

Development and scale-up of structured catalytic reactors for steam methane reforming

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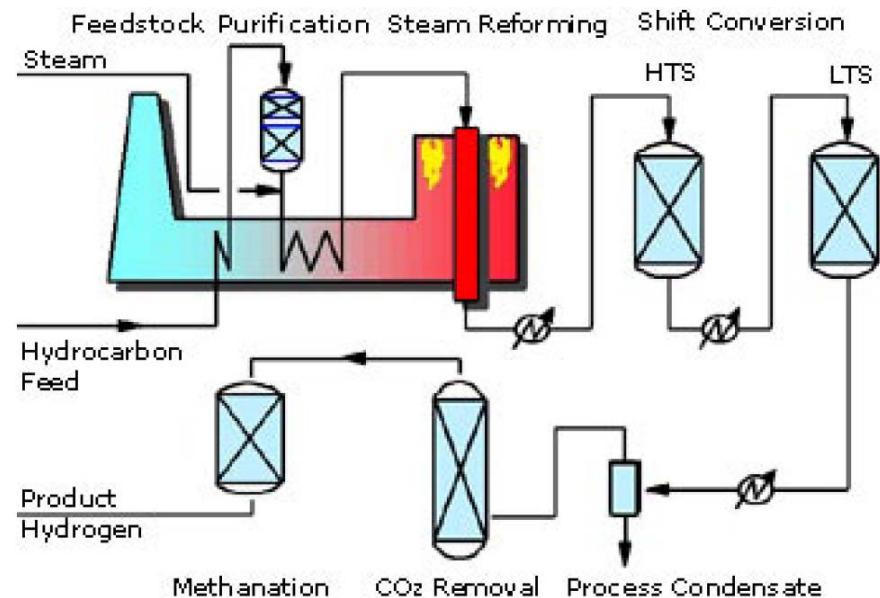
Steam Methane Reforming

- H₂ & Syngas production (H₂ & CO)
- Downstream conversion into:
 - Methanol
 - Ammonia
 - Hydrogen
 - Synthetic fuels (Fischer-Tropsch)
- Accounts for:
 - 95% of the H₂ produced in the US
 - 48% of the H₂ produced globally

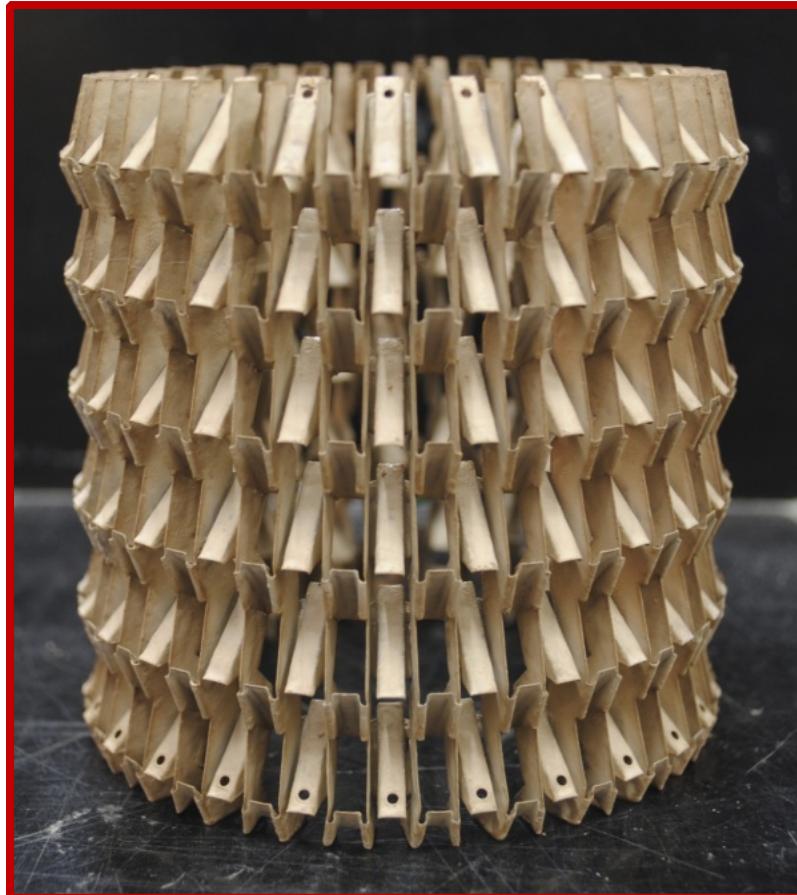


(Topsoe)

- Strongly endothermic reactions
 - Multi-tubular fixed bed reactor
 - Ni/Mg-Al₂O₄ spinel cat.
 - T(gas): 750-800°C, P: 29 bar
- Intra-particle diffusion limitations
=> Low cat. effectiveness factors
- Pressure drop limitations
- Heat transfer limitations (wall-gas)
=> Diameter tube: 10 cm
=> Heat flux ⇔ Tube skin temp.
- Coke formation: S/C-ratio & local T



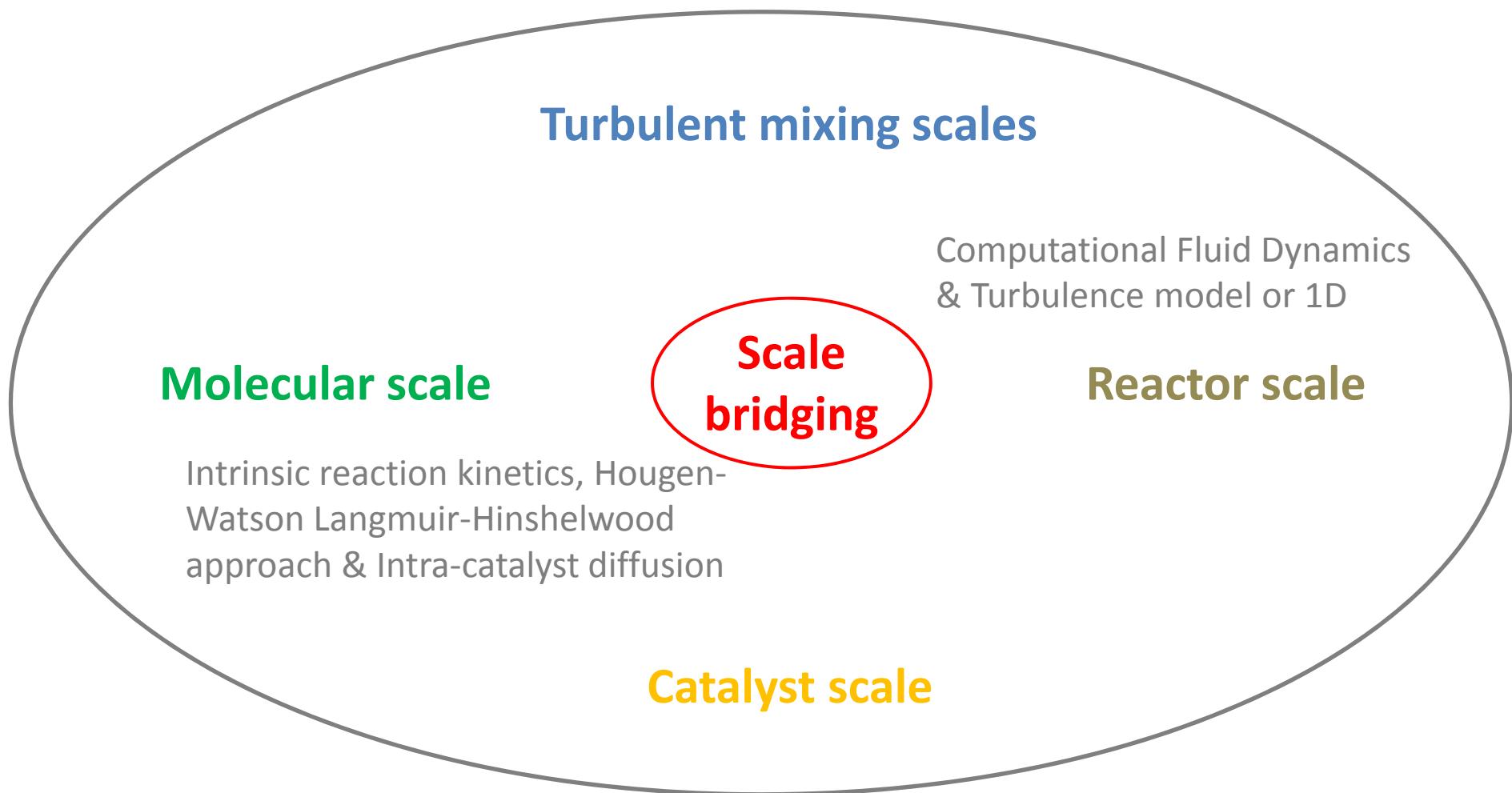
ZoneFlow™ structured catalytic reactors



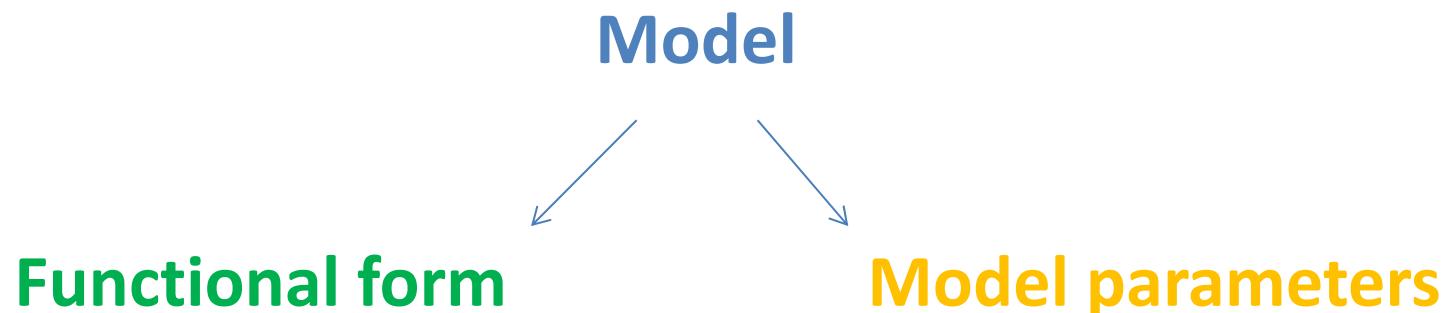
Near-wall Casing:

- Intensified heat transfer
- Reduced pressure drop
- Increased specific interfacial surface area
- Improved catalyst effectiveness
- Mechanical strength (no crushing)

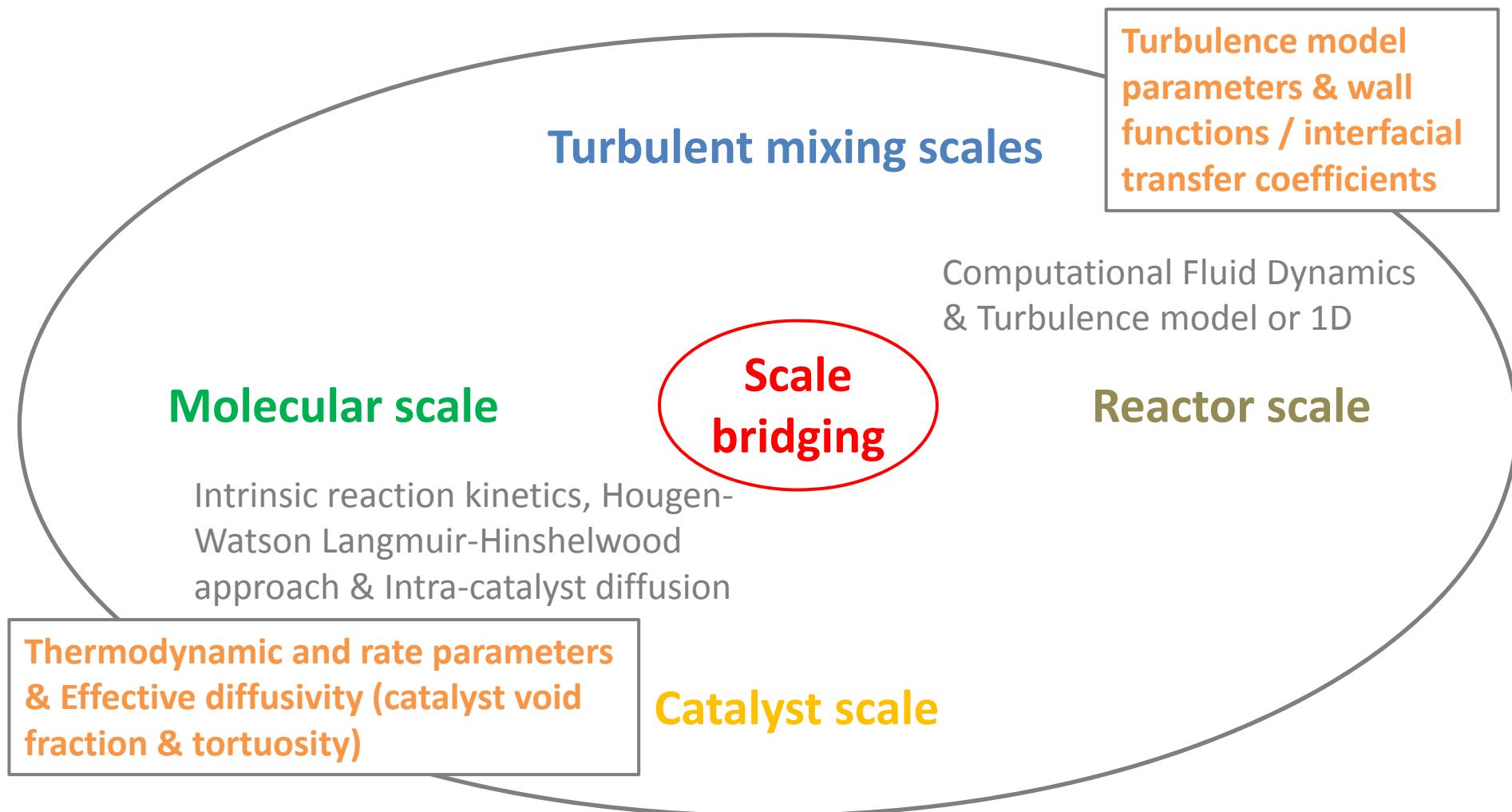
Multiscale modelling for scale-up & optimization



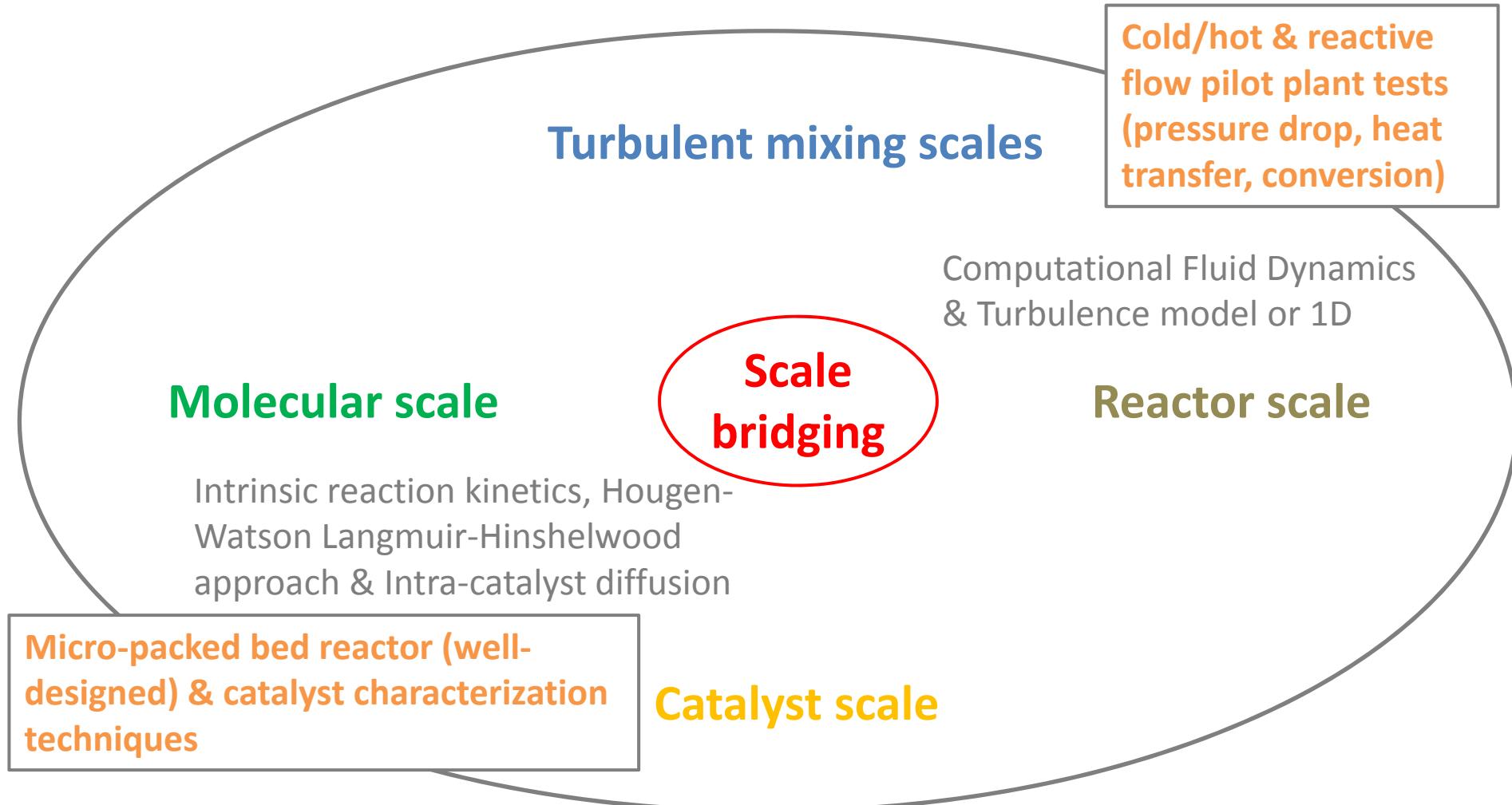
Multiscale modelling for scale-up & optimization



Multiscale modelling for scale-up & optimization



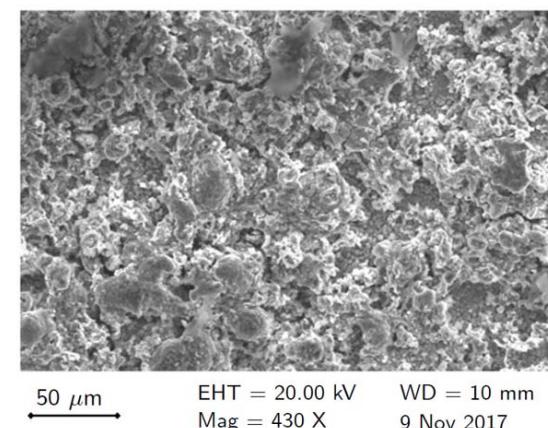
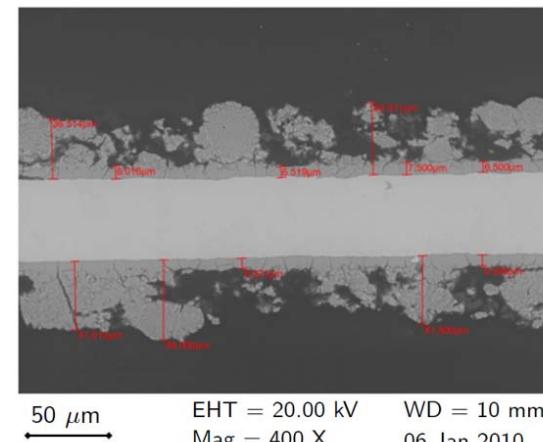
Multiscale modelling for scale-up & optimization



ASC catalyst

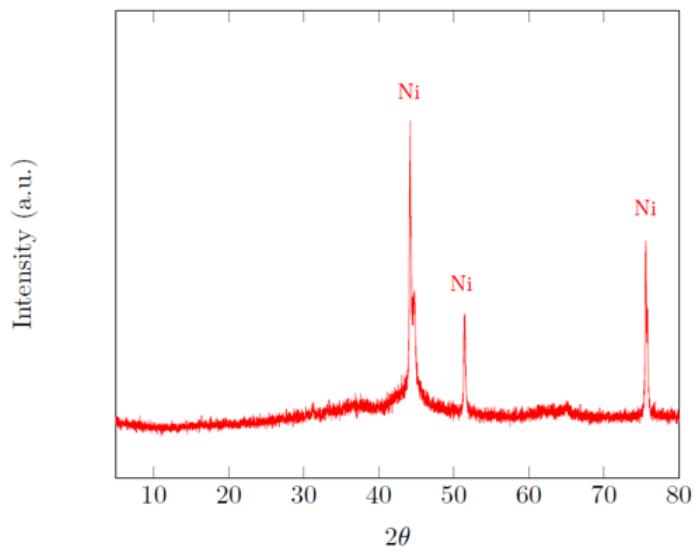
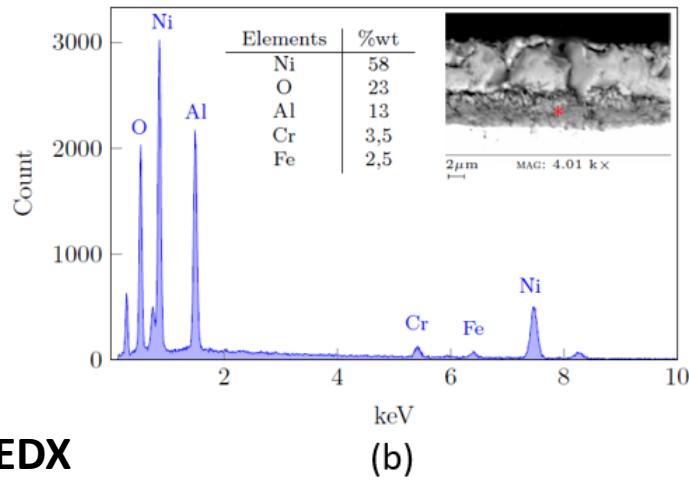
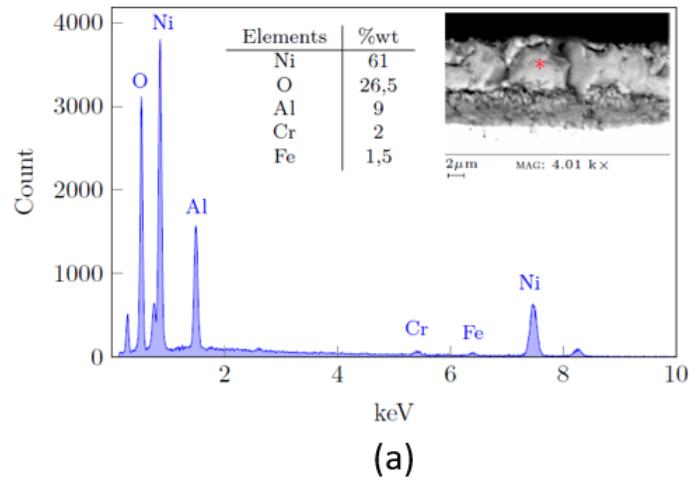
- A metal structure with a thin, nanostructured and adherent high surface area coating
 - Integral bonding of nanostructured catalytic layers
 - Can be used as a catalyst or catalyst support
 - Can take on various form factors
 - ✓ Foil
 - ✓ Fiber
 - ✓ Mesh
 - ✓ Tube
- Mechanical robustness
 - Reactor geometry formed after coating
 - Potential to eliminate washcoat layer
 - No delamination under severe process conditions

Coating thickness (μm)	10
Coating mass fraction ($\text{g}_{\text{coat}}/\text{g}_{\text{tot}}$)	0.075
Ni content (wt.%) (reduced state)	75-85
BET surface area ($\text{m}^2/\text{g}_{\text{coat}}$)	7.4
Density ($\text{g}_{\text{coat}}/\text{cm}^3_{\text{coat}}$)	5.78
Pore volume ($\text{cm}^3_{\text{g}}/\text{g}_{\text{coat}}$)	0.0145
Porosity ($\text{cm}^3_{\text{g}}/\text{cm}^3_{\text{coat}}$)	0.084

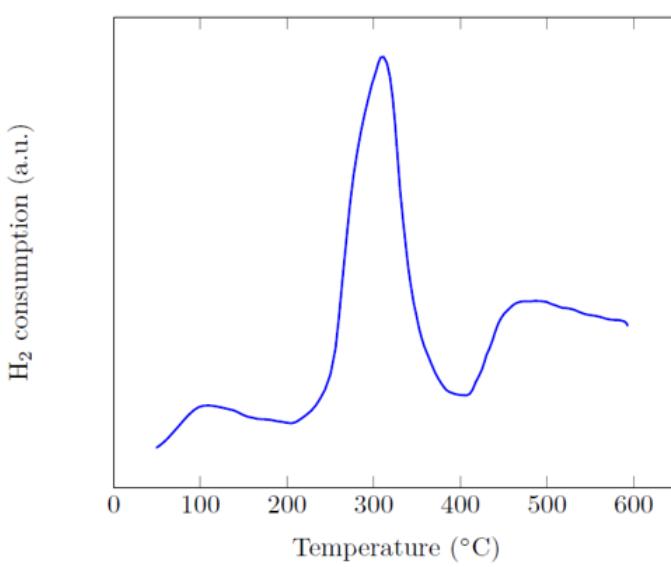


Catalyst coating can be done before creating the structure

ASC catalyst

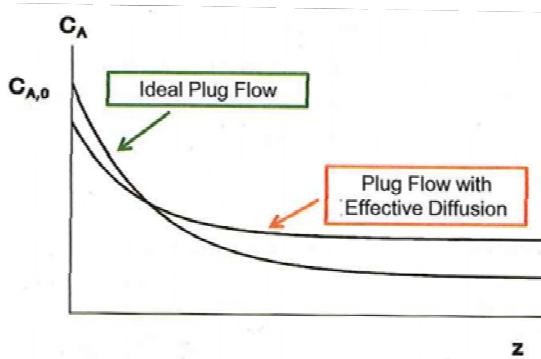


(c) XRD



(d) TPR

Measuring intrinsic reaction kinetics



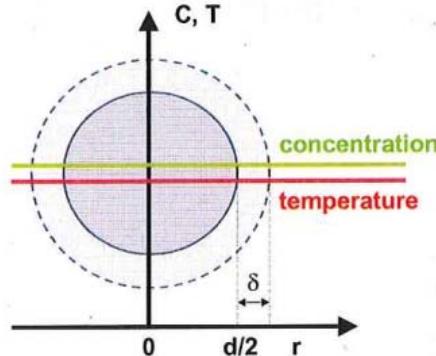
Goal : intrinsic kinetics

- Not affected by transport phenomena
- Specific design considerations
- Well defined operating conditions

Packed bed reactor:

- Plug flow: $Re_p > 20$ [Carberry, 1976] $Re_p = 22$ ✓
- Negligible axial dispersion:
 - $L/d_p > 20-50$ [Carberry & Wendel, 1963; Carberry, 1976] $L/d_p = 250$ ✓
- Negligible radial dispersion:
 - $d_t/d_p > 8-10$ [Chu & Ng, 1989; Froment et al., 2010] $d_t/d_p = 250$ ✓
- Isothermal operation:
 - d_t sufficiently small
 - $\Delta T_{r,B} = |-\Delta H| \cdot r_A \cdot \rho_B \cdot (d_t)^2 / (32 \cdot \lambda_{er}) < \Delta r_{rel} \cdot R \cdot (T_w)^2 / E$ ($d_t/d_p > 100$) [Mears, 1971] $0,5 < 3,5$ ✓
 - $\Delta T_{w,BC} = (1+8 \cdot Bi_w \cdot d_p/d_t) \cdot |-\Delta H| \cdot r_A \cdot \rho_B \cdot (d_t)^2 / (32 \cdot \lambda_{er}) < \Delta r_{rel} \cdot R \cdot (T_w)^2 / E$ ($d_t/d_p < 100$) $0,65 < 3,46$ ✓
- Bed dilution: $b_{max} = \Delta x_{rel} / (\Delta x_{rel} + 0.5 \cdot x_{dil} \cdot d_p / L)$ [Berger et al., 2002]

Measuring intrinsic reaction kinetics



Pressure (bar)	1.8 - 3.57
Temperature (°C)	448 - 602
H ₂ O/CH ₄ molar	2.87 - 5.53
H ₂ /CH ₄ molar	1.25

Packed bed reactor:

- Negligible interphase mass & heat transfer limitations:
 - $\Delta T_{gs} = |-\Delta H| \cdot r_A \cdot \rho_B \cdot d_p / (6 \cdot h_{gs}) < 0.05 \cdot R \cdot (T)^2 / E$ (Mears, 1971) $0,04 < 2,1$ ✓
 - $\Delta C_{A,gs} = r_A \cdot \rho_s / (k_g \cdot a_{v,s}) < R I_{im,r} \cdot C_A / n$ (Mears, 1971) $5,8 \times 10^{-4} < 7 \times 10^{-4}$ ✓
 - Experimental verification by varying W/F
- Negligible intra-particle diffusion limitations:
 - $\Phi = [(n+1)/2] \cdot [(r_A \cdot \rho_s) / (D_{A,eff} \cdot (C_{A,s})^s \cdot (a_{v,s})^2)] << 1$ [Weisz & Prater, 1954] $\Phi = 0,066$ ✓
 - Experimental verification by varying d_p
- Negligible intra-particle heat transfer resistance:
 - $\Delta T_{int,s} = |-\Delta H| \cdot r_A \cdot \rho_s \cdot (d_p)^2 / (60 \cdot \lambda_s) < 0.05 \cdot R \cdot (T)^2 / E$ [Anderson, 1963] $5,7 \times 10^{-3} < 2,1$ ✓
- Sufficiently small pressure drop:
 - $\Delta P < 0.2 \cdot P_{tot} / n$ with: $\Delta P = f \cdot \rho_g \cdot (u_{sup})^2 \cdot L / d_p$ [Ergun, 1952] $10^3 < 31 \times 10^3$ ✓

Kinetic modelling

Integral method of kinetic analysis

$$\frac{W}{F_{A0}} = \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{r_A}$$

Regression: $S(\beta) = \sum_{I=1}^n [y_I - f(\mathbf{x}_I, \beta)]^2 \xrightarrow{\beta} \text{Min}$

Statistical testing:

- Model discrimination / adequacy:

$$F_c = \frac{\sum_{I=1}^n \frac{\hat{y}_I^2}{p}}{\sum_{I=1}^n \frac{(y_I - \hat{y}_I)^2}{n-p}} ? F(p, n-p; 1-\alpha)$$

- Confidence intervals :

$$b_j - t\left(n-p; 1-\frac{\alpha}{2}\right)s(b_j) \leq \beta_j \leq b_j + t\left(n-p; 1-\frac{\alpha}{2}\right)s(b_j)$$

- t - value

$$t_c = \frac{|b_j - 0|}{s(b_j)}$$

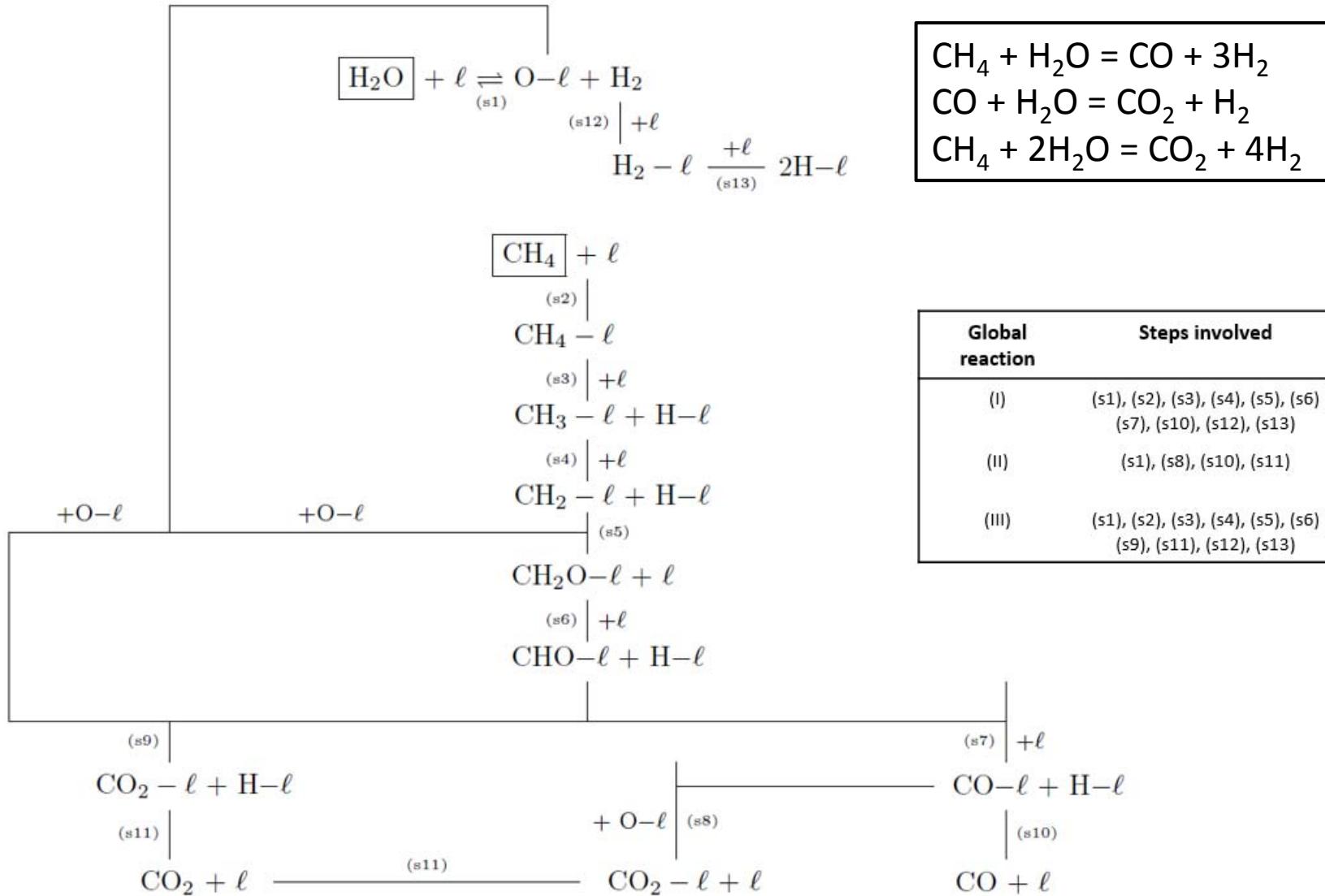
Physicochemical testing:

- $E_a > |\Delta H|$

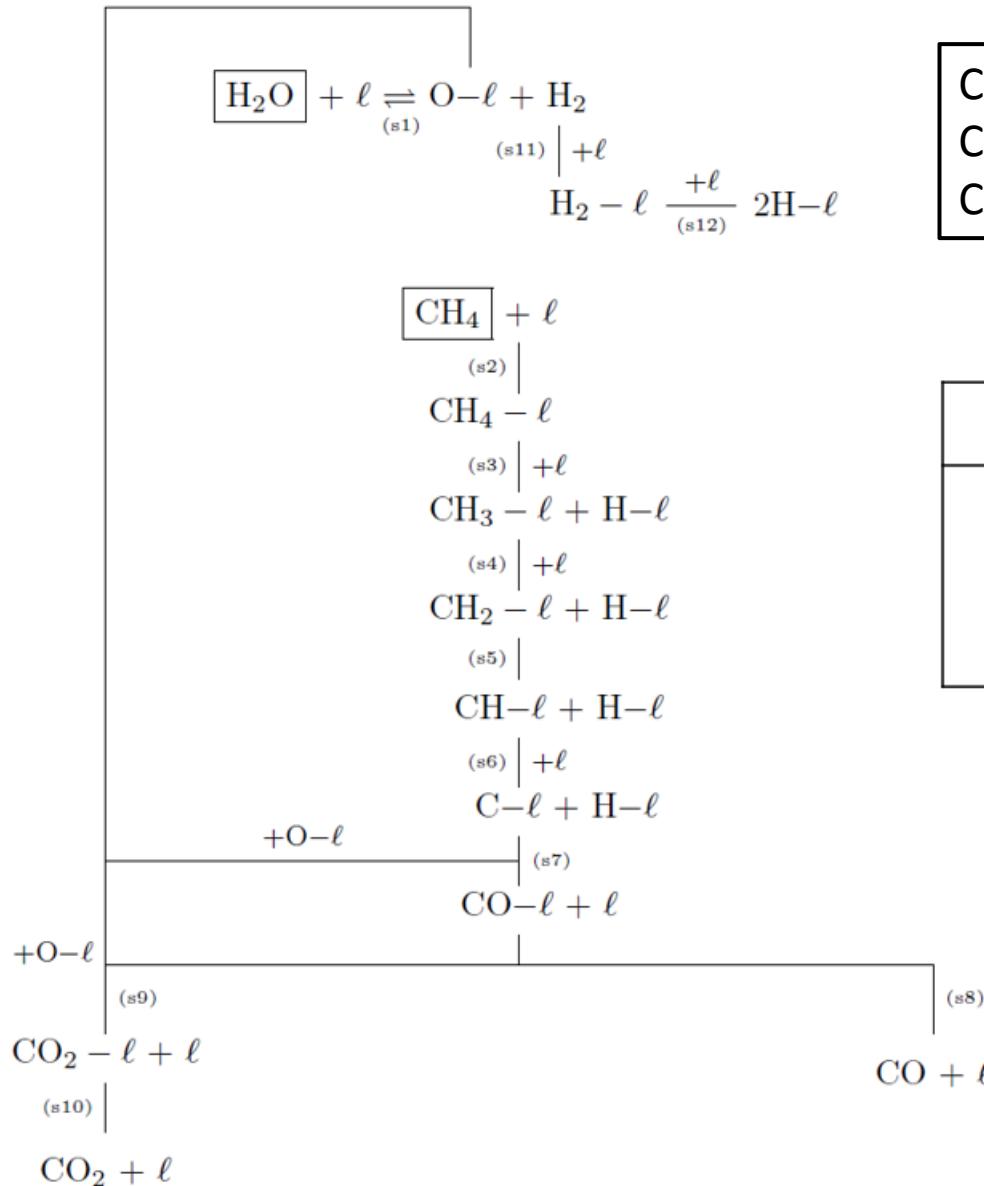
Kinetic modelling

T (°C)	$W/F_{CH_4}^0$ (g _{cat} .hr/mol)	S/C ratio	x_{CH_4} (%)	x_{CO_2} (%)	Approach to Equilibrium (%)
448	0.8025	3.44	0.37	0.37	5.30
449	0.6010	3.53	0.29	0.29	5.70
449	1.2067	3.54	0.40	0.40	5.88
512	1.1655	4.47	4.87	4.39	29.27
513	0.5850	3.04	1.95	1.63	15.03
513	1.1665	3.03	5.31	4.73	22.92
514	0.5850	3.04	1.21	0.98	8.09
546	1.2028	3.53	9.45	8.85	27.98
549	0.6026	3.54	6.69	6.15	28.27
549	0.8038	3.45	8.78	8.22	27.27
567	1.1678	2.89	15.04	12.50	34.75
574	1.1678	5.53	15.84	13.36	59.87
576	0.5850	2.87	8.66	6.57	30.69
601	0.6023	3.54	13.35	11.92	44.76
602	0.8039	3.45	16.78	15.20	45.68
602	1.2071	3.54	20.35	18.24	47.00

Kinetic modelling



Kinetic modelling



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

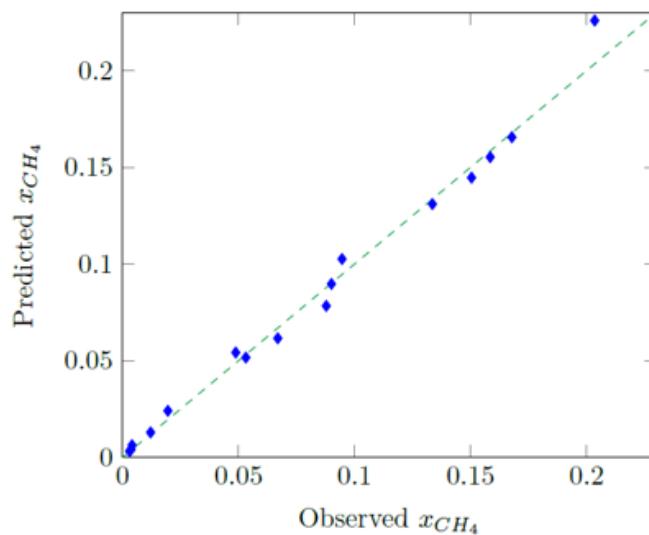
Kinetic modelling

Model	Mechanism	r.d.s. reaction (I)	r.d.s. reaction (III)	Physicochemical tests	F-value	R ²
1	1	(s1)	(s1)	Equation (6) not satisfied	150.7	0.935
2	1	(s2)	(s1)	Equation (6) not satisfied	352.7	0.959
3	1	(s3)	(s1)	Equation (6) not satisfied	182.7	0.959
4	1	(s6)	(s1)	Equation (6) not satisfied	627	0.984
5	1	(s7)	(s1)	Equations (6) and (7) not satisfied	646.4	0.984
6	1	(s10)	(s1)	Equation (6) not satisfied	305.9	0.967
7	1	(s1)	(s2)	Equations (6) and (7) not satisfied	292.5	0.949
8	1	(s2)	(s2)	Equation (6) not satisfied	268.3	0.962
9	1	(s3)	(s2)	Equations (6) and (7) not satisfied	182.7	0.96
10	1	(s6)	(s2)	Equations (6) and (7) not satisfied	204.7	0.964
11	1	(s7)	(s2)	Equations (6) and (7) not satisfied	203.7	0.964
12	1	(s10)	(s2)	Equation (6) not satisfied	306.6	0.975
13	1	(s1)	(s3)	Equation (6) not satisfied	228.1	0.956
14	1	(s2)	(s3)	Equations (6) and (7) not satisfied	252.4	0.961
15	1	(s3)	(s3)	OK	57.6	0.699
16	1	(s6)	(s3)	Equation (6) not satisfied	633.1	0.984
17	1	(s7)	(s3)	Equations (6) and (7) not satisfied	646.8	0.984
18	1	(s10)	(s3)	Equation (6) not satisfied	399.1	0.974
19	1	(s1)	(s6)	Equation (6) not satisfied	633	0.984
20	1	(s2)	(s6)	Equation (6) not satisfied	633	0.984
21	1	(s3)	(s6)	Equation (6) not satisfied	401.9	0.98
22	1	(s6)	(s6)	Equation (6) not satisfied	633.9	0.984
23	1	(s7)	(s6)	OK	661.4	0.984
24	1	(s10)	(s6)	Equation (6) not satisfied	633.1	0.984
25	1	(s1)	(s9)	Equations (6) and (7) not satisfied	365.9	0.972
26	1	(s2)	(s9)	Equations (6) and (7) not satisfied	329.9	0.977
27	1	(s3)	(s9)	OK	325.5	0.976
28	1	(s6)	(s9)	Equation (6) not satisfied	460.5	0.983
29	1	(s7)	(s9)	OK	447.8	0.977
30	1	(s10)	(s9)	Equation (7) not satisfied	295.1	0.974
31	2	(s2)	N.A.	Equation (6) not satisfied	106.4	0.731
32	2	(s3)	N.A.	Equations (6) and (7) not satisfied	397.2	0.962
33	2	(s7)	N.A.	OK	465.5	0.972
34	2	(s8)	N.A.	OK	343.3	0.947
35	Wei and Iglesia model (2004)	N.A.	N.A.	Equation (6) not satisfied	256.6	0.894

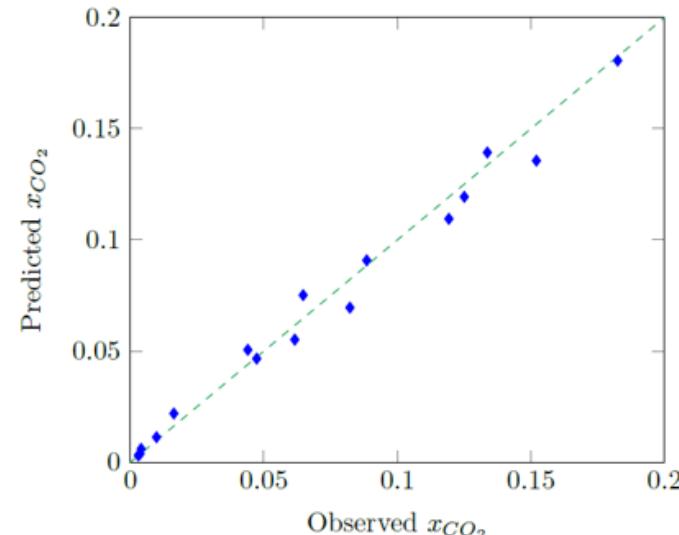
Kinetic modelling

Parameter	Value	Unit	t-value	95% Confidence intervals
$A(k_1)$	7.48×10^{12}	$mol \cdot bar^{1/2} / (kg_{cat} \cdot s)$	27.98	$7.48 \pm 0.54 (\times 10^{12})$
$A(k_2)$	5.43×10^5	$mol / (kg_{cat} \cdot s \cdot bar)$		Xu and Froment (1989)
$A(k_3)$	9.56×10^{11}	$mol \cdot bar^{1/2} / (kg_{cat} \cdot s)$	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		"

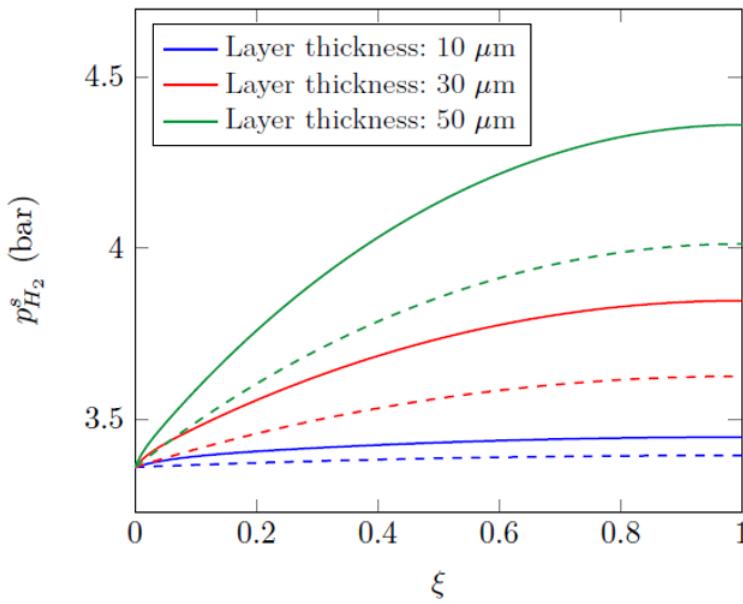
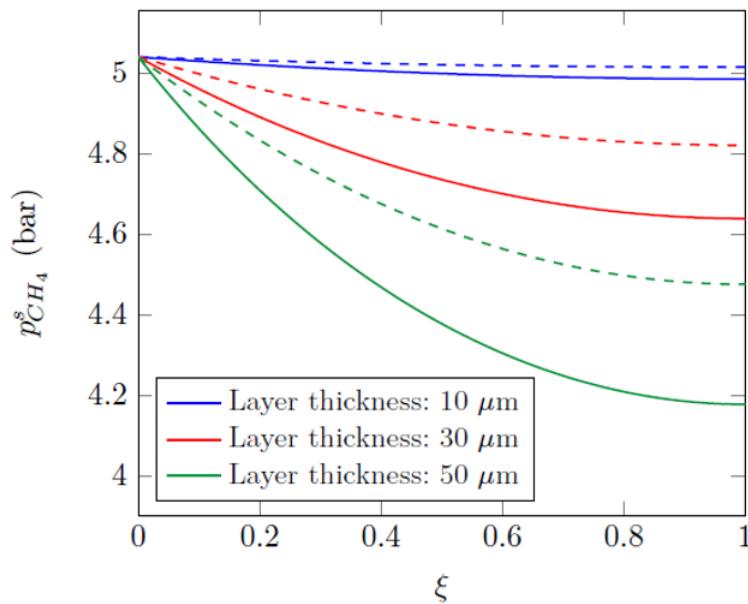
CH₄ molar conversion



CO₂ molar conversion



Intra-catalyst diffusion-reaction modelling



Layer thickness	Model A		Model B	
	η_I	η_{III}	η_I	η_{III}
10 μm	0.959	0.909	0.995	0.998
30 μm	0.784	0.620	0.954	0.978
50 μm	0.606	0.454	0.884	0.937

Computational Fluid Dynamics

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

Species A:

$$\nabla \cdot (\rho m_A \bar{u}) = \nabla \cdot (D_{A\text{m,eff}} \nabla m_A)$$

Total mass:

$$\nabla \cdot (\rho \bar{u}) = 0$$

Momentum:

$$\nabla \cdot (\rho \bar{u} \bar{u}) = -\nabla P_{\text{eff}} + \nabla \cdot (\bar{\sigma}_{\text{eff}}) + \bar{b}$$

Energy:

$$\nabla \cdot (\rho E \bar{u}) = -\nabla \cdot (\bar{u} P_{\text{eff}}) + \nabla \cdot (\bar{\sigma}_{\text{eff}} \cdot \bar{u}) + \nabla \cdot (\lambda_{f,\text{eff}} \nabla T) + Q_{\text{rad}} - \nabla \cdot \left(\sum_i h_i J_i \right)$$

+ Standard k- ϵ turbulence model

(De Wilde & Froment, 2012)

Computational Fluid Dynamics

- 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:

$$\begin{aligned}\tilde{k}_{g,A} (m_{As}^s - m_A) &= \rho_s d M_A \sum_k \alpha_{A,k} \eta_k r_k (\bar{m}_s^s, T_s) \\ &= (1 - \varepsilon) \rho_s M_A \sum_k \alpha_{A,k} \eta_k r_k (\bar{m}_s^s, T_s) / a_v\end{aligned}$$

$$\begin{aligned}h_f (T_s - T) &= \rho_s d \sum_k \eta_k r_k (\bar{m}_s^s, T_s) (-\Delta H_k) \\ &= (1 - \varepsilon) \rho_s \sum_k \eta_k r_k (\bar{m}_s^s, T_s) (-\Delta H_k) / a_v\end{aligned}$$

Heated wall:

$$Q_{hw} = h_{f,hw} (T_{hw,i} - T) + Q_{rad}$$

(Jayatilleke, 1969)

Coupled Flow-Reaction Simulation

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

Methane steam reforming:



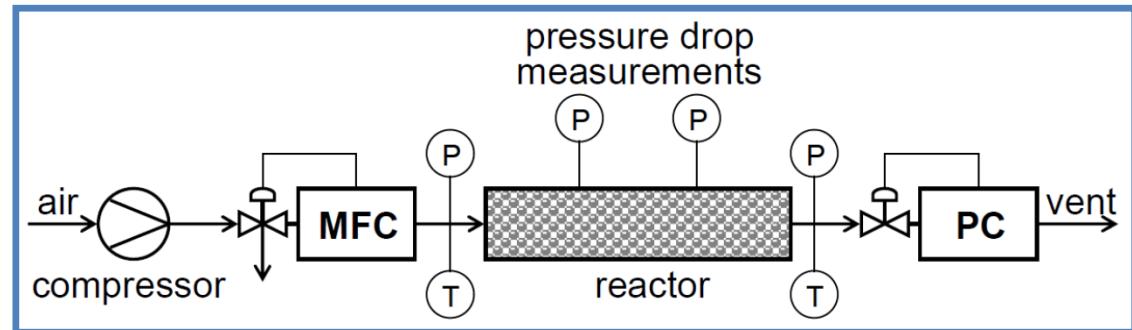
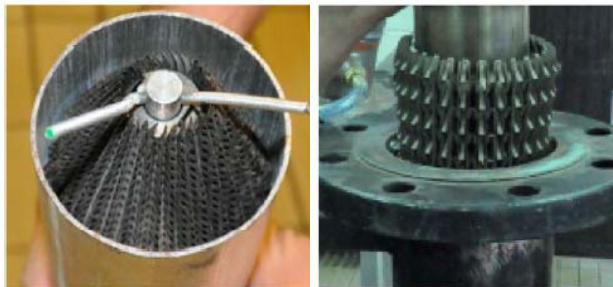
Coke formation and gasification:



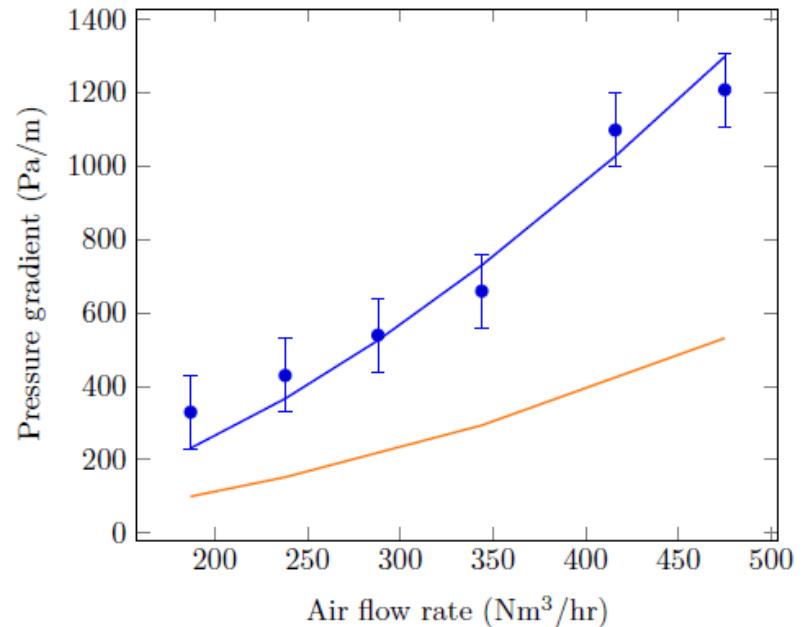
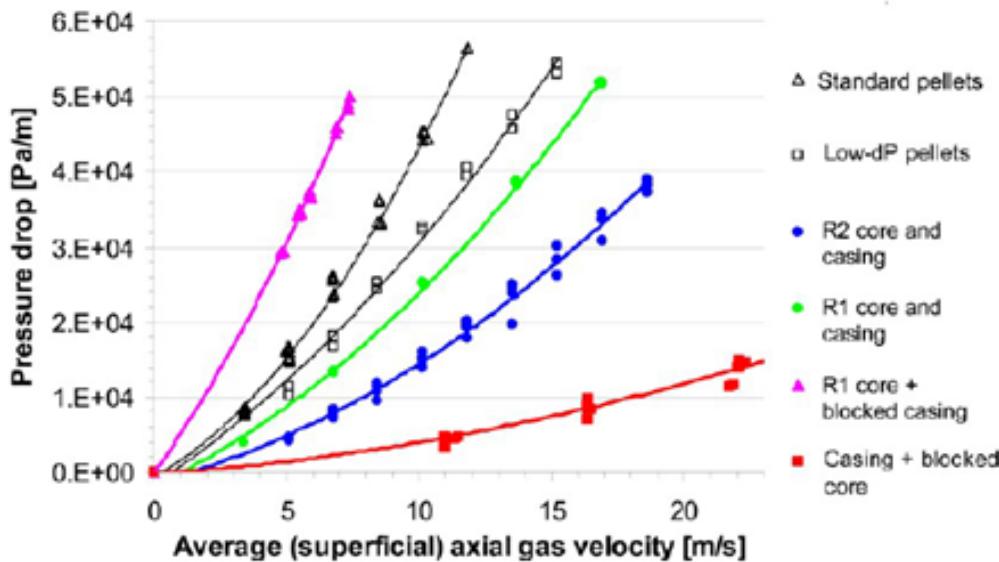
(Xu & Froment, 1989; Snoeck & Froment, 2002)

Computational Fluid Dynamics

Cold flow pilot plant



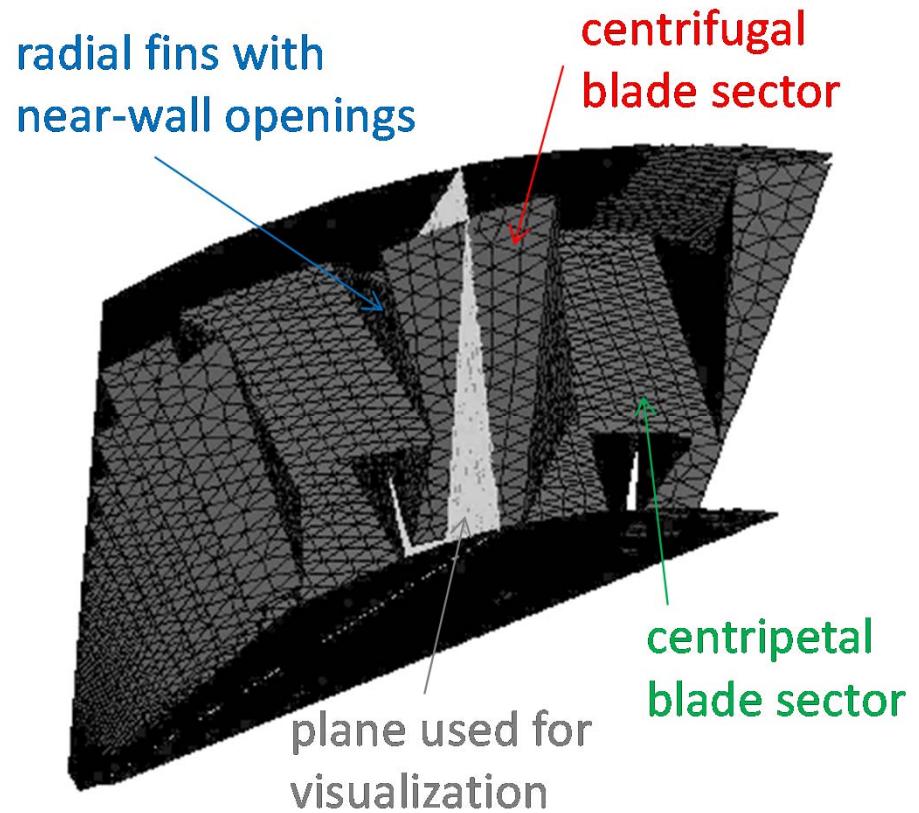
Turbulence model (parameters)



(De Wilde & Froment, 2013)

Computational Fluid Dynamics

Hot & Reactive flow pilot plant



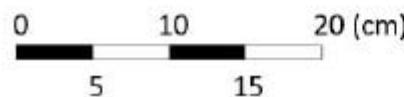
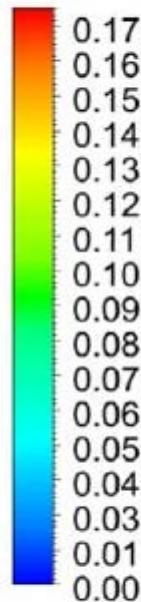
Interfacial mass & heat transfer (parameters)
& Radiative heat transfer & Model validation

Computational Fluid Dynamics

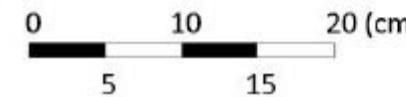
Reactive flow pilot plant

SV = 1,198. Nm³/h/m³

CH₄ mass fraction



CH₄ mass fraction



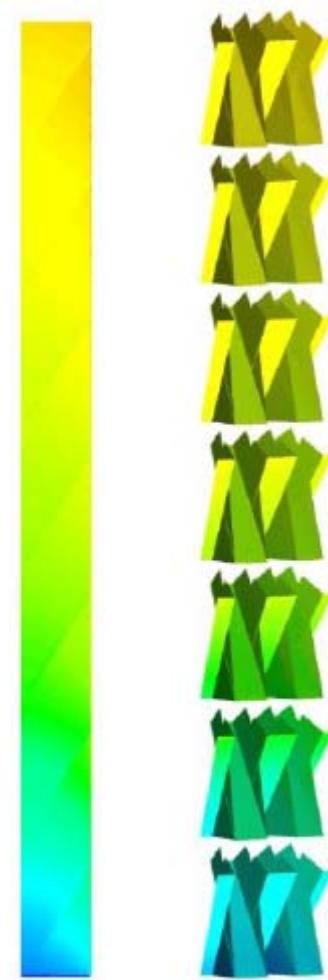
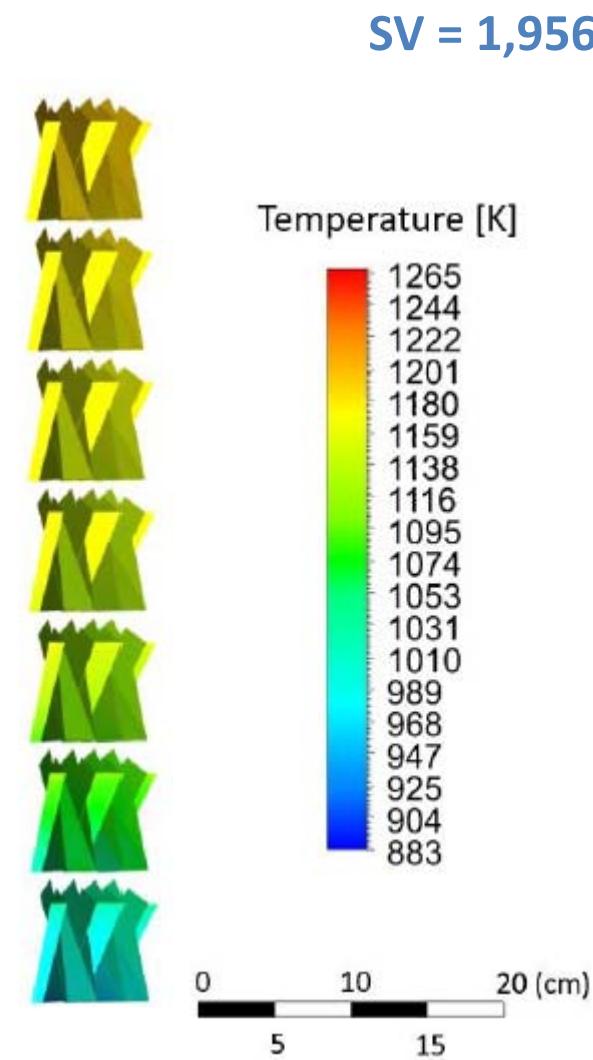
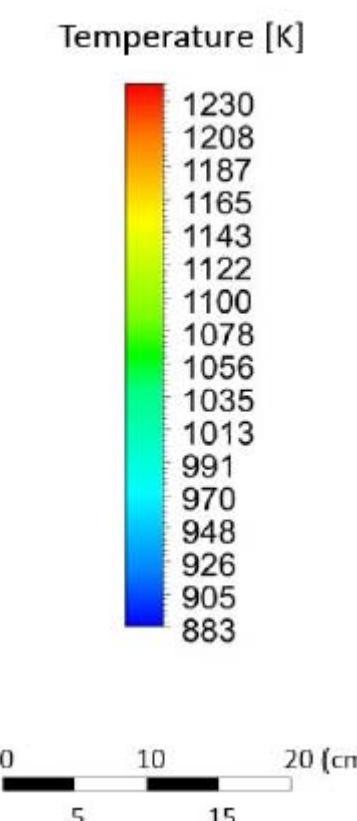
SV = 1,956. Nm³/h/m³



Computational Fluid Dynamics

Reactive flow pilot plant

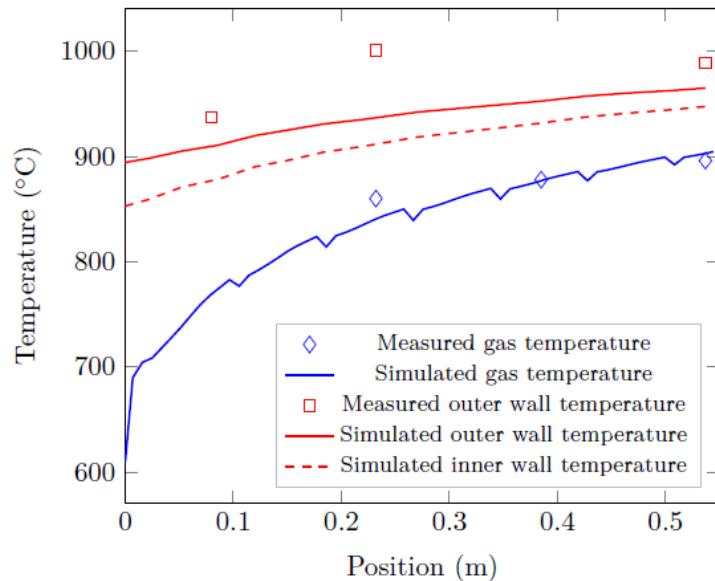
SV = 1,198. Nm³/h/m³



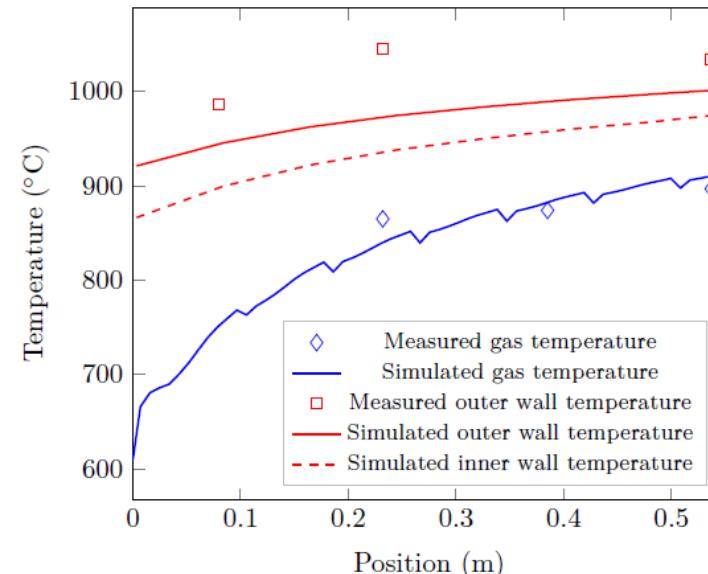
Computational Fluid Dynamics

Reactive flow pilot plant

$SV = 1,198. \text{ Nm}^3/\text{h/m}^3$



$SV = 1,956. \text{ Nm}^3/\text{h/m}^3$

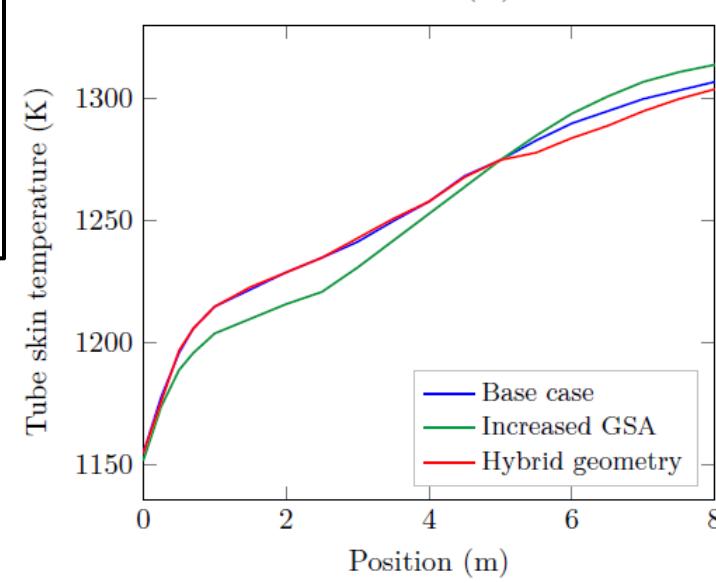
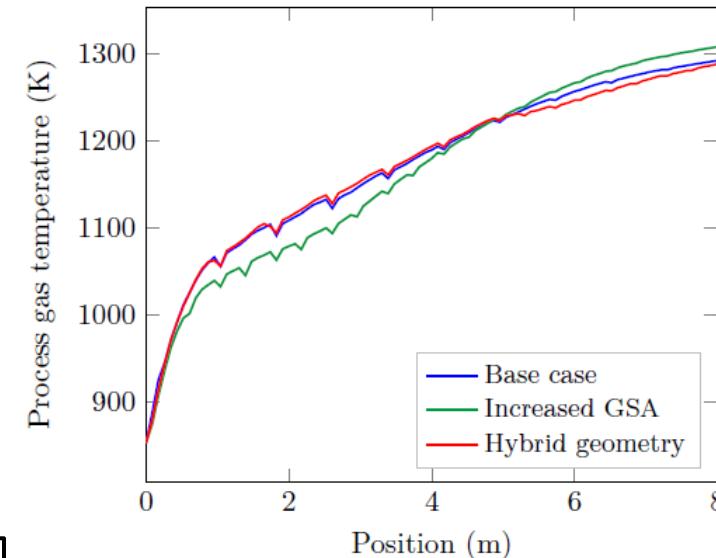
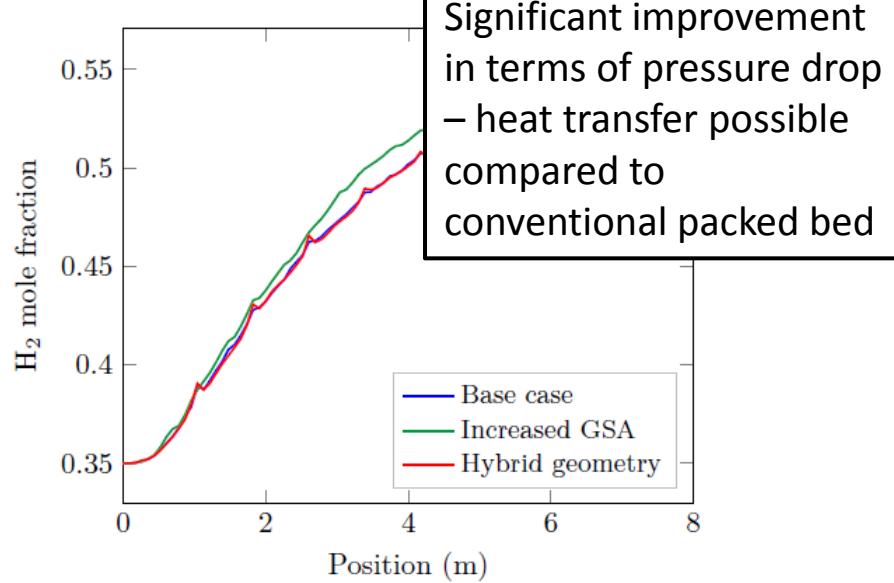
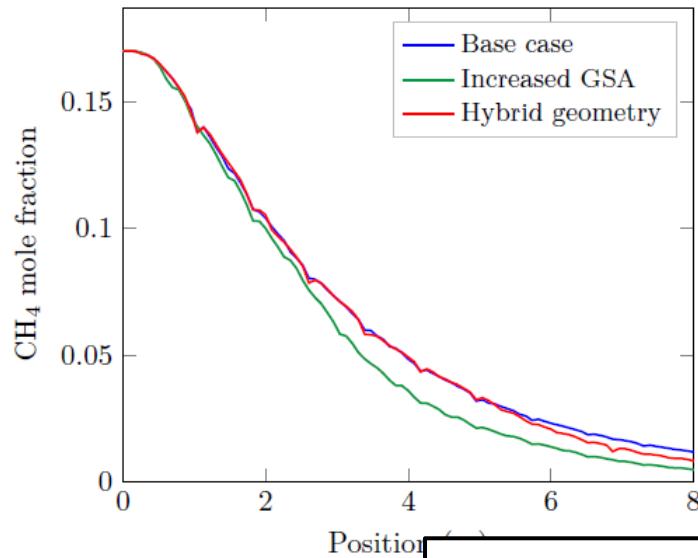


	Measured Mol%, Dry	Simulated Mol%, Dry
CH_4	10.23	9.85
H_2	48.34	49.54
CO_2	8.73	8.64
CO	28.92	28.76
N_2	3.47	3.21

	Measured Mol%, Dry	Simulated Mol%, Dry
CH_4	11.76	11.70
H_2	47.23	47.35
CO_2	10.37	10.14
CO	26.93	26.89
N_2	3.71	3.92

Computational Fluid Dynamics

Commercial scale & optimization



New SMR pilot plant at IMAP with ZoneFlow Reactor Technologies, LLC



Conclusions

- Scale-up and optimization of reactors and processes facilitated by detailed modelling and simulation
- Multi-scale approach and scale-bridging strategies required
- Different aspects to be studied separately with specifically designed equipments
- Fundamental approach feasible with modern computational power
- Approach used to study scale-up and optimization of the promising structured reactor for Steam Methane Reforming of ZoneFlow Reactor Technologies, LLC