and inherent strength, thus enabling several distinctive and* ***attractive applications in steam reforming****.*

ZF design can be customized for the required optimum between heat transfer and pressure drop, and to fit in any commercial SMR tube size. Another major distinction of ZF against pellet catalysts is that their customized designs can also be loaded horizontally, thus enabling their deployment in the reformer convection section existing process coils for achieving ***in-situ non-adiabatic convective pre-reforming***

(ZF-CPR). This solution can offer appreciable reforming capacity increase with minimized modifications and investment, along with the merit of amenable pressure drop and no to minimal additional reformer firing depending upon the extent of capacity increase.

*Furthermore, for the proven capacity revamp solutions of a **heat exchange post-reformer** like KBR's KRES and Topsoe's HTER, ZF technology, with its enhanced heat transfer capability (ZF-PR), can provide substantial value by making the post reformers much smaller.*

*ZF performance parameters have been validated through advanced CFD analysis, and are currently being demonstrated through extensive pilot plant testing under commercial operating conditions. Based on the described features, ZF technology offers several attractive opportunities **for enabling cost-effective steam reformer capacity increase of up to 30%** based on different levels of front-end modifications and investment.*

This paper provides relevant details of the ZF technology development, the pilot plant progress for testing under commercial range of S/C ratio, pressure and temperature conditions as well as selective case analysis for ammonia plant revamping.

ZoneFlow Reactor Technology - an Innovative Breakthrough

The steam reforming catalysts so far have stayed by and large as "pellets", with improvements mainly in terms of pellet geometry for specific needs or applications. These developments around the shapes and sizes of the pellet form have been mostly for achieving marginal improvements in catalyst pressure drop, heat transfer and to some extent crush strength. The pellet-based steam reforming catalyst put as random packing in the reformer tubes carry accepted tolerances on the inherent pressure drop variance or mal-distribution over the multiple tubes and also its gradual increase over the operating life attributable to the limited crush strength, eventually leading an appreciable non-uniformity of flow, heat and temperature distribution.

ZoneFlow(R) Reactor Technologies LLC (ZFRT) has developed a proprietary, radically innovative structured catalytic system, called the ZoneFlow Reactor (ZF) consisting of a formed metal foil structure (the "substrate") coated with catalyst, it provides high heat transfer, low pressure drop, high geometric surface area (GSA), uniform flow and heat distribution, and long-term structural integrity. The use of ZF allows significant capital and operating cost reduction in steam reforming both for new plants as well as Revamps.

The geometry of the ZF (Figure-1) is carefully designed to optimize heat transfer, which is further promoted by features that eliminate gaps between the substrate and the tube wall. Occupying less than half the volume of the tube (depending on the tube diameter), ZF substantially reduces the pressure drop.

ZF's relatively high GSA permits more than adequate catalyst loading in the otherwise heat-transfer constrained steam reforming application. Alternating columns of centrifugal and centripetal flow channels promote uniform radial mixing and heat transfer within and across tubes.

ZF's unique combination of inherent mechanical strength and ability to expand and contract with the tube ensures proximal contact with the wall and thus avoid any by-pass axial gaps.

Figure-1 : ZF module & loading

This distinctive of ZFdesign feature thus offers robust catalyst with much high crush strength for longer operating life, stable low pressure drop combined with higher heat transfer compared to pellets. In sum, the innovative, flexible design of the ZF Reactor allows simultaneous, targeted improvements of heat transfer, kinetics, and pressure drop.

Merits of ZF Reactors vs. Conventional 'Pellet' Steam Reforming Catalyst

Based on ZF Reactor's basic design features described above, it enables two primary advantages over conventional “pellet” steam reforming catalysts :

- Superior heat transfer – replacing the random distribution of pellets with the carefully engineered substrate of the ZF significantly enhances heat transfer, permitting process intensification and operation at lower steam-to-carbon (S/C) ratios.
- Reduced pressure drop (dP) – the ZF uses pressure drop only to enhance the 'hydraulic' heat transfer, avoiding to large extent the “unutilized" pressure drop in overcoming flow and diffusion resistance typical of random pellet packed column.

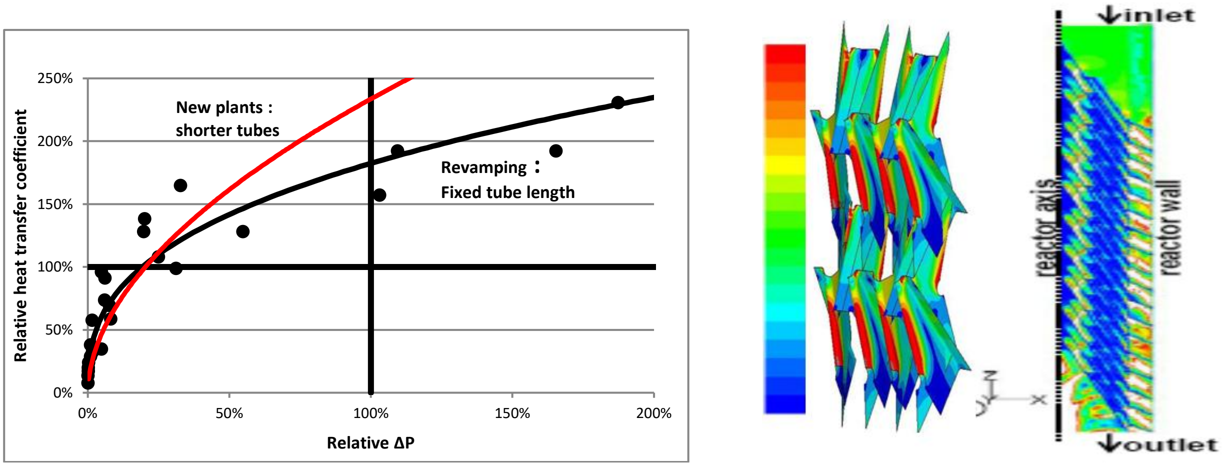


Figure 2: ZF Reactor Hydraulic and Heat Transfer Characteristics

The extraordinary combined effect of these two factors results in the unique ZF advantage of higher heat transfer coefficient at the same dP or same HTC at lower dP are shown in Figure-2. Also shown is one of the several CFD modelling results further confirming such hydraulic and heat transfer benefit.

Additionally, as described, ZF carries following significant advantages compared to pellets :

- Superior geometric surface area, allowing delivery of more than adequate and available catalyst to support reforming
- Uniform heat transfer and fluid flow throughout the length of the reformer tube, eliminating hot spots that can restrict full-load operation and shorten tube life
- Uniform heat transfer and fluid flows across multiple tubes, eliminating variations among tubes that must otherwise be accommodated by less than full-load operation
- Long-term structural integrity, including mechanical features to accommodate thermal cycling, so avoiding pressure drop increases over time related to progressive deterioration of pellets

ZF Reactor Development History and Current Status

ZFRT has achieved the following development milestones based on the extensive development work over recent years:

- Bench-scale validation of the ZF technology in the Hydrogen Performance labs at the University of California at Davis. ZF Reactors were tested against commercially available steam reforming pellets to compare performance with respect to heat transfer, conversion, and pressure drop.

- Extensive independent Computational Fluid Dynamic (CFD) analysis was conducted for numerous alternative reactor designs by Professors Juray DeWilde of Universite Catholique de Louvain, Belgium and Gilbert Froment of Texas A&M, USA to optimize the ZF Reactor for the desired combination of heat transfer and pressure drop improvements.

- Finite Element Analysis (FEA) was undertaken by CAE Associates, Middlebury, CT, USA, to establish mechanical robustness and long-term durability.

- Extensive physical testing was done to confirm that the ZF Reactors can be loaded into and removed from reformer tubes without distorting or damaging either the reactor modules or the tubes.

- ZF Reactors were installed in two tubes of a 204-tube commercial SMR and operated under commercial, high-severity reforming (Oxo-syngas application) conditions for close to 2 years, further validating their physical robustness and suitability. It also provided the much desirable opportunity for direct comparative assessment of ZF reactor catalyst system versus conventional BAT pellet catalyst under the same operating conditions. Table-1 below summarizes the observed ZF performance results (also see Figure -3)

Table-1 : Results of ZF Demonstration in Commercial SMR

Parameter	Demonstrated ZF performance
Pressure drop over catalyst tube	> 20% lower (allowing up to 40% more throughput per tube)
Heat transfer properties	Up to 60^o C lower tube wall temp
Robustness / physical strength	Intact after >15,000 hrs operation (including few transient / thermal cycles)

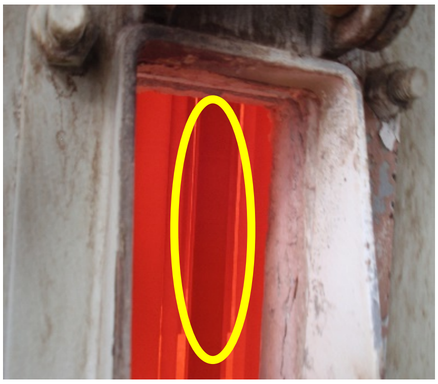


Figure-3 : Cooler ZF loaded (2) tubes comapred to adjacent conventional catalyst loaded tubes

- Currently, ZFRT is distinctively nearing the completion of its own designed and built pilot plant to further validate the performance of its various ZF Reactor designs under commercial conditions of S/C ratios, temperatures and pressures. The Pilot plant test campaign is planned by 1Q 2018 for confirming the merits for taking them to the market. ZFRT is also working with several large SMR users and engineering companies to develop initial commercial opportunities.

ZFRT Pilot Plant

The Pilot facility installed within the Université Catholique de Louvain, Belgium (UCL) is a fully equipped and instrumented self-designed and built plant unit with the objective of conducting the various ZF performance and integrity tests under a broad range of commercial operating conditions in terms of S/C ratios, pressures and temperatures with near commercial flows derived.

The range of these conditions cover S/C ratios from state-of-the-art level of 2.5 to 3.0 down to severe (HyCO) levels of 1.5 combined with the range of 10-30 bar pressures and reformer outlet temperatures well above 880 C for covering the extensive campaigns for testing the ZF reactor designs on and even beyond commercial conditions (including ZF-Bayonet recuperative reforming design for New SMRs)

The UCL pilot plant (see Figure-4) consists of a feed compression and desulphurization section, a furnace-reactor section with electrical multi-element heated and controlled full bore single tube (> 6 m long) for steam reforming, a heat recovery and cooling section leading to safe flaring of the product syngas. The reforming tube has several heating zones which can be independently controlled along with an extensive temperature monitoring cluster.

Figure-4 : UCL Pilot plant under construction

The allied sections of steam generation, BFW pumping & preheating and process condensate handling are carefully integrated into the facility to allow repeatable smooth start-ups, normal operation and safe shut-downs.

The facility is adequately supported by state-of-the-art analytical provisions including on-line and off-line GCs as well as advanced DCS based process control and safe guarding system. All the utilities in terms of feed supply, Demineralized water, cooling water, electric power, fuel gas as well as process and steam condensate handling are in place. The pilot plant is mostly inside a building, with some equipment like compressor and flare etc outside. The facility has gone through the rigorous safety and operability auditing and for strict compliance with all regulations, codes and standards.

IP Status

ZFRT has several patents which have been granted and/or applied for covering:

- Alternative reactor geometries to produce the desired heat transfer and pressure drop results
- Alternative related process and method patents
- Mechanical designs to ensure minimal casing-tube wall gap despite tube creep
- Reactor concepts and designs for convective pre-reforming integrated in the heat recovery section of the SMR

Ammonia Plant Revamping Using ZF Reactors

Presently, about 25% of the world ammonia production capacity is older than 30 years and more than 50% is older than 15 years. Although aging itself is an aspect to attend to , the more prominent issues in these older plants are around achieving the (name plate) capacity and desired operating efficiencies . These plants, however, do have larger hardware design margins, than the newer plants, making them not only qualifying but favourable candidates for revamps aiming at capacity and energy improvements.

A good portion of ammonia capacity growth globally is expected to be realized through incremental capacity from existing facilities via debottlenecking and revamping based on few favourable factors in comparison to new facilities. For most of these opportunities syngas availability from the existing plant in terms of the primary reformer capacity acts as the major limiting factor and scope for capacity increase in the syngas generation section.

The technical and economic potential available for revamping an ammonia plant is dependent on its flowsheet (see Figure-5) and its current operational efficiency. Developments in, converter design, synthesis catalysts and purge gas recovery etc frequently allow a synthesis loop capacity increase of 20-30% or even beyond in some cases, along with simultaneous energy savings per ton ammonia (depending upon the retrofit margins and level of modifications). The critical and controlling requirement, however, comes upon expanding the capacity of front-end make-up synthesis gas production.

Often the allowable pressure drop and tube temperature increase, apart from resulting impact on feed conversion (methane slip), severely limit the extent of primary reformer capacity increase. Moreover, in many cases, increasing capacity not only increases (compression) energy requirements but also pushes the operating conditions closer to their design (pressure) limits against safe limits thus getting restricted.

Based on typical natural gas feed the basic overall reaction for ammonia conversion is (see Figure-5) :

$$0.448\ CH_4 + 0.604\ H_2O + 0.5\ N_2 + 0.146\ O_2 \Rightarrow NH_3 + 0.448\ CO_2 + 8850\ Kcal$$

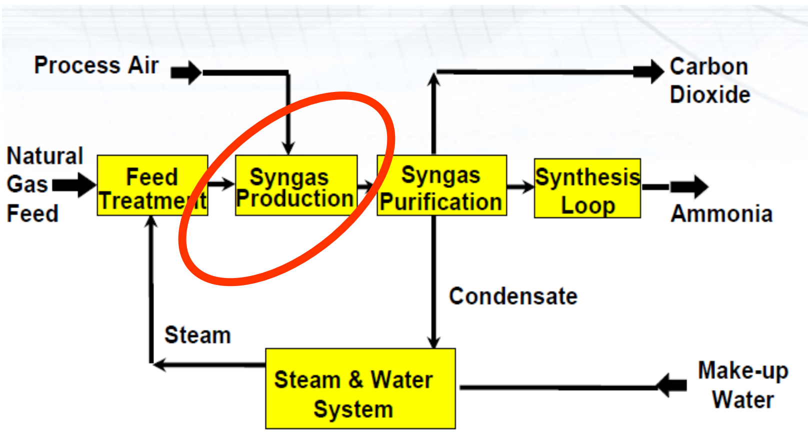


Figure-5: Typical Ammonia Plant Block Diagram

Syngas generation (including steam system but excluding CO_2 removal) consumes almost 2/3rd of the energy and also is the more capital-intensive section of an ammonia facility. Thus the emphasis is not only to get the additional syngas capacity through advanced technological options but also to have then cost-effective , efficient and reliable.The attributes of ZF Reactors effectively enable capital and energy cost reductions in syngas capacity upgrades of existing plants through application of differentiated ZF products.

Following ammonia plant debottlenecking and revamp strategic categories have been considered to highlight ZF application potential :

1. Stressed Primary Reformers : replacement of existing conventional SMR catalyst with ZF Reactors for removing the governing bottlenecks
2. Simple Debottlenecking for incremental capacity based on ZF Reactor replacing existing SMR catalyst combined with judicious process optimization without any major equipment modification.
3. ZF-CPR in primary reformer mixed feed preheat convection coil for in-situ non-adiabatic convective pre-reforming utilizing high level flue gas heat thereby shifting radiant duty
4. ZF-catalyst employed in a heat-exchange Post-reformer integrated with Secondary reformer

Case 1 Stressed Primary Reformer Make-over

- Primary reformers suffering from **under-nameplate capacity limitations** on process (catalyst tube) side due to either pressure drop or tube temperatures or both; possibly caused by catalyst breakage from thermal cycling and reduced catalyst activity / effectiveness
- Propagative loss of related heat transfer and feed conversion
- Operation on forced higher S/C ratios to limit outlet temperatures in conjunction with above which further puts constraints on achievable throughput
- Reformer capacity curtailed in order to is operate to maintain TSM limits and also to avoid hot spots with the ultimate objective of conserving tube life
- ZF replacement can overcome these governing bottlenecks and further optimize reformer conditions with slightly lower S/C ratio, slightly higher outlet temp with lower approach to equilibrium and lower than original pressure drop, while staying within the original design tube design temperature and bridge wall temperature.

Table-2 SMR De-Stressing		Design (Top Fired)	Stressed SMR Operation	ZF-Radiant Operation
Relative Capacity,	%	100	95	100
Capacity limitations		-	dP, TSM	removed
S/C Ratio		3.3	3.5	3.2
Outlet temp,	C	800	796	804
Approach to Equilibrium EOR	C	-10	-12	-7
CH_4 slip,	vol %	12	12	12
Radiant Pressure drop,	bar	2.8	2.8	2.3
Relative Radiant duty	%	100	96	99
Avg heat flux	kW/m2	75	72	75
Bridgewall temp,	C	950	950	948
TSM	C	860	860	857

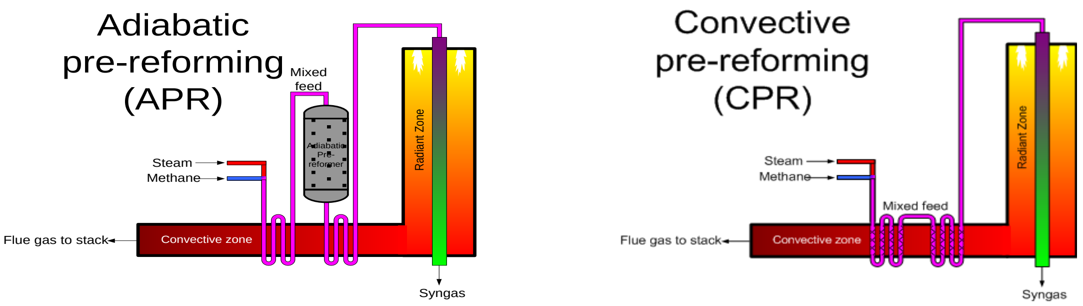
Case 2 Simple Debottlenecking of Primary Reformer

- Achieving an **incremental reforming capacity without exceeding TSM or Bridgewall** temp
- Optimized operation and reforming severity in terms of T out and S/C
- Marginal utilization of available design margins on burners and fans
- dP slightly lower than design even on increased capacity
- Slightly higher average heat flux without exceeding tube design or bridgewall temp
- Better temperature uniformity leading to extended tube life and improved reliability
- Better catalyst robustness, performance and “life cycle” costs based on longer operating life
- Better catalyst performance and “life cycle” costs

Table-3 : SMR Debottlenecking	Reference	ZF-Radiant
Relative Capacity, %	100	105
Capacity limitations	dP, TSM	removed
S/C Ratio	3.3	3.1
Outlet temp, C	800	810
Approach to Equilibrium C	-10	-7
CH4 slip, vol %	12	12
Radiant Pressure drop, bar	2.8	2.5
Relative Radiant duty %	100	103
Avg heat flux kW/m2	75	77
Bridgewall temp, C	950	950
TSM C	860	860

Case 3 ZoneFlow™ Convective Pre-reforming (ZF-CPR)

ZFRT has designed and engineered a ultra-low pressure drop structured catalytic reactor with high surface area / low cross section for non-adiabatic convective pre-reforming reactor module design ZF CPR™ (CPR). It is a special structured catalyst that can be inserted into the existing Mixed feed preheat (MFPH) coil in the convection with some modifications to its layout if needed (to have counter-current configuration).



It accomplishes in-situ non-adiabatic pre-reforming (including conventional reheat) providing 8-15% additional reforming capacity by transferring convective heat to radiant duty. ZF-CPR operate at higher reforming temperatures and higher kinetic reaction rates than the conventional adiabatic pre-reforming.

CPR fully exploits ZF's core advantages on heat transfer and dP and when combined with ZF in the radiant section, the net pressure drop increase is marginal since off-set by appreciably lower dP in the radiant catalyst part

Table-4 : ZF-CPR based SMR Revamp	Existing	ZF + CPR
Relative Capacity, %	100	115
S/C Ratio	3.4	2.8
SMR inlet temp, C	550	550 / 575 1)
SMR outlet temp, C	804	804 / 821 2)
Approach to Equilibrium C	-10	-7
CH4 slip, vol %	12	13.2 / 12
Radiant Pressure drop, bar	2.5	2.3
Avg heat flux kW/m2	75	75-77
Relative Radiant duty	100	100 / 103
Bridgewall temp, C	950	< 960
TSM C	860	845/ 865 1) 2)

Notes
1) possible exploiting of existing plant design margins
2) With lower ATE and enhanced heat transfer, tube skin and bridgewall temps increase are minimal

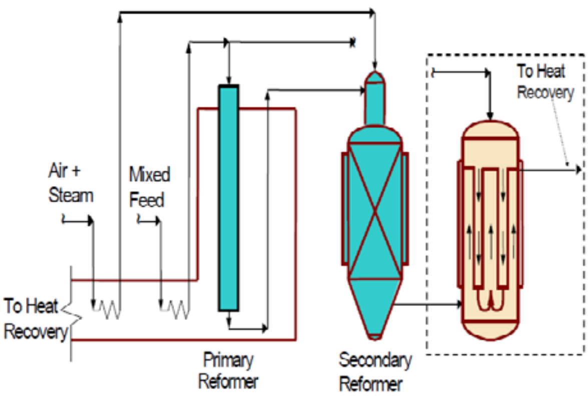
Additional advantages of ZF-CPR include :

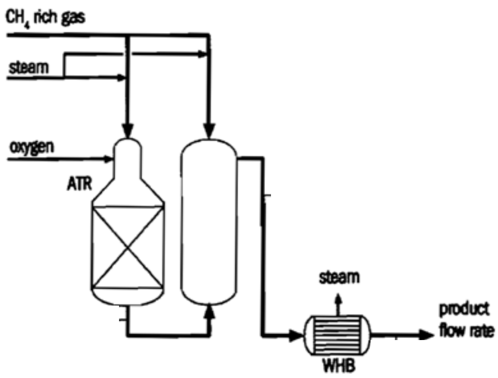
- No concerns over horizontal loading catalyst settling ,run attrition and related feed by-passing
- Minimized modifications and related downtime (can be executed within a typical turnaround depending upon case-specific factors)
- Shifts steam loads to U&O thus also lowering core-plant C-footprint

Case 4 ZF - PR in Heat Exchange / Post Reforming with Secondary Reformer-

For achieving ammonia plant revamp capacity expansions of more than 15% (up to 30%) in the make-up Syngas generation, an effective and proven solution is to install a heat exchange post reformer integrated with the Secondary reformer in a 2IN-1OUT configuration i.e. the secondary exit gas is mixed with the post reformer catalyst effluent gas before exchanging / providing heat for reforming. The high grade heat of secondary reformer exit gas is used for reforming the additional feed in a convective heat-exchange reformer instead of steam raising.

However the usual challenges are the size scalability and protection from potential metal-dusting. Since the post reforming is heat-transfer limited, application of enhanced heat transfer **ZF-PR structured catalyst** system can effectively reduce the surface area requirements and thus size of the post reformer and thereby the installed cost of this expensive piece of equipmemt.This in turn also allows larger capacities within the heat exchange reformer scalability limits.





ZF-PR is a pressure-drop optimized enhanced heat transfer structured catalyst design that can be ideally applied to smaller ID heat exchange tubes, while also providing extended operating life.

- Allows up to 30% additional reformed gas without increasing primary reformer radiant duty
- Can achieve more effectively when combined with ZF-CPR
- Modular add-on with minimized modifications and related downtime
- Fully exploits ZF's core advantages on heat transfer and dP

Table-5 : Post Reformer based Revamp	Existing	ZF-PR + CPR
Relative Capacity, %	100	130
S/C Ratio SMR / PR	3.4	2.8 / 3.2
Inlet temp SMR / PR C	550	550 / 500
Outlet temp, SMR / PR tube C	804	804-820* / 915
CH4 slip SMR / PR vol %	12	12 / 3.5
Relative SMR radiant duty	100	100
Seco Reformer outlet temp, C	990	1050
H2/N2 ratio in MUG	3.0	~ 3.0
Total inerts in MUG vol %	1.5	2.5

* Possible exploiting of available design margin in existing SMR

The post reformer syngas contribution being devoid of N2, the process air flow to the secondary needs to be proportionately increased for eventually bringing H2/N2 ratio in the make-up syngas to the desired level of ~ 3.0. Accordingly, the secondary reformer exit temp increases due to more process air flow, which in turn is good for getting a higher mixed temp at the bottom of the pre-reformer for better temp approach or conversion in the post reformer.

Overall Economic Benefits Analysis and Case Selection

Based on the above Case simulation evaluations, the Pre-and Post revamp OPEX and CAPEX analysis with reference to the overall existing plant can be conducted in order to short-list or select the more attractive, applicable or conforming ZF revamp option.

Since the energy costs, economic criteria, and the level of modifications required in the existing plant as well as investment in additional equipment can vary over a wide range on a case-to-case basis for evaluating and assessing the various Revamp options, only a typical / generic listing of parameters and variables are listed below for doing the comparative full Economic Benefits Analysis :

- OPEX (w.r.t existing plant)
  - Feed + fuel - excess steam — MJ
  - Specific Energy improvement, — MJ/Nm3.h
  - Energy costs savings / yr — MM$/y
  - Catalyst life, — Years
  - Catalyst costs / year — MM$/y
  - NET OPEX Savings — MM$/y
- CAPEX (w.r.t. Existing plant)
  - Delta SMR radiant, — MM$
  - Delta SMT convection + fans — MM$
  - Delta PAC — MM$
  - CPR — MM$
  - Post refo — MM$
  - Delta PGB — MM$
  - Delta CO2 removal — MM$
  - Delta MUG compressor — MM$
  - CAPEX NPV — MM$/y
- TOTAL Benefit (Opex + Capex) — MM$/y

Conclusions

The presented description and high-level details of the ZoneFlow™ Reactor (ZF) development and its product platform potential is should be encouraging enough for establishing it as an innovative, advanced, unmatched and differentiating structured catalyst technology.

ZF product developments, together with the ensuing pilot plant testing and collaboration with some of the prominent players in the syngas space, carry a lot of promise as a enabling technology. When combined with the state-of-the-art steam reformer and related advanced revamp options, ZF Reactor technology is poised to be a strong contender for cost-effective , efficient, reliable and thus distinctly attractive solutions for Ammonia plant revamp applications and opportunities.