ZoneFlow Reactor Technologies, LLC

ZoneFlow™ Structured Catalyst System – Innovation for the future in Steam Reforming

Sanjiv Ratan, ZFRT, USA
&
Prof. Juray de Wilde, UCL, Belgium

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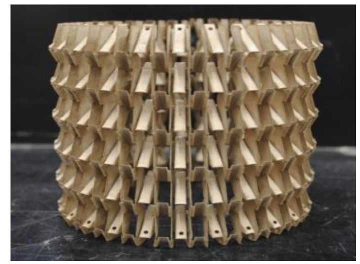
Presentation Outline

- **From** current BAT 'pellet' steam reforming catalyst - Status quo **to** ZoneFlow^{TM} (ZF) structured catalytic reactor technology - an innovative breakthrough
- ZF product development update and validation programs
- Application merits and advanced solutions of ZF reactor technology

ZoneFlow™
innovative breakthrough for Steam Reforming

Conventional pellet SMR catalyst



ZoneFlow™ structured catalytic reactor system

Structured near-wall casing:

- Intensified heat transfer
- Reduced pressure drop
- High interfacial surface area
- Improved catalyst effectiveness
- Robust mechanical strength

ZoneFlow™ Advantages against Pellets (BAT)

Property	BAT - Status quo	ZoneFlow – differntited merits
Substrate	Ceramic	Metallic foil
Geometry	Pellets in various shapes	Structured annular casing
Loaded pattern	Random, non-uniformity	Aligned stack, fully uniform
Strength and Voidage	Limited (mutually)	Robust, flexible. high voidage
Flow / temp mal-distr	Inherent (catalyst packing)	None or minimized - entire life
Thermal cycling effects	Attrition & settling ; dP >>	No attrition & settling, stable dP
Utilization of catalyst volume	Partial (thermal gradient); sporadic wall contact	Full, peripheral proximity - in cold AND hot condition
GSA access / activity	Intra diffusion limitations	Full open-access to coated fins
Catalyst effectiveness	**Low , inherent**	**Higher (by multi-fold)**
Pressure drop	**Base, increasing over life**	**Lower; same over entire life**
Heat transfer	**Base, stagnant inner film**	**Higher; near-wall turbulence**

ZF Validation Program

- **New generation (cost) optimized design validated**
- **Specific applications enhancement “enabling” technology**
  - Single-pass (ZF-SP)
  - Bayonet (ZF-B)
- **Verification / validation of performance at near-commercial conditions**
  - ✓ CFD modelling (1D & 3D)
  - ✓ Feedback from commercial demo (15 months run)
  - ✓ Heat transfer and pressure drop (HTPD) Test Rig at UCL
  - ✓ Kinetics Lab at UCL for (intrinsic) evaluations of catalysts
  - ✓ Pilot plant coming up for commercial hot reactive testing
  - ✓ Demo with strategic partners and customers
- **Readiness for Commercial Roll-out**

Computational Fluid Dynamics (CFD) Modeling

- Detailed 3D geometry (periodic domain)
- Detailed reaction kinetics (coupled)
- Reynolds-Averaged Navier-Stokes approach

Boundary conditions: (De Wilde & Froment, 2012)

Solid internals coated with catalyst:

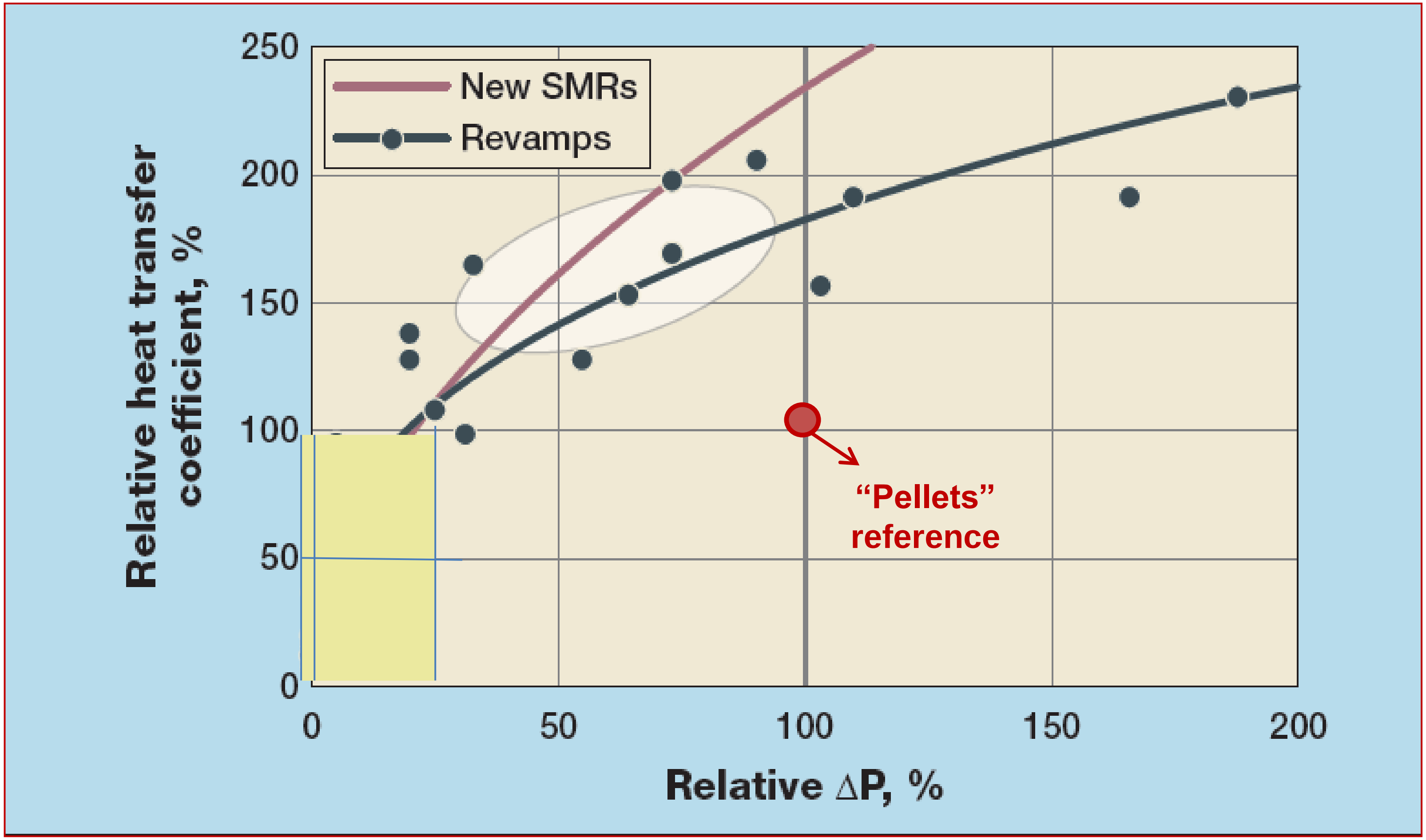
$$\tilde{k}_{g,A}\left(m^{s}_{As} - m_{A}\right) = \rho_{s} d M_{A} \sum_{k} \alpha_{A,k} \eta_{k} r_{k}(\overline{m}^{s}_{s}, T_{s})$$

$$= (1-\varepsilon)\rho_{s} M_{A} \sum_{k} \alpha_{A,k} \eta_{k} r_{k}(\overline{m}^{s}_{s}, T_{s}) / a_{V}$$

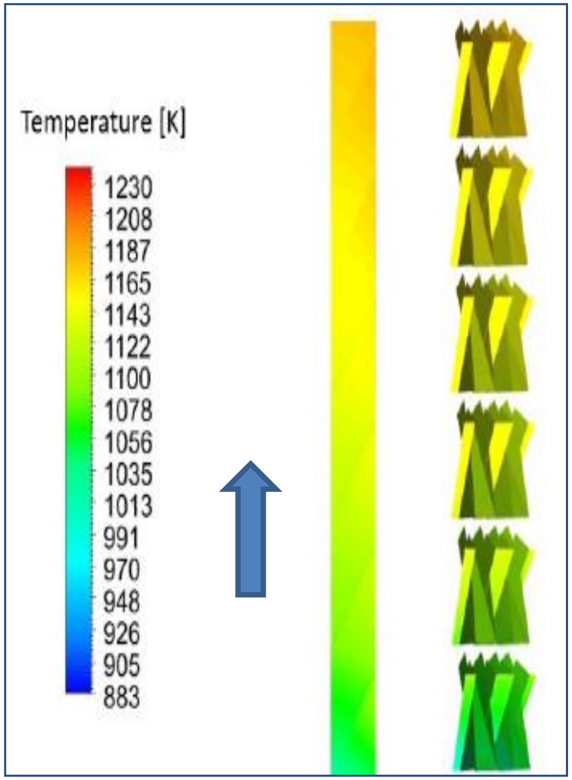
$$h_{f}(T_{s} - T) = \rho_{s} d \sum_{k} \eta_{k} r_{k}(\overline{m}^{s}_{s}, T_{s})(-\Delta H_{k})$$

$$= (1-\varepsilon)\rho_{s} \sum_{k} \eta_{k} r_{k}(\overline{m}^{s}_{s}, T_{s})(-\Delta H_{k}) / a_{V}$$

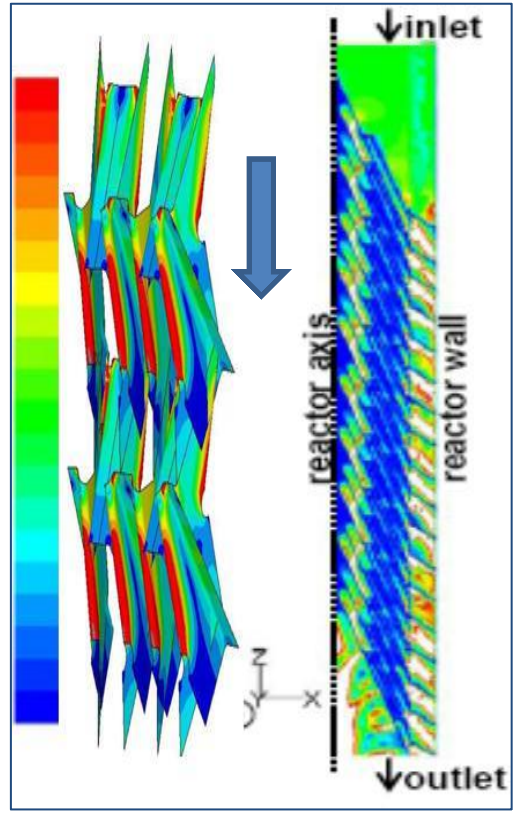
CFD Modeling Results



Rigorous CFD and FEA Results

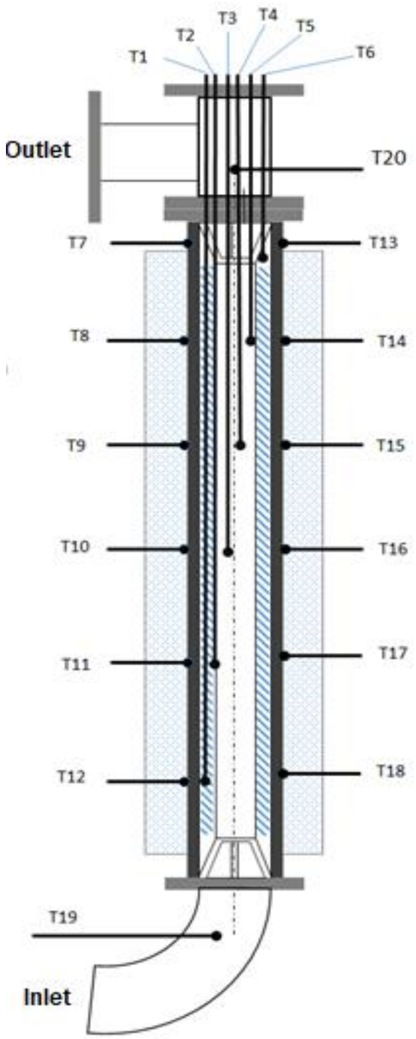


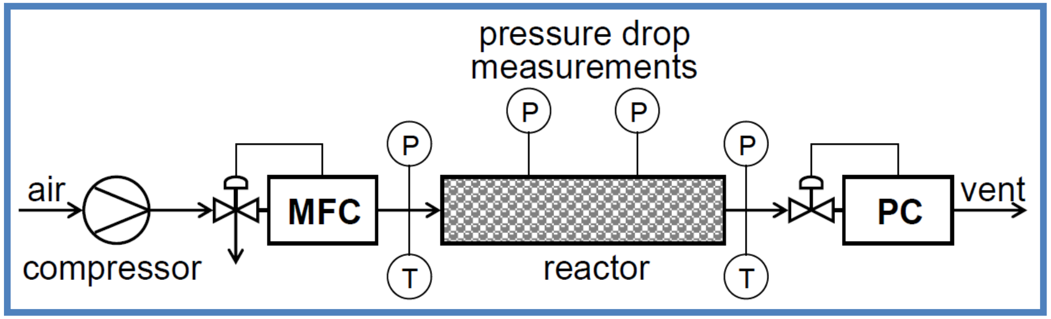
Temp Profiles



FE Analysis

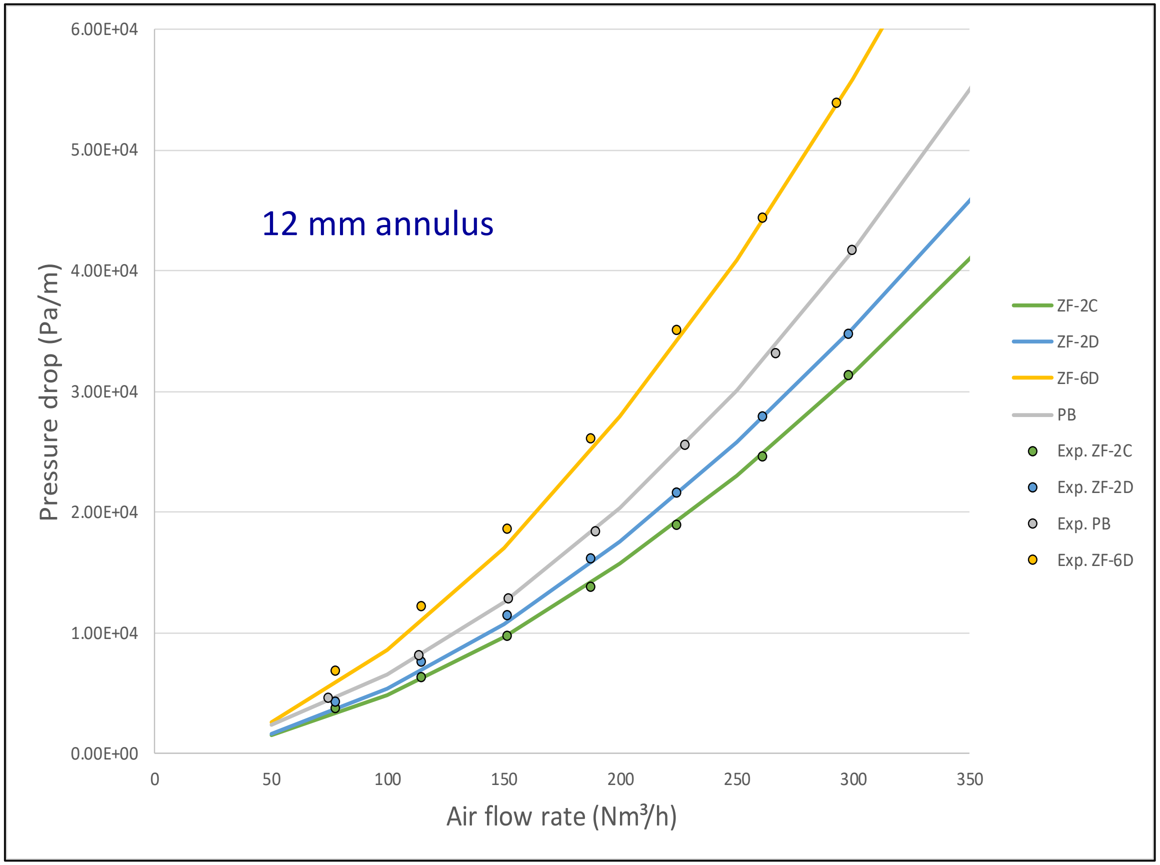
HTPD Test Rig





Air flow 75-300 Nm³/h, temperature 100-500°C

Pressure Drop Testing : ZF v/s Pellets



Turbulence model (CFD) / friction factor (1D)

$$\frac{dP}{dZ} = -f\frac{\rho_g u_s^2}{L}$$

ZoneFlow:

$$f = \frac{16}{Re} + a_1 Re^{-a_2}$$

Packed bed:

$$f = \frac{1-\varepsilon}{\varepsilon^3}\left[a_3 + \frac{a_4(1-\varepsilon)}{Re_p}\right]$$

95% confidence intervals model parameters determined

Heat Transfer Testing : ZF v/s Pellets

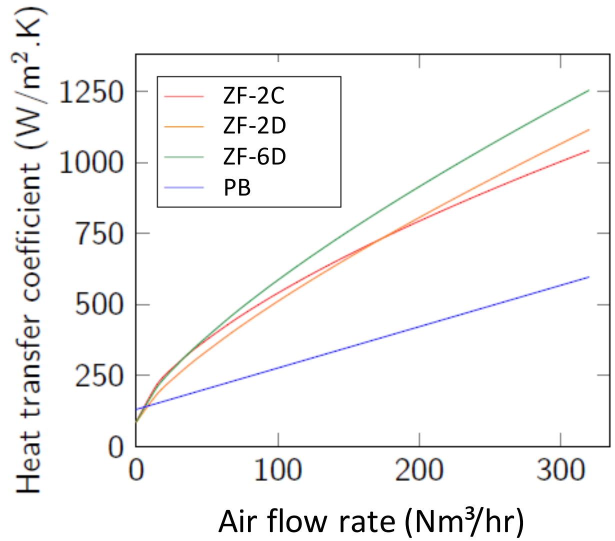
ZoneFlow:

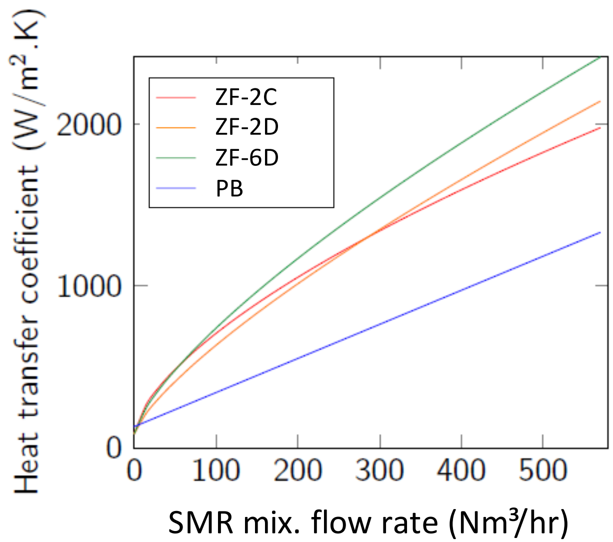
$$Nu = \frac{86L}{\lambda_g} + a_5 Re^{a_6} Pr^{1/3}$$

Packed bed:

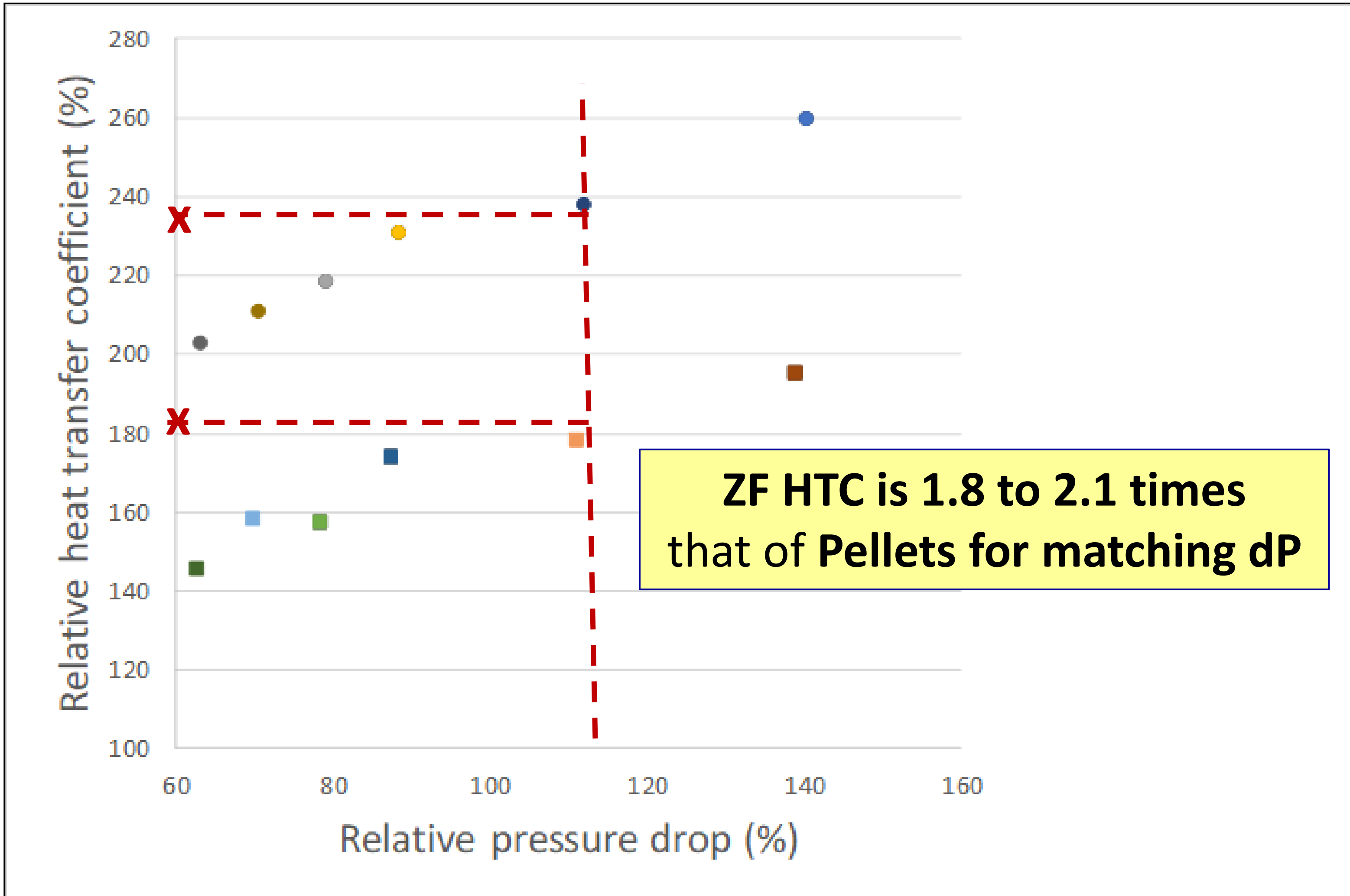
$$Nu_p = \frac{a_7 d_p}{\lambda_g} + a_8 Re_p Pr$$

- **95% confidence intervals model parameters determined**
- **Fast generation turbulence in the near-wall region confirmed**

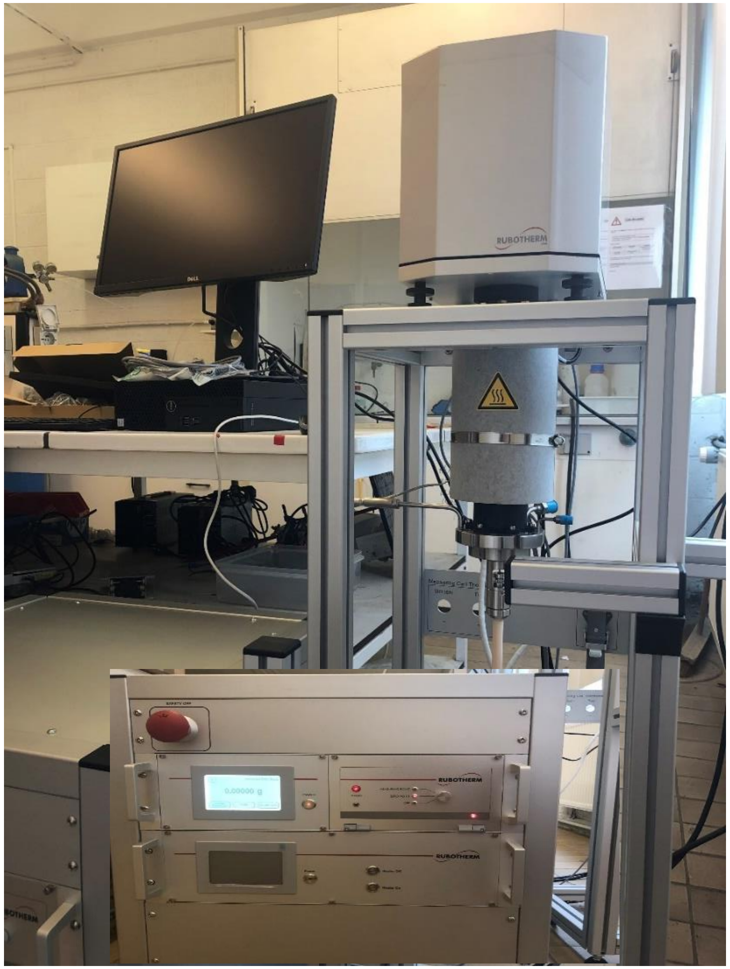




ZF v/s Pellets : dP - HTC Results



Catalyst Kinetics Evaluation Lab



Kinetic Modeling

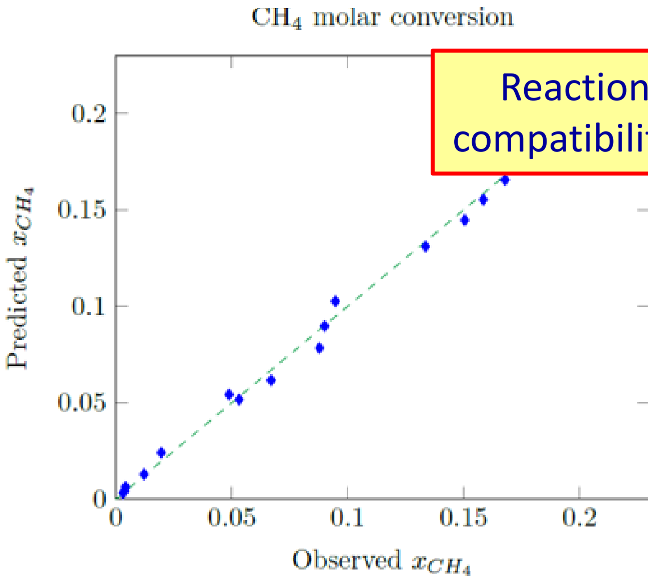
$$r_1 = \frac{\left(k_1/p_{H_2}^{2.5}\right)\left(p_{CH_4}p_{H_2O} - \frac{p_{CO}p_{H_2}^3}{K_I}\right)}{DEN^2}$$

$$r_2 = \frac{\left(k_2/p_{H_2}\right)\left(p_{CO}p_{H_2O} - \frac{p_{H_2}p_{CO_2}}{K_{II}}\right)}{DEN^2}$$

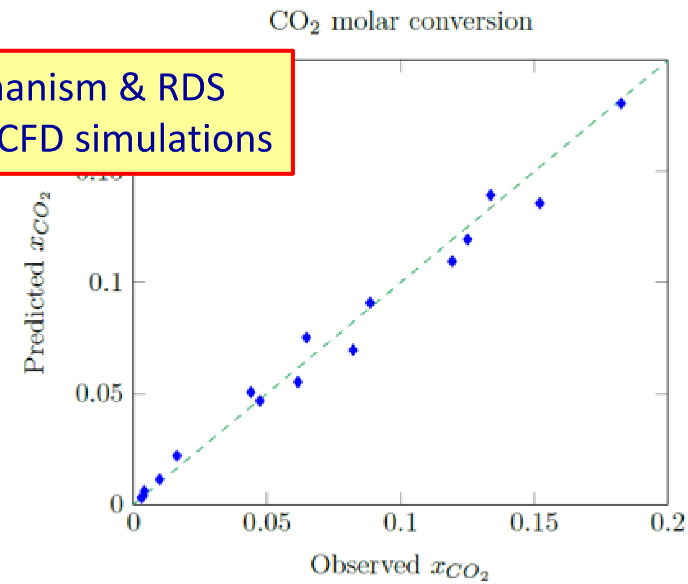
$$r_3 = \frac{\left(k_3/p_{H_2}^{3.5}\right)\left(p_{CH_4}p_{H_2O}^2 - \frac{p_{CO_2}p_{H_2}^4}{K_{III}}\right)}{DEN^2}$$

$$DEN = 1 + K_{CH_4}p_{CH_4} + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{H_2O}\frac{p_{H_2O}}{p_{H_2}}$$

Parameter	Value	Unit	t-value	95% Confidence intervals
$A(k_1)$	7.48×10^{12}	$mol.bar^{1/2}/(kg_{cat}.s)$	27.98	$7.48 \pm 0.54\ (\times 10^{12})$
$A(k_2)$	5.43×10^5	$mol/(kg_{cat}.s.bar)$		Xu and Froment (1989)
$A(k_3)$	9.56×10^{11}	$mol.bar^{1/2}/(kg_{cat}.s)$	28.43	$9.56 \pm 0.68\ (\times 10^{11})$
E_{a1}	226.4	kJ/mol	60.16	226.4 ± 7.5
E_{a2}	67.13	kJ/mol		Xu and Froment (1989)
E_{a3}	210.4	kJ/mol	59.03	210.4 ± 7.2
$A(K_{H_2O})$	2.09×10^5		71.29	$2.09 \pm 0.06\ (\times 10^5)$
ΔH_{H_2O}	88.68	kJ/mol		Xu and Froment (1989)
$A(K_{CH_4})$	2.68×10^{-4}	bar^{-1}	1.2	$2.68 \pm 2.03\ (\times 10^{-4})$
ΔH_{CH_4}	-38.28	kJ/mol		Xu and Froment (1989)
$A(K_{CO})$	8.23×10^{-5}	bar^{-1}		"
ΔH_{CO}	-70.65	kJ/mol		"
$A(K_{H_2})$	6.12×10^{-9}	bar^{-1}		"
ΔH_{H_2}	-82.90	kJ/mol		(Minette et al., 2018)

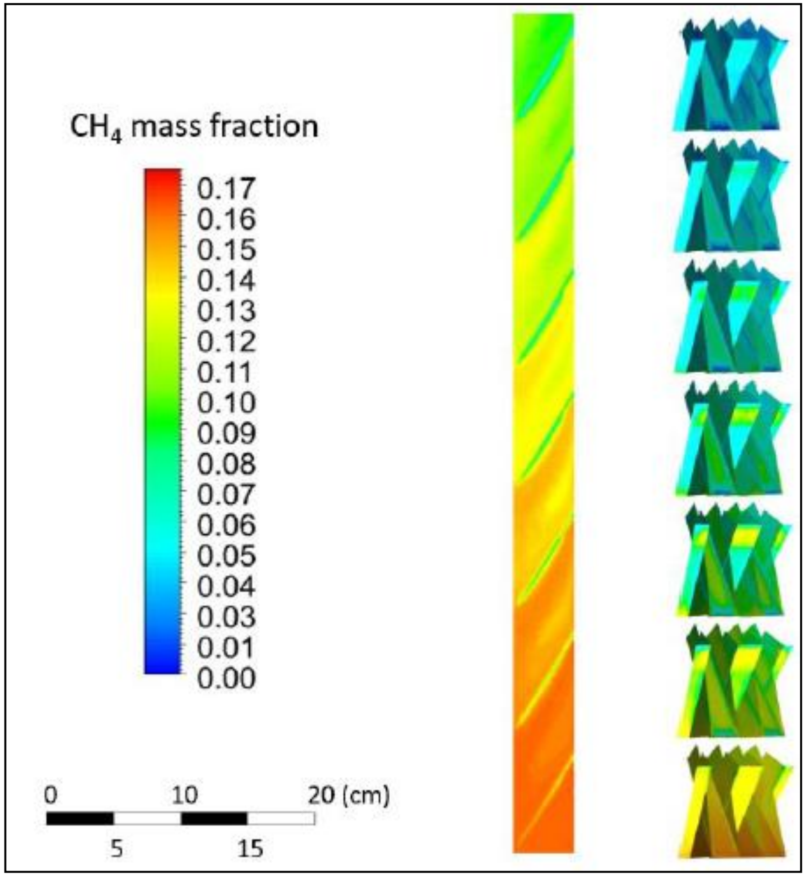


Reaction mechanism & RDS compatibility for CFD simulations

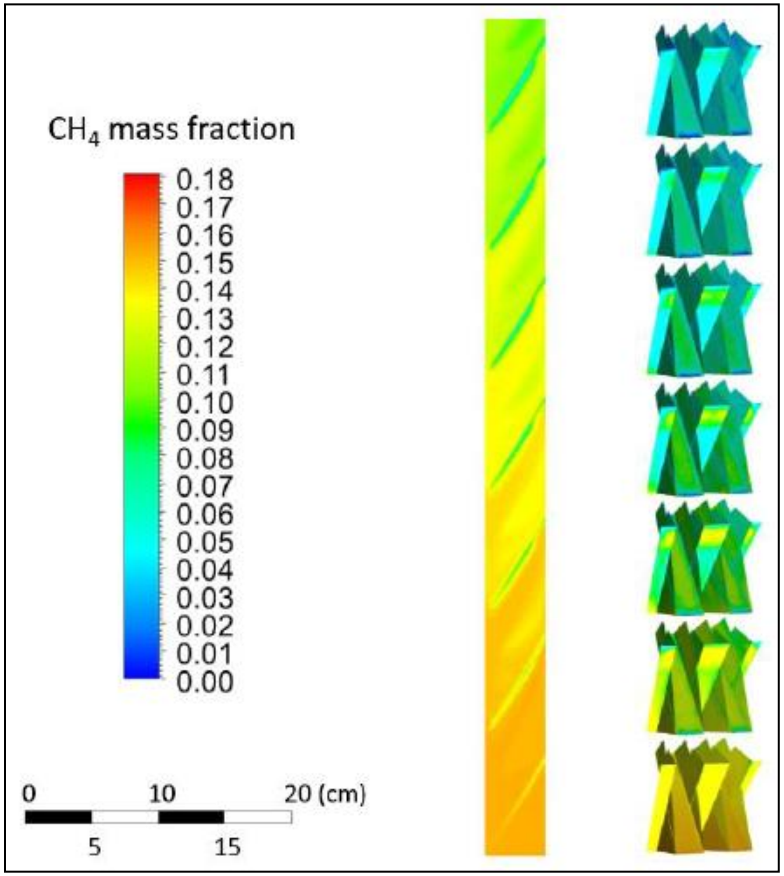


ZF Reactive Model Validation

SV = 1,198. Nm³/h/m³



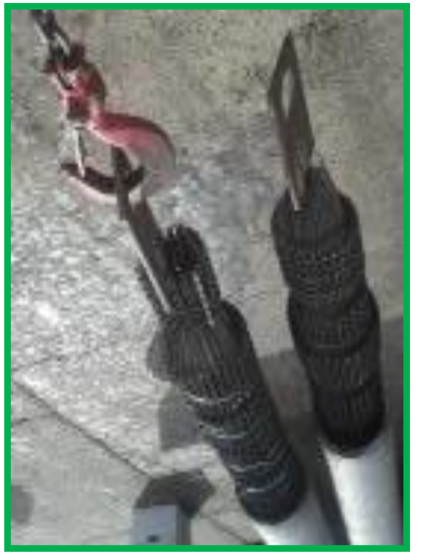
SV = 1,956. Nm³/h/m³



ZF's Commercial Demonstration

Installation

Operation

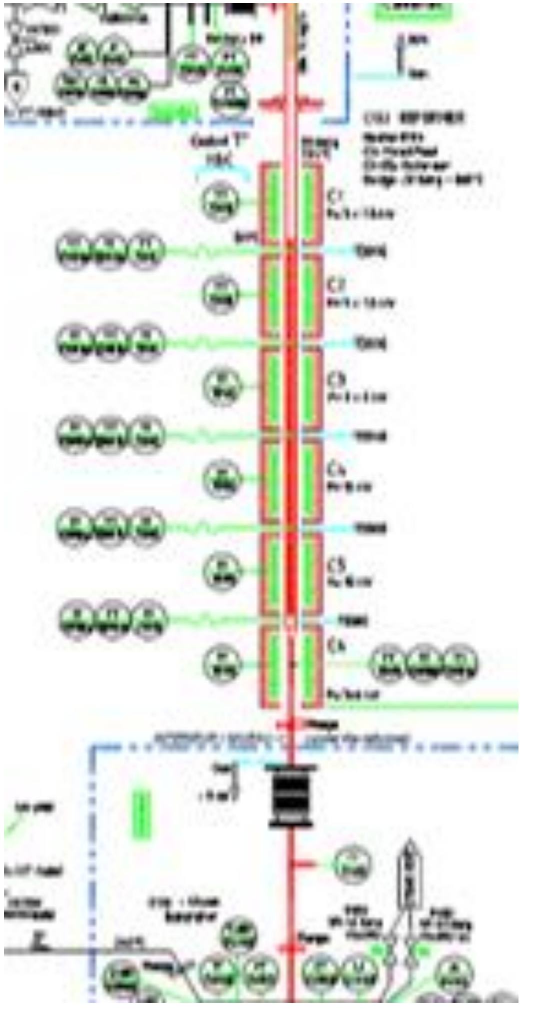


Extraction

- 2 tubes in a 204 tubes Oxo-SMR in Texas
- Up to 80^{o} C lower TMT compared to adjacent tubes
- Up to 24% lower pressure drop
- No hot spots
- ZF structure intact in original form after >15,000 hrs operation and with 5 thermal cycles

ZFRT Pilot Plant Project

- World class unit with extensive design and instrumentation with stringent safety audit and Hazop/LOPA (a small extract of SMR P&ID is depicted)
- At Université Catholique de Louvain (UCL), Belgium, in collaboration with Prof. Froment and Prof. de Wilde
- Rigorous test plan and comprehensive procedures for testing under and beyond commercial conditions
- Site construction nearing completion in coming months



Glimpses of Pilot Plant Installation

ZF Applications in SMRs: Core-Merit and Benefits

- ZF's lower dP, higher HTC and higher catalyst effectiveness allow the following underlying advantages, especially for retrofits :
  - higher throughput without increasing pressure drop
  - higher SMR outlet temp without increasing maximum tube skin temperature (TSM)
  - higher heat flux (average and peak) and/or higher reforming severity with minimized increase in bridge-wall temperature and thus related firing and flue gas
  - lower approach to equilibrium
- Exploitation of ZF's annular structure supports "recuperating reforming"

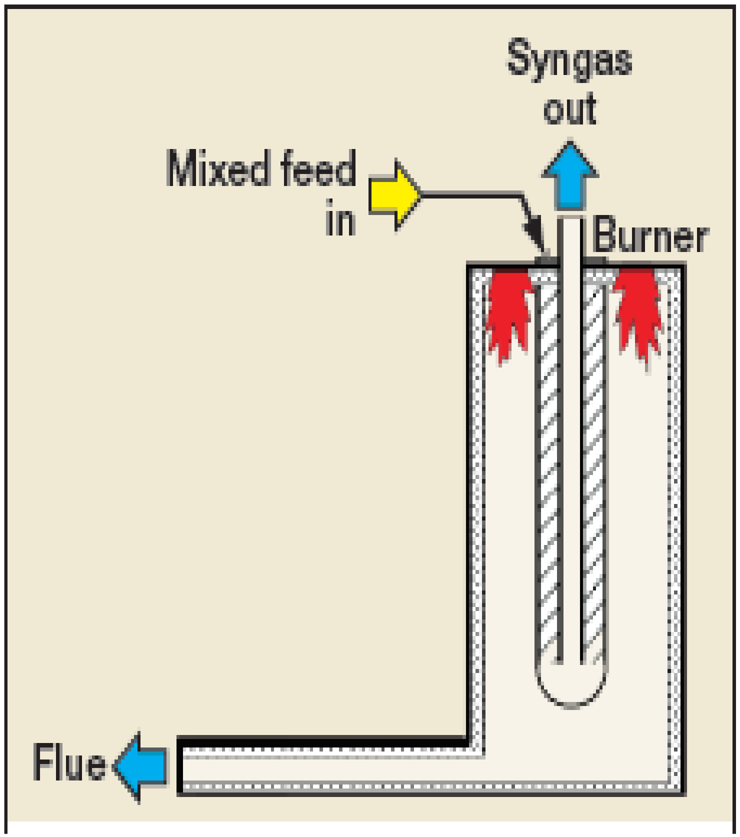
ZF Advanced Solutions for SMRs

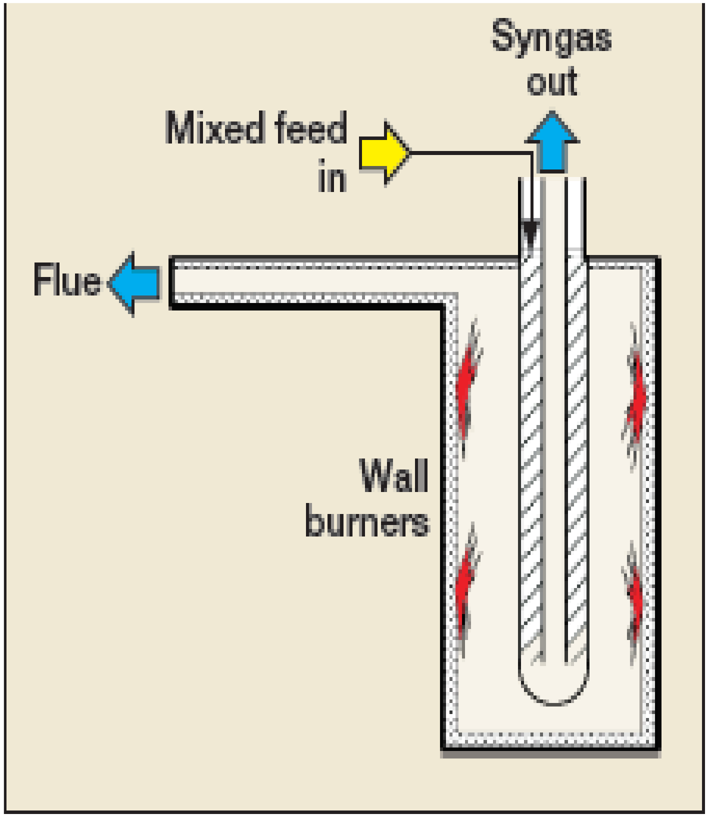
- **ZF-Single pass (ZF-SP)**
  - De-stressing and/or debottlenecking of existing SMRs (upto 15%) with no or minimum modifications
  - Higher average heat flux, cost-effective and more reliable new SMRs
- **ZF-Bayonet (ZF-B)**
  - ZF design inherently suitable for recuperative reforming in new SMRs, overcoming the challenges with Pellets

ZF-SP for SMR Debottlenecking

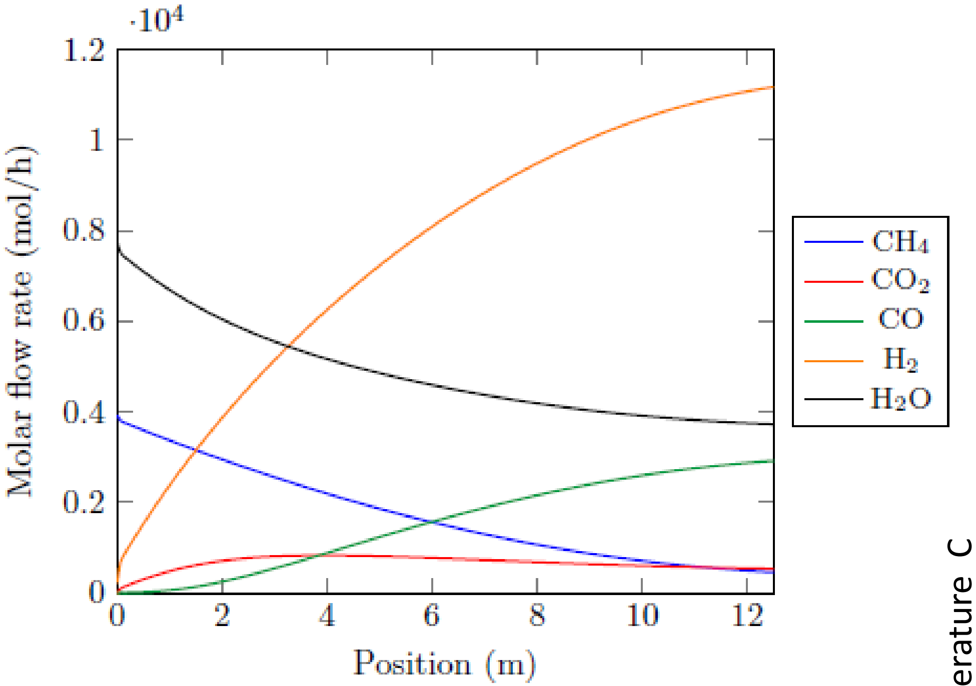
		De-stressing	Upgrading
Max. current capacity,	%	**95**	**100**
Post ZF retrofit capacity,	%	**100**	**115**
S/C Ratio		3.1	2.8
Outlet temp,	C	860	**872**
Approach to equilibrium	C	-10	-7
CH_4 slip,	vol % dry	5.5	5.5
Catalyst pressure drop (design 2.8 bar),	bar	**< 2.8**	**2.8**
Relative Radiant duty	%	100	114
Avg heat flux	kW/m2	75	86
Bridgwall temp,	C	1008	1020
Max. Tube Skin Temp (design 940 C)	C	**< 940**	**940**

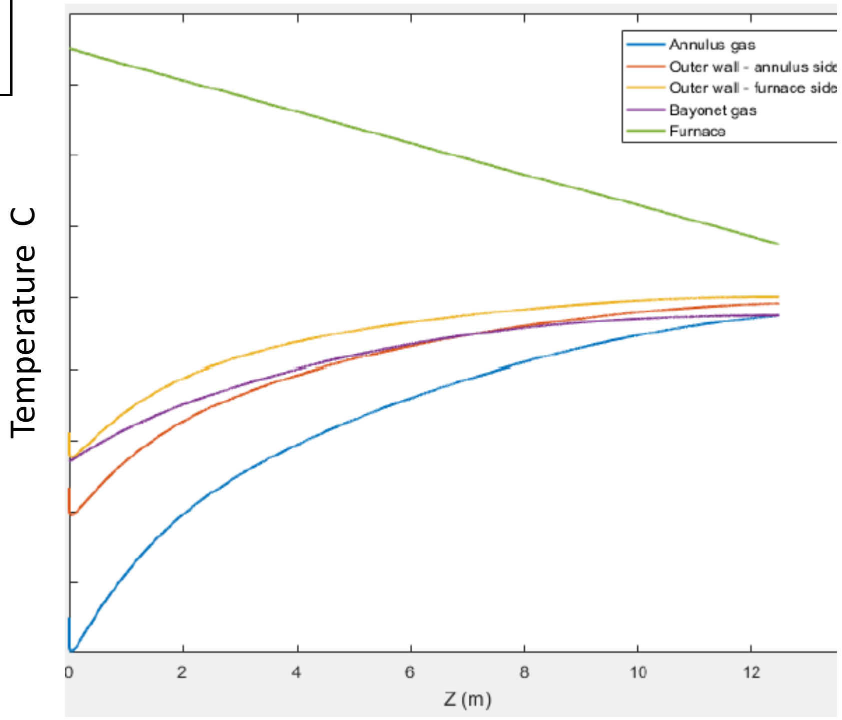
ZF-Bayonet Configurations





ZF-Bayonet Modeling Results





Drivers and Benefits of ZF-Bayonet

- Direct exploitation of ZF's inherent annular design
- Overcomes innate limitations of the "pellet" catalyst against crushing from differential expansion / thermal cycling
- SMR size reduction up to 20% based on high grade heat recovery for reforming
- Allows "Zero export steam" hydrogen plants for :
  - remote, stand-alone or "distributed " hydrogen plants not having a steam host
  - cases where export steam has low or no credit compared to fuel
- Allows lowering of carbon-footprint from reduced firing per unit H2
- Compact / modularized SMR units
- Applicable in various SMR configurations and designs

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Thank You !

For additional information, contact:

Sanjiv Ratan
Director of Marketing and Prod Dev
sratan@zoneflowtech.com
+1-951-538-5501