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ZoneFlow Reactor Technologies, LLC

Innovative ZoneFlow™ Structured Catalyst System
- Gearing for the Future in Steam Reforming

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

Presentation Outline

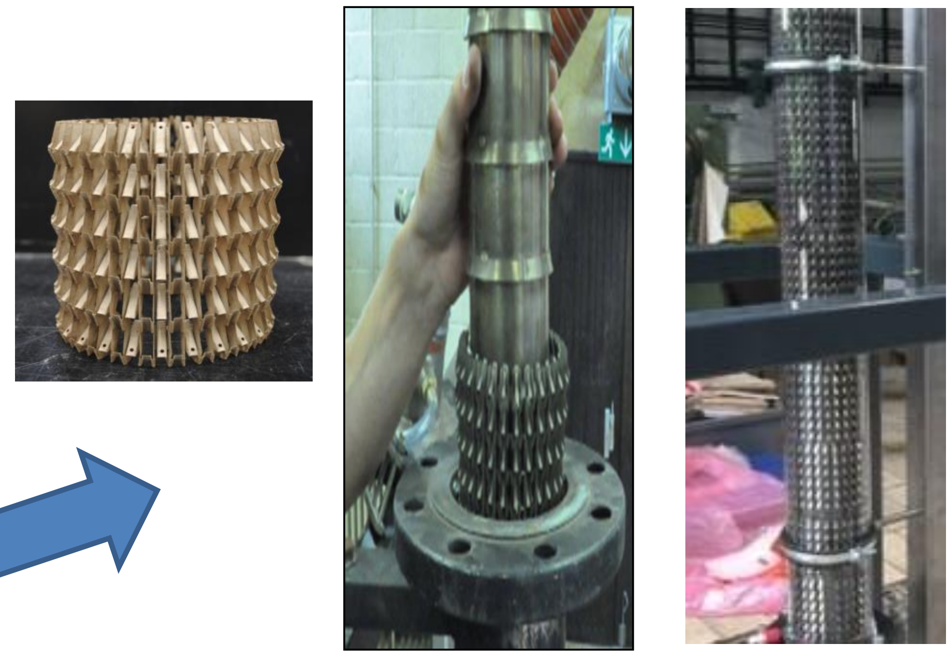
- Introduction
- From current BAT ‘pellet’ steam reforming catalyst - Status quo to ZoneFlow^{TM} (ZF) structured catalytic reactor technology - an innovative breakthrough
- ZF product development update and validation programs
- Application merits and advanced solutions of ZF reactor technology
- Conclusions

Introduction

- Steam (methane) reforming (SMR) is the most prominent process and ‘technology of choice’ for hydrogen-syngas generation
- State-of-the-art steam reforming catalysts have by and large stayed “pellet-based” and so have the inherent deficiencies
- Various attempts have been made in the past for developing structured catalyst for SMR but weren’t very successful due to few core challenges till lately
- ZoneFlow Reactor Technologies (ZFRT) has developed an advanced, innovative and breakthrough ZoneFlow™ structured catalyst reactor system (ZF) for steam reforming which overcomes most of the pellet catalyst deficiencies :

ZoneFlow™
Gearing for the Future in Steam Reforming

Conventional pellet SMR catalyst



ZoneFlow™ structured catalytic reactor system

ZF Merits overcome BAT Deficiencies

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	Diffusion limited	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 Product Development Path and Milestones

- Concept design and Cold-flow testing
- Bench-scale unit at HyPaul lab UC Davis
- Manufacturing and mechanical performance
- Demo in commercial plant
- New generation (cost) optimized design development
- Specific application need based ZF products – as enabling technology
    - Single-pass (ZF-SP)
    - Bayonet (ZF-B)
- Commercial roll-out

ZF Validation Program

- Focus on verification and validation of performance at near-commercial conditions
  - CFD modelling (1D & 3D)
  - Heat transfer and pressure drop test rig (UCL)
  - Commercial-scale pilot plant for hot reactive testing (UCL)
  - Kinetics (intrinsic) evaluations of prospective catalysts (UCL)
  - Pilot and demonstration installations at strategic customer sites

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:

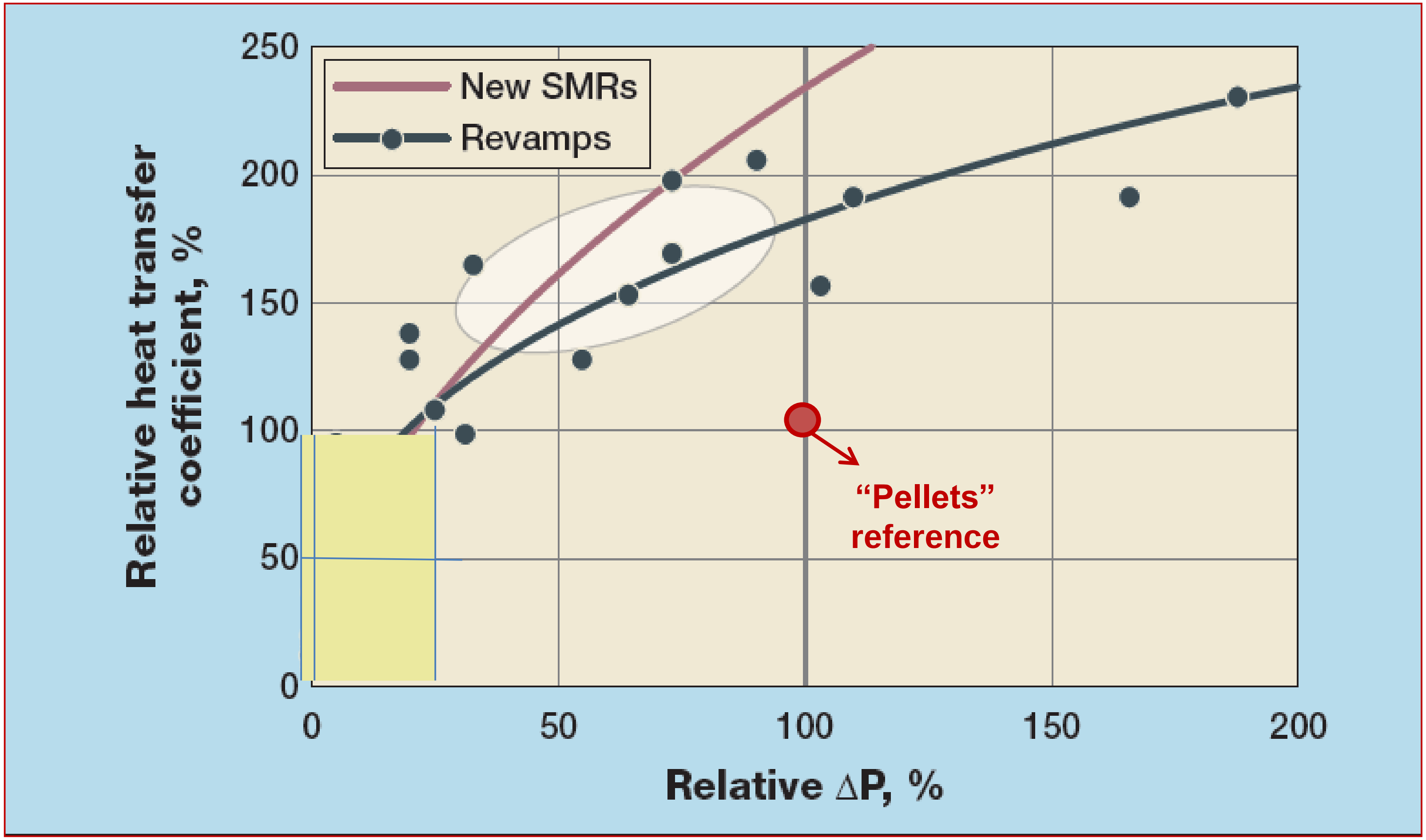
$$\tilde{k}_{g,A}\left(m_{As}^{s} - m_{A}\right) = \rho_s d M_A \sum_k \alpha_{A,k}\eta_k r_k(\overline{m}_s^{s}, T_s)$$

$$= (1-\varepsilon)\rho_s M_A \sum_k \alpha_{A,k}\eta_k r_k(\overline{m}_s^{s}, T_s)/a_V$$

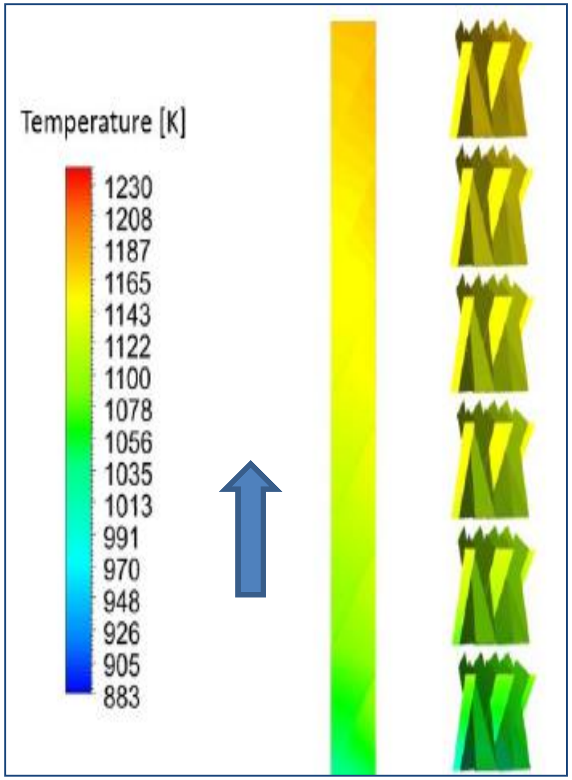
$$h_f(T_s - T) = \rho_s d \sum_k \eta_k r_k(\overline{m}_s^{s}, T_s)(-\Delta H_k)$$

$$= (1-\varepsilon)\rho_s \sum_k \eta_k r_k(\overline{m}_s^{s}, T_s)(-\Delta H_k)/a_V$$

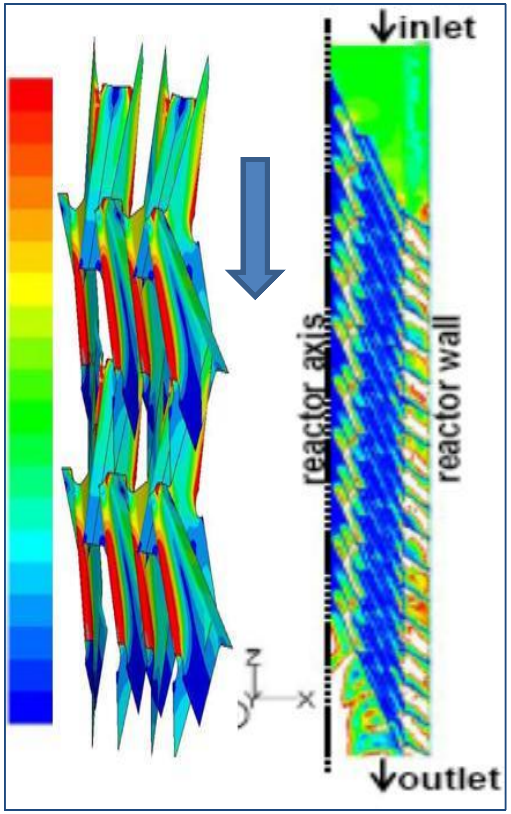
CFD Modeling Results



Rigorous CFD and FEA Results

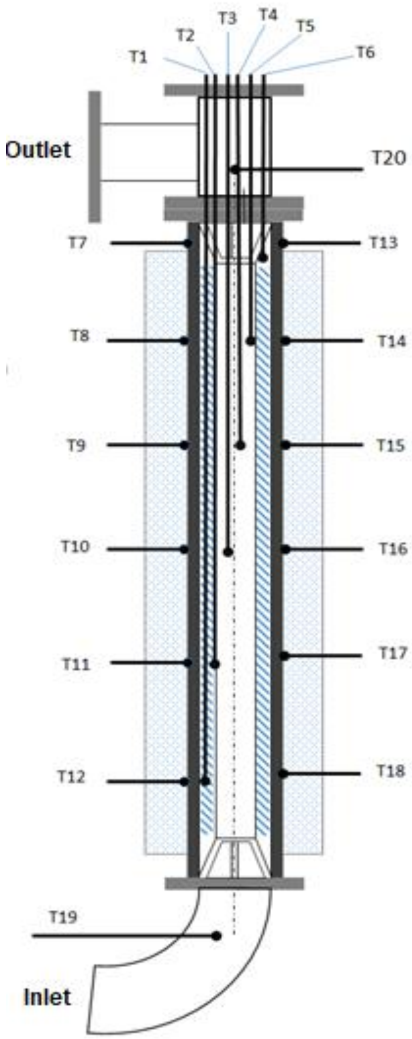


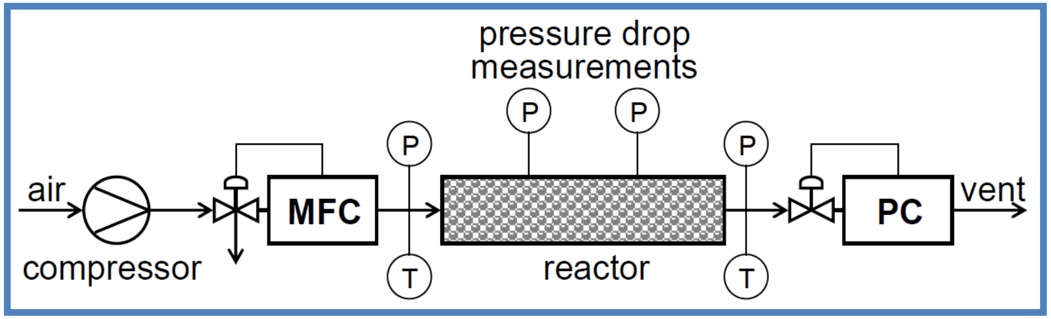
Temp Profiles



FE Analysis

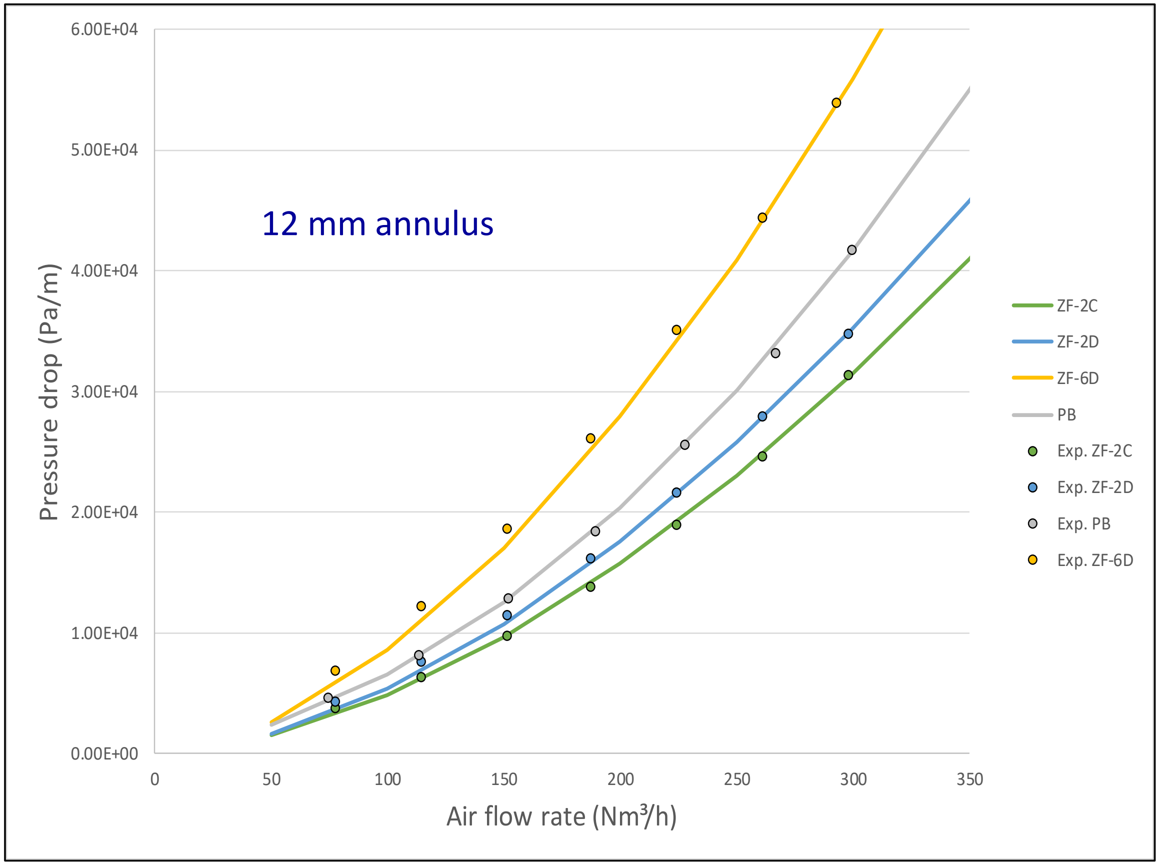
Pressure Drop - Heat Transfer Test Rig





Air flow 75-300 Nm^3/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

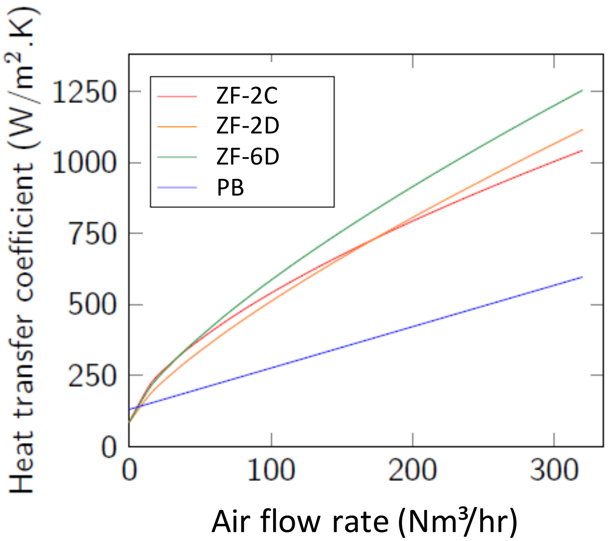
ZoneFlow:

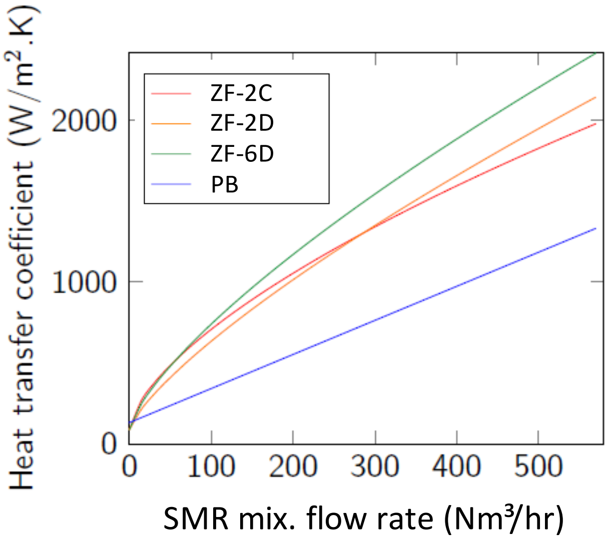
$$Nu = \frac{86L}{\lambda_g} + a_5 Re^{a_6} Pr^{1/3}$$

Packed bed:

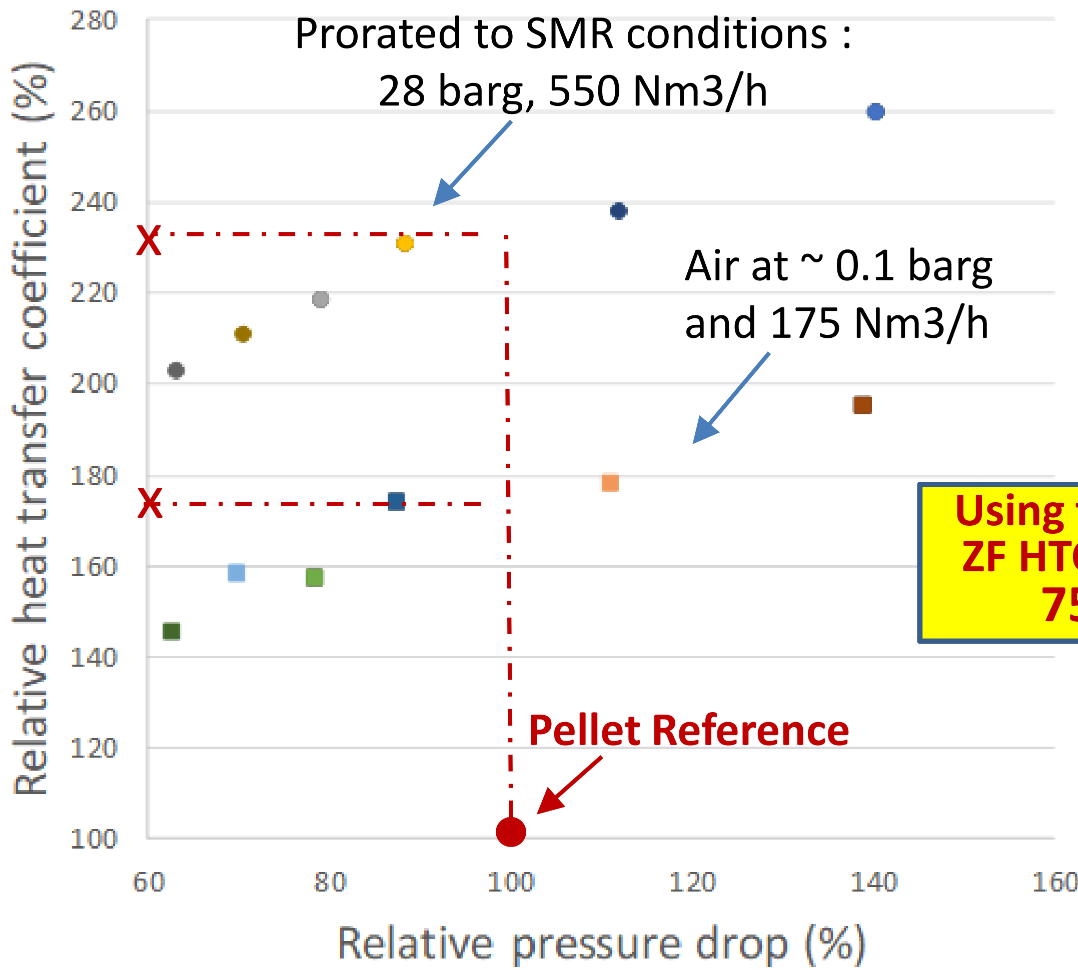
$$Nu_p = \frac{a_7 d_p}{\lambda_g} + a_8 Re_p Pr$$

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



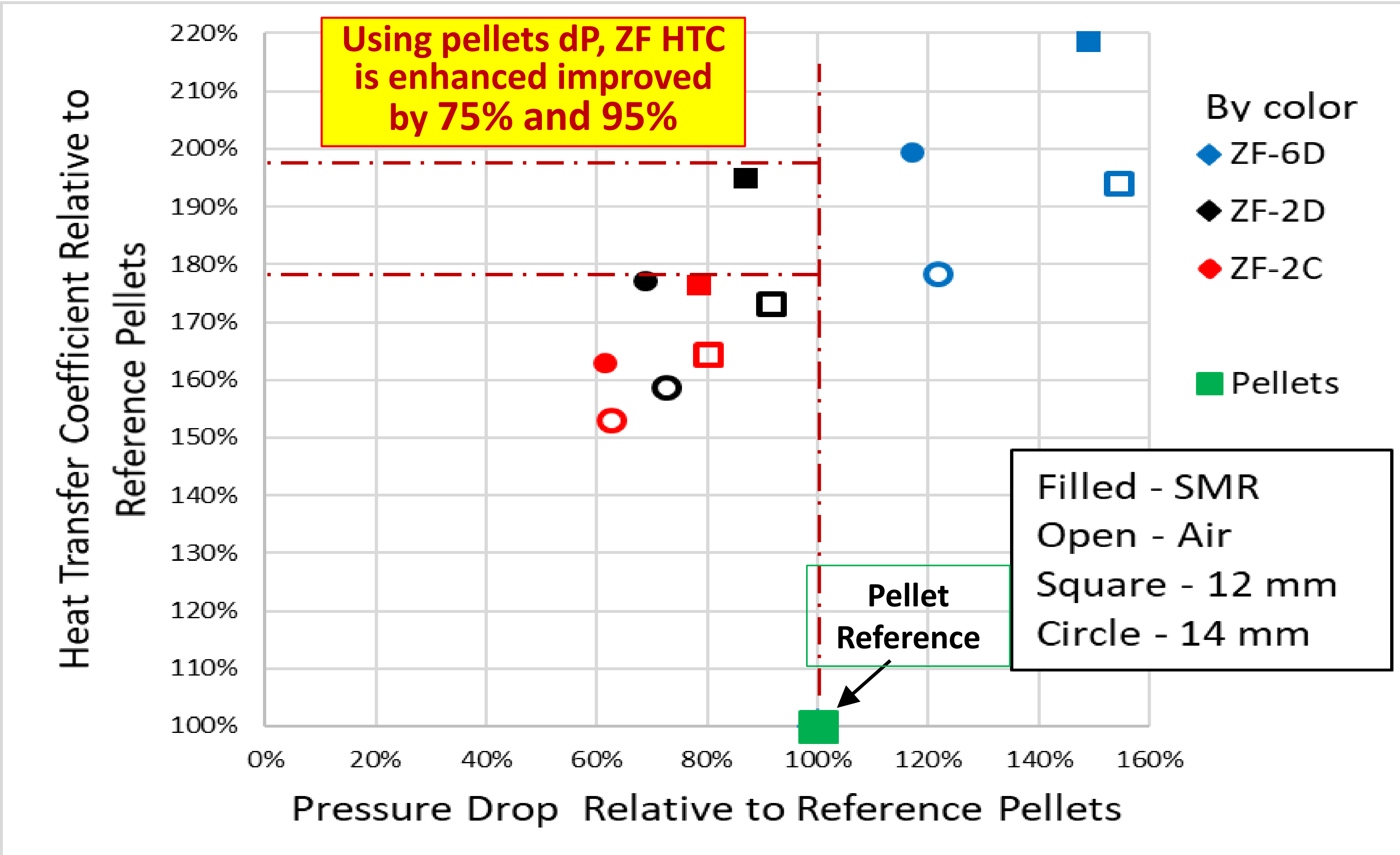


ZF v/s Pellets A : dP-HTC Relation



Using full dP of pellets, ZF HTC is enhanced by 75% to 130%

ZF v/s Pellets B : dP-HTC Relation



Catalyst Kinetics Evaluation Lab

Kinetic Modeling

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

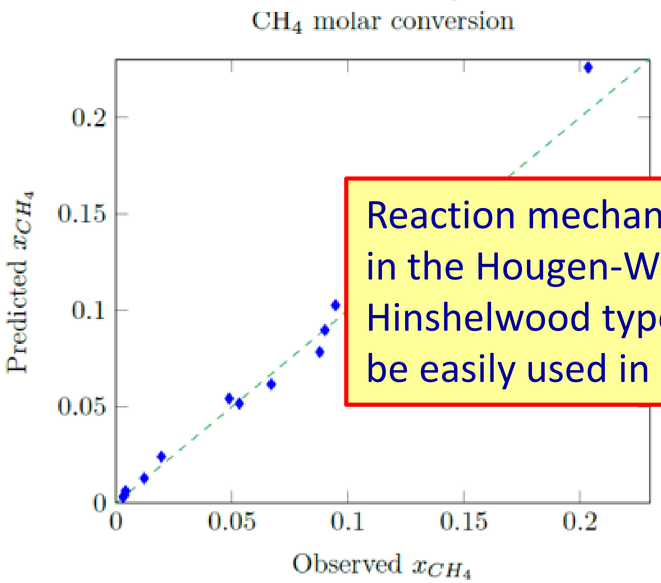
$$r_2 = \frac{\left(k_2/p_{H_2}\right)\left(p_{CO}p_{H_2O} - \frac{p_{H_2}p_{CO_2}}{K_{II}}\right)}{DEN^2}$$

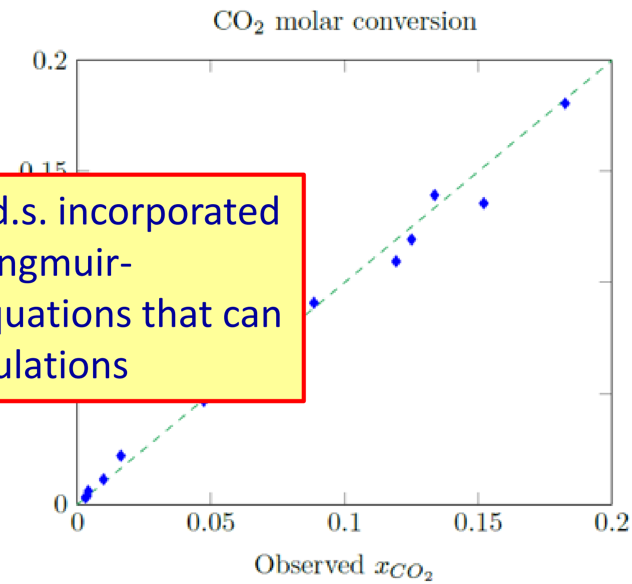
$$r_3 = \frac{\left(k_3/p_{H_2}^{3.5}\right)\left(p_{CH_4}p_{H_2O}^2 - \frac{p_{CO_2}p_{H_2}^4}{K_{III}}\right)}{DEN^2}$$

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

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)

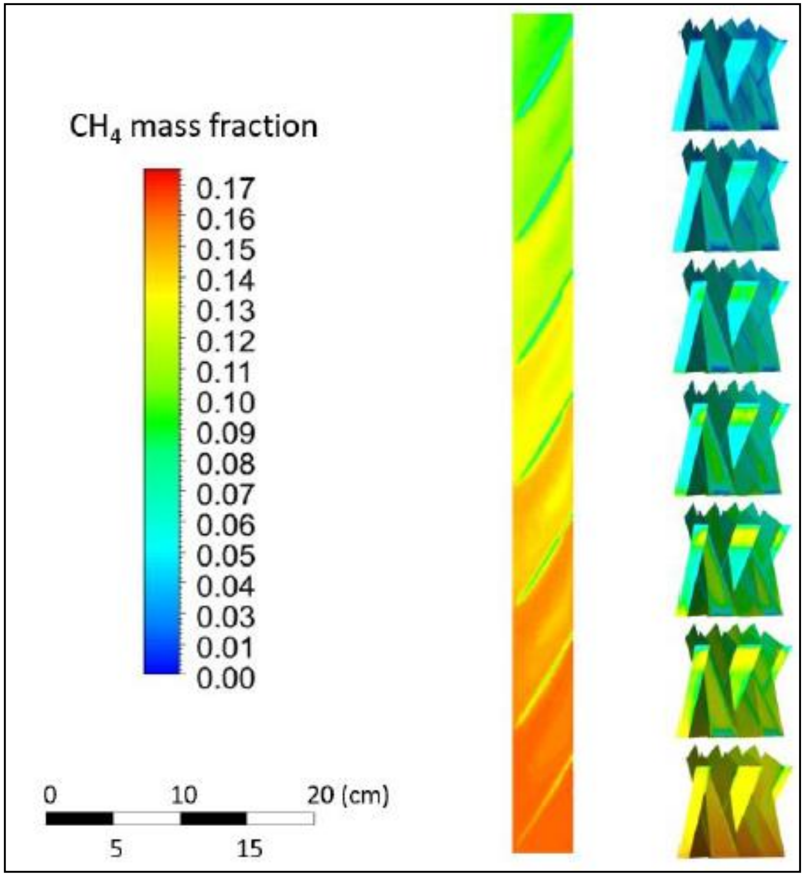




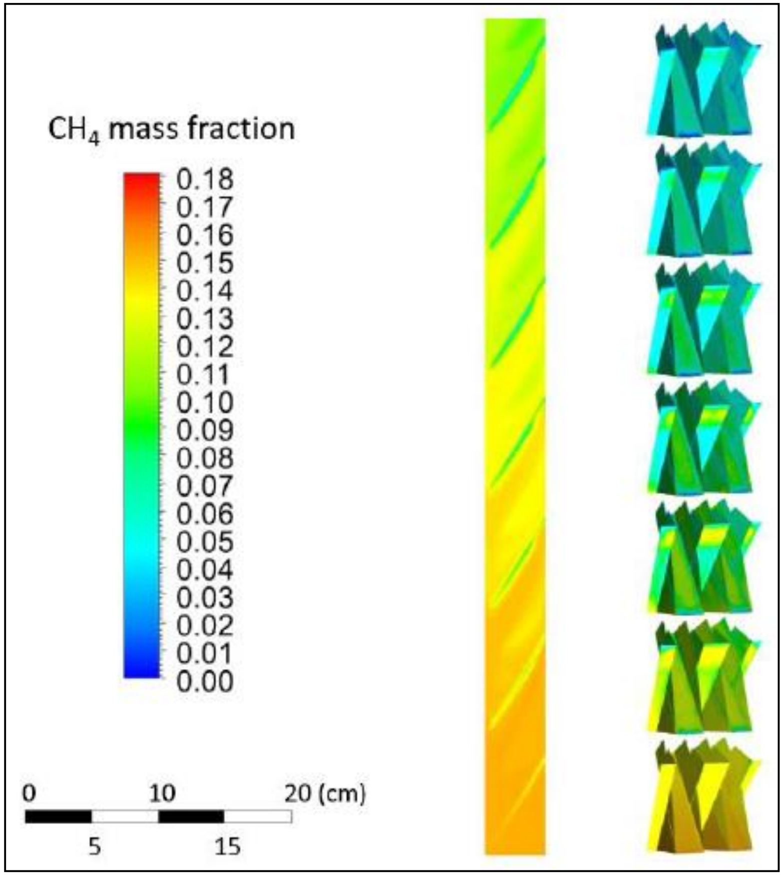
Reaction mechanism & r.d.s. incorporated in the Hougen-Watson Langmuir-Hinshelwood type rate equations that can be easily used in CFD simulations

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 80º 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 Installation

- At Université Catholique de Louvain (UCL), Belgium
- Fully equipped and instrumented for rigorous testing under commercial conditions
- In collaboration with Prof. Froment and Prof. de Wilde
- Operational 4Q 2019

Glimpses of Pilot Plant Execution

Glimpses of Pilot Plant Execution (cont'd)

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 <u>without</u> increasing maximum tube skin temperature (TSM)
  - higher heat flux (average and peak) and/or higher reforming severity with minimal 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

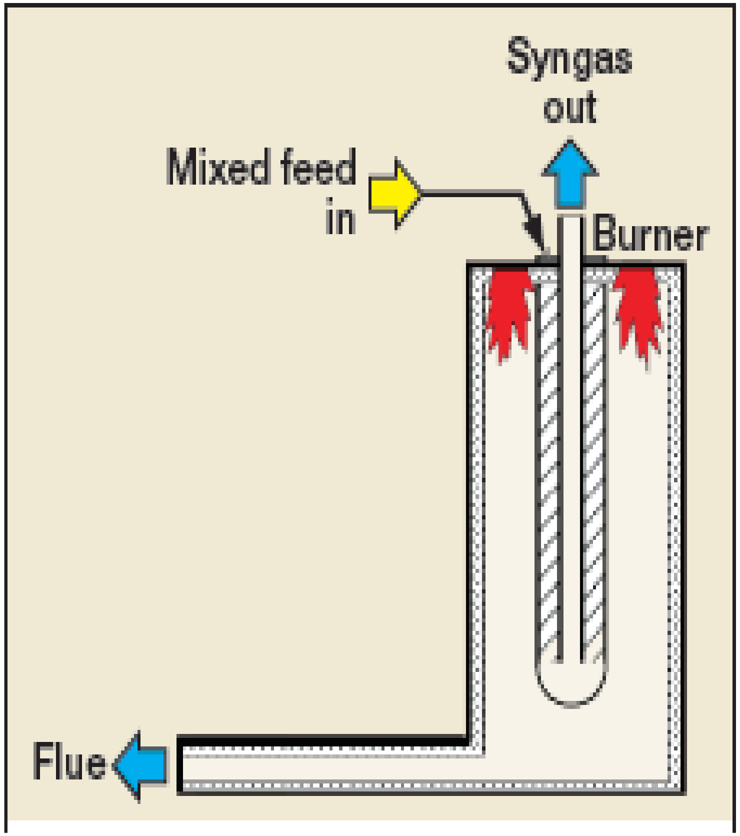
- **ZF-Single pass (ZF-SP)**
  - De-stressing and/or debottlenecking of existing SMRs (upto 15%) with no or minimum modifications
  - Higher average heat flux, cost-effective and more reliable new SMRs

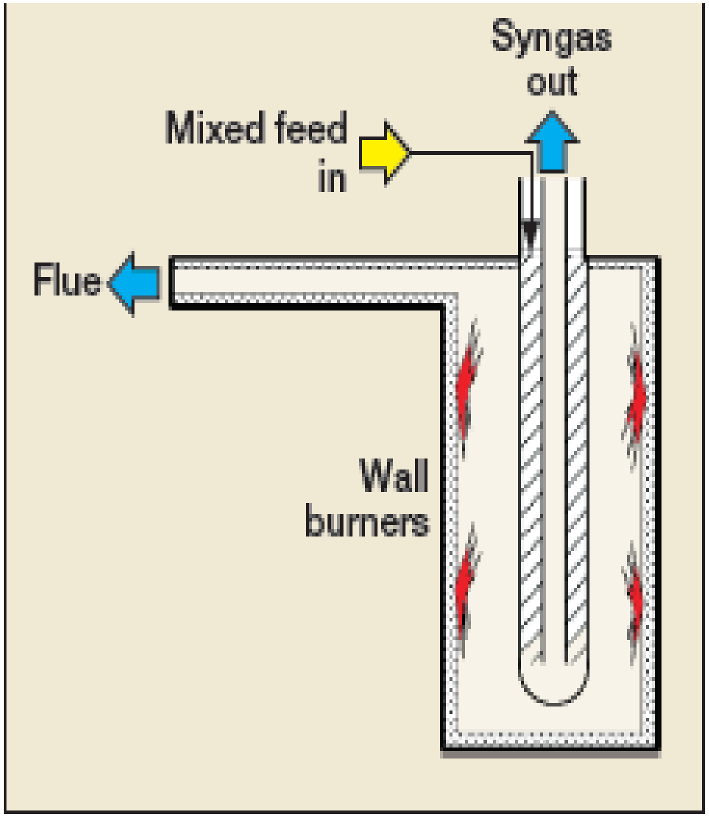
- **ZF-Bayonet (ZF-B)**
  - ZF design inherently suitable for recuperative reforming in new SMRs, overcoming the challenges with Pellets

ZF-SP for SMR Debottlenecking

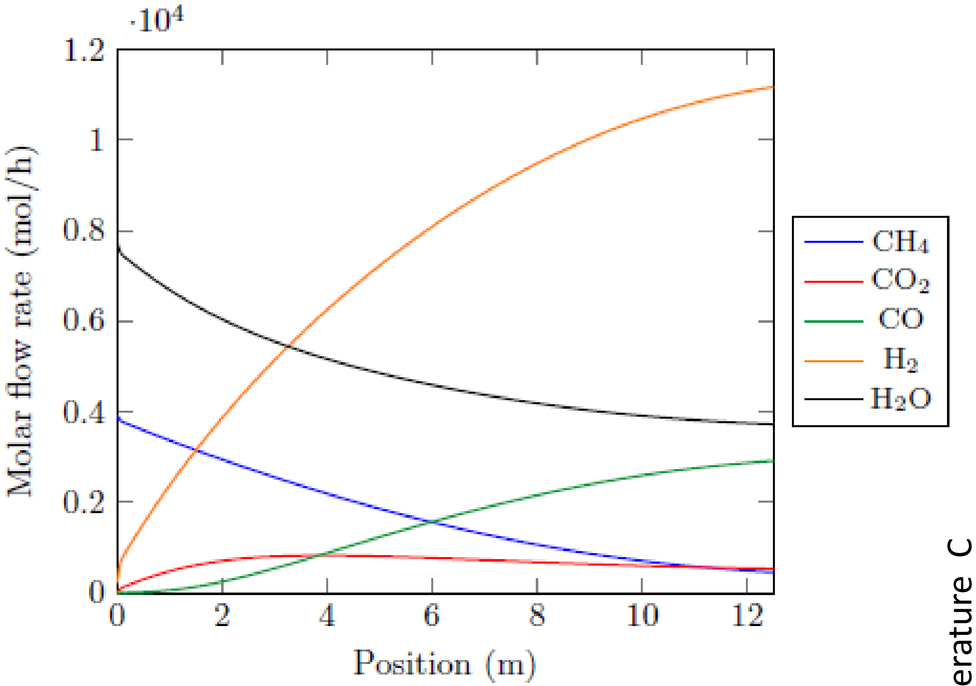
	De-stressing	Upgrading
Max. current capacity, %	**95**	**100**
Post ZF retrofit capacity, %	**100**	**115**
S/C Ratio	3.1	2.8
Outlet temp, C	860	**872**
Approach to equilibrium C	-10	-7
CH4 slip, vol % dry	5.5	5.5
Catalyst pressure drop bar (design 2.8 bar),	**< 2.8**	**2.8**
Relative Radiant duty %	100	114
Avg heat flux kW/m2	75	86
Bridgwall temp, C	1008	1020
Max. Tube Skin Temp C (design 940 C)	**< 940**	**940**

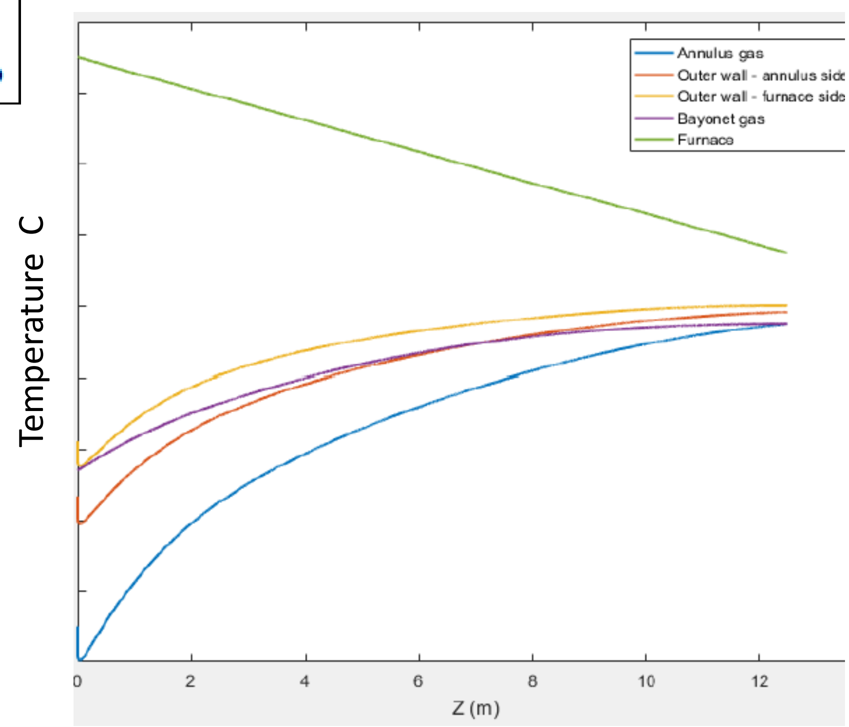
ZF-Bayonet Configurations





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

Conclusions

- Steam Reforming has been the predominant technology for Hydrogen - Syngas generation
- SMR catalyst governs to a large extent its capacity rating, performance, operational reliability and tube life
- Current pellet catalysts have inherent deficiencies, thus limiting the extent of improvements.
- ZoneFlow Reactor Technologies (ZFRT) has developed breakthrough and innovative structured catalyst reactors for steam reforming
- ZoneFlow^{TM} (ZF) suite of catalysts offer exceptional and advanced solutions for revamping as well as new SMRs, providing attractive Capex and Opex benefits.
- After successful demo and test rig results, the upcoming world class pilot plant will allow extensive testing under commercial conditions and beyond for establishing its merits.

ZoneFlow Reactor Technologies, LLC

Thank You !

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