A “Pas de Deux” of methane: Chemical Engineering and Catalysis

G.B. Marin

Laboratory for Chemical Technology

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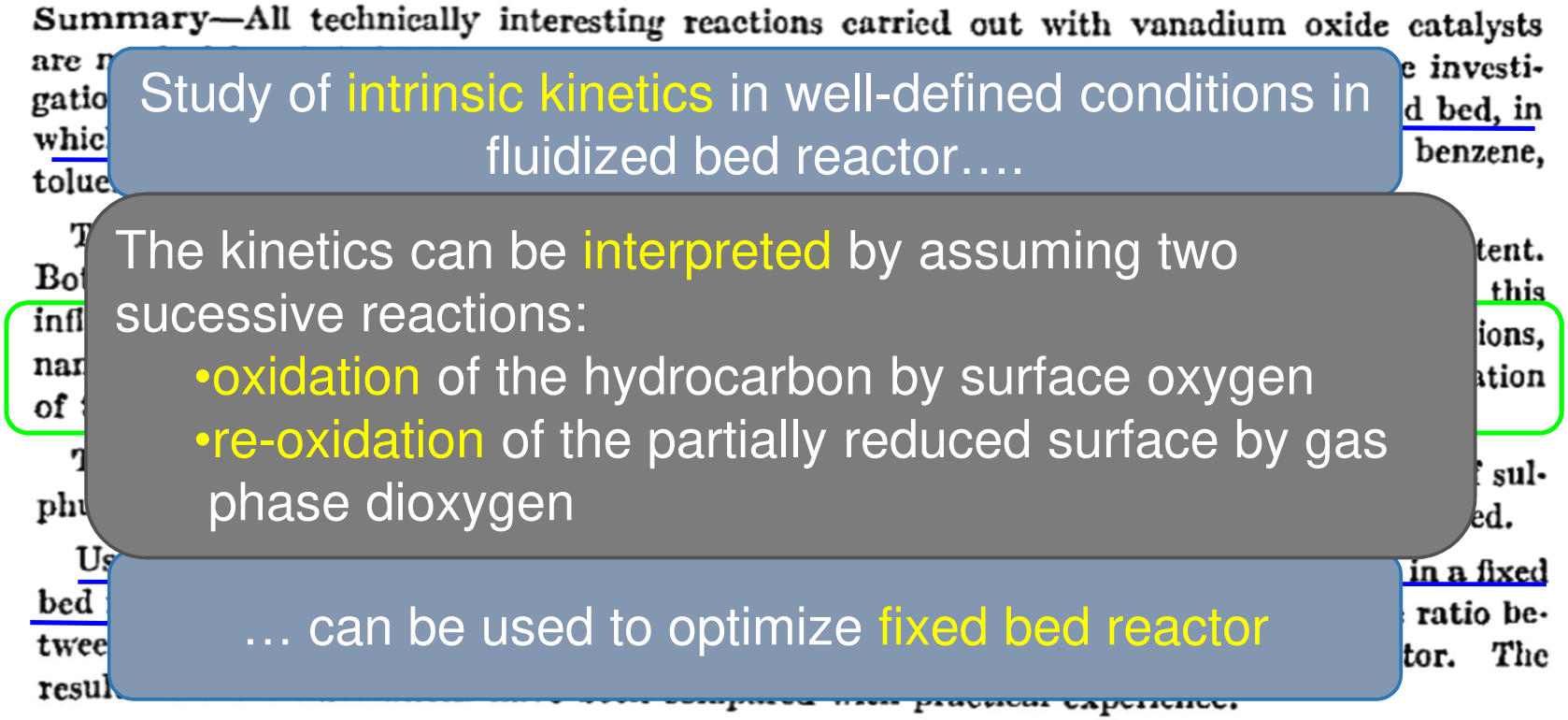
CSC Centre for Sustainable Chemistry

ENERGY X

ERIC European Research Institute of Catalysis

M2D2R2C

Chemical Engineering and Catalysis



Summary—All technically interesting reactions carried out with vanadium oxide catalysts

Study of intrinsic kinetics in well-defined conditions in fluidized bed reactor….

The kinetics can be interpreted by assuming two sucessive reactions:

- oxidation of the hydrocarbon by surface oxygen
- re-oxidation of the partially reduced surface by gas phase dioxygen

… can be used to optimize fixed bed reactor

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Mars - van Krevelen mechanism

Special Suppplement to Chemical Engineering Science, vol. 3, 1954.

Oxidations carried out by means of vanadium oxide catalysts

P. MARS and D. W. VAN KREVELEN

Staatsmijnen in Limburg, Central Laboratory, Geleen, Netherlands

Figure 1 Diagram of apparatus

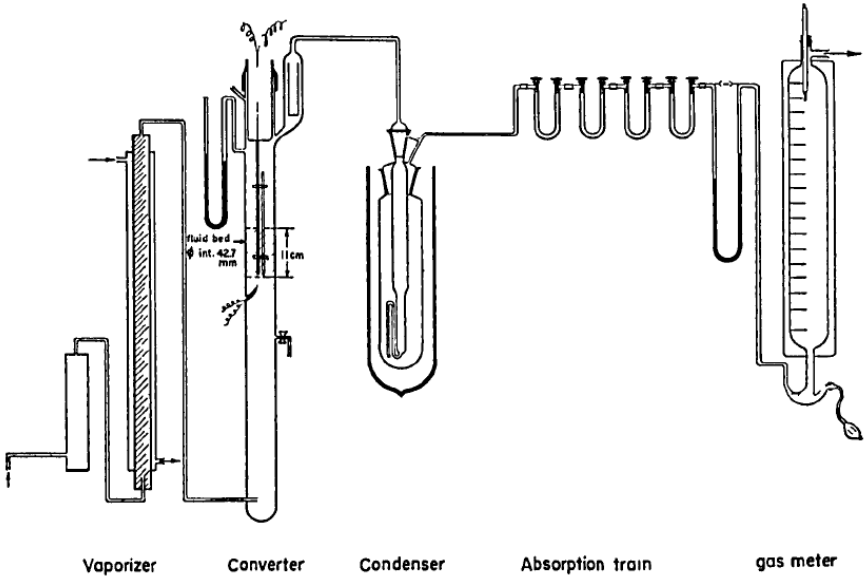
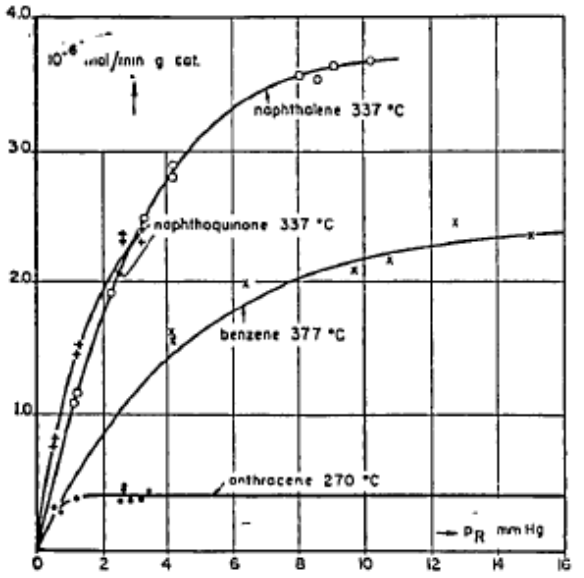
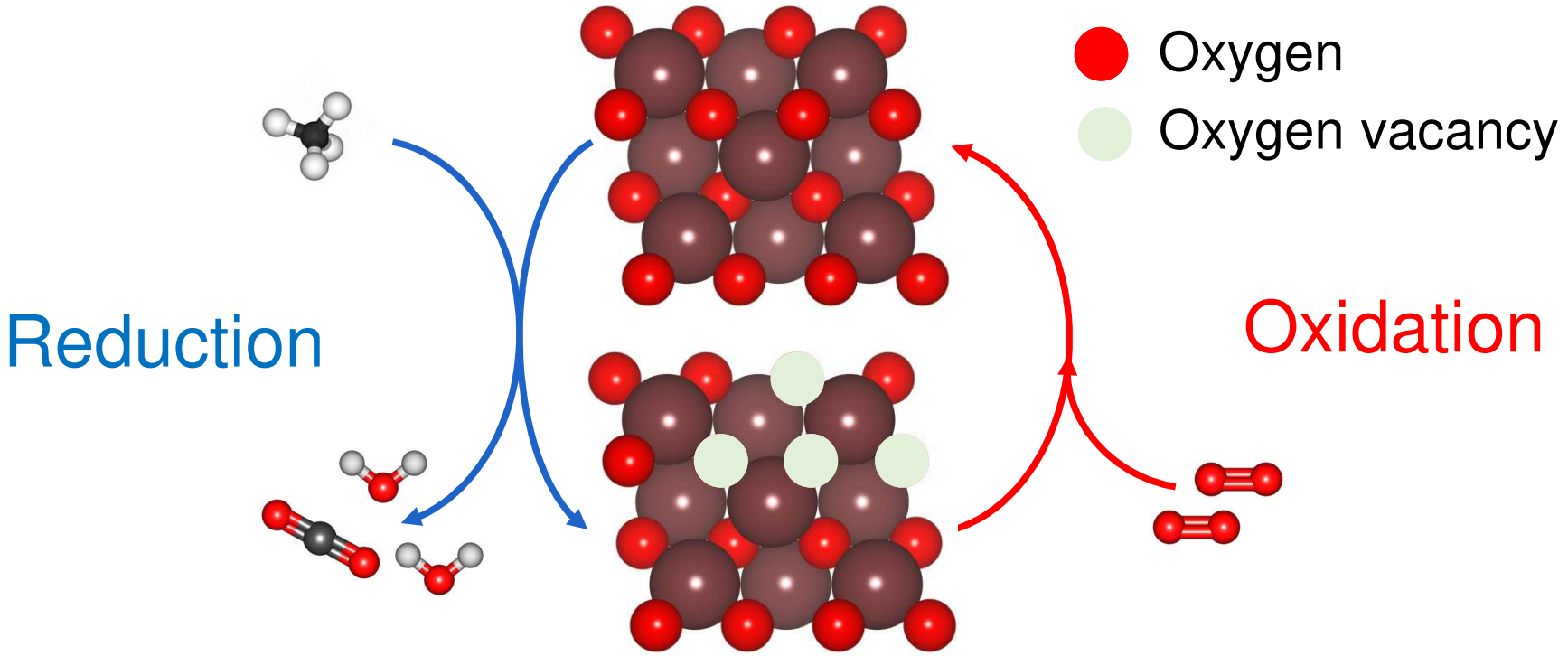


Figure 2 Conversion as a function of partial pressure of the reactant.



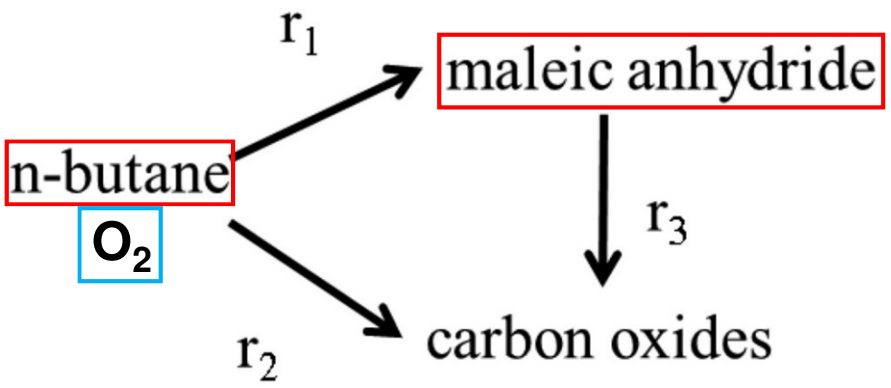
Redox cycle: ab initio calculations and in situ characterization

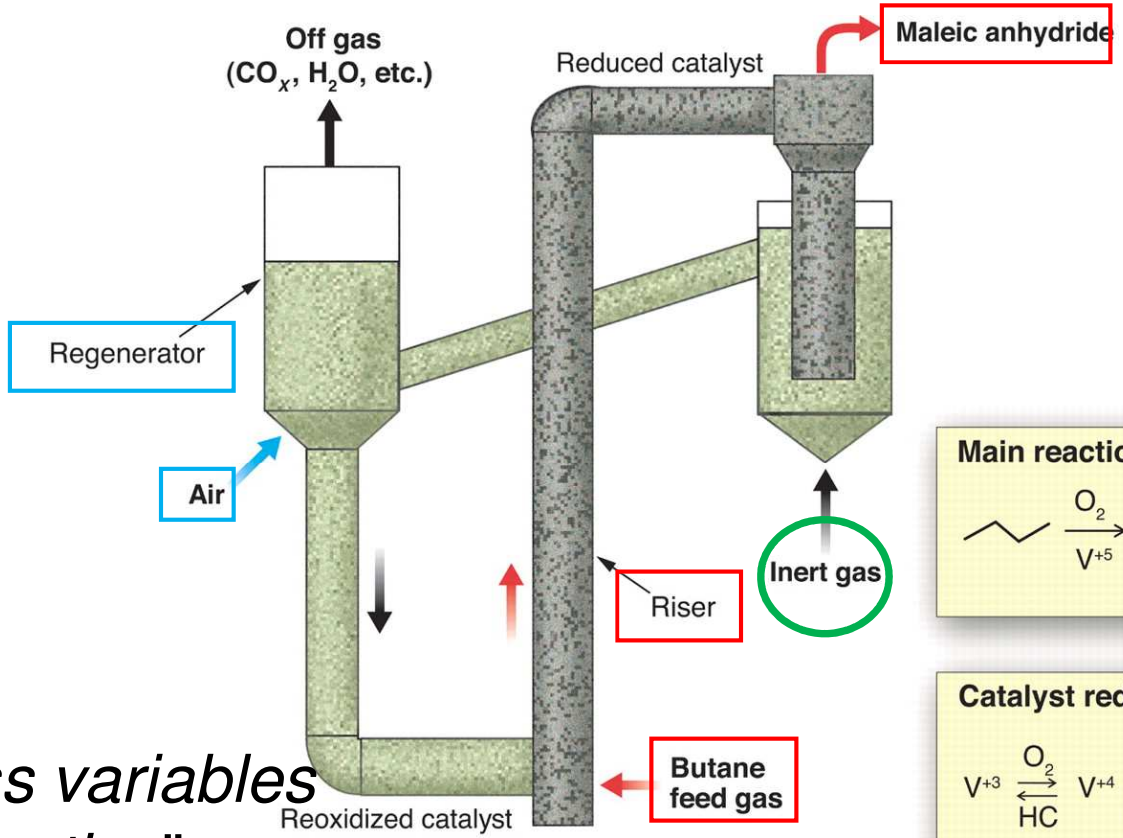


+ Diffusion of lattice oxygen from bulk to surface

Nibbelke R.H. et al., J. Catal. 1995, 156, 106 Menon U. et al., J. Catal., 2011 283,1
Alexopoulos K. et al., Appl. Catal. B 2010, 97, 381
Mathias F. et al., Angew. Chem. Int. Ed. 2018, 57 (38), 12430;
Angew. Chem. Int. Ed. 2019, 58, 2

Selective n-butane oxidation to maleic anhydride





"*independent control of the process variables for the two steps of the redox operation*"

Circulating Fluid Bed

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Rashmi M. Contractor CES vol. 54 (1999) 5627-5632 : Dupont's CFB technology for maleic anhydride

Milorad P. Dudukovic, Science 325 (2009) 698-701: Frontiers in reactor engineering

Catalytic vs Cyclic/Chemical Looping process

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

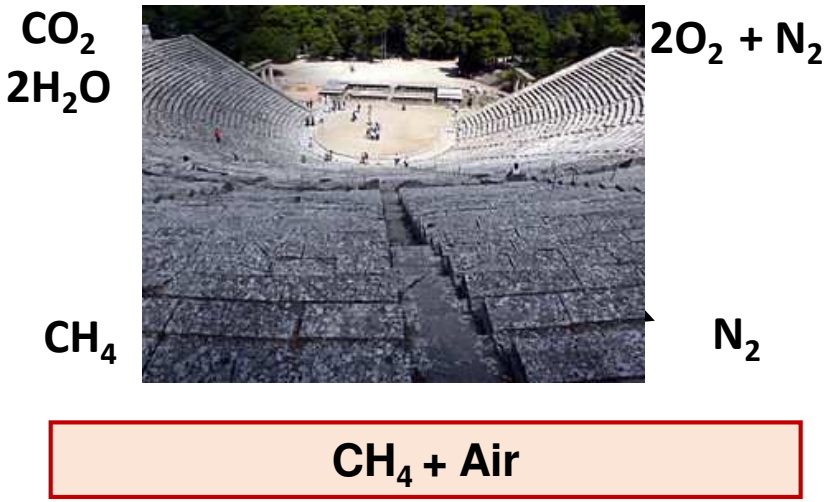
Catalytic process

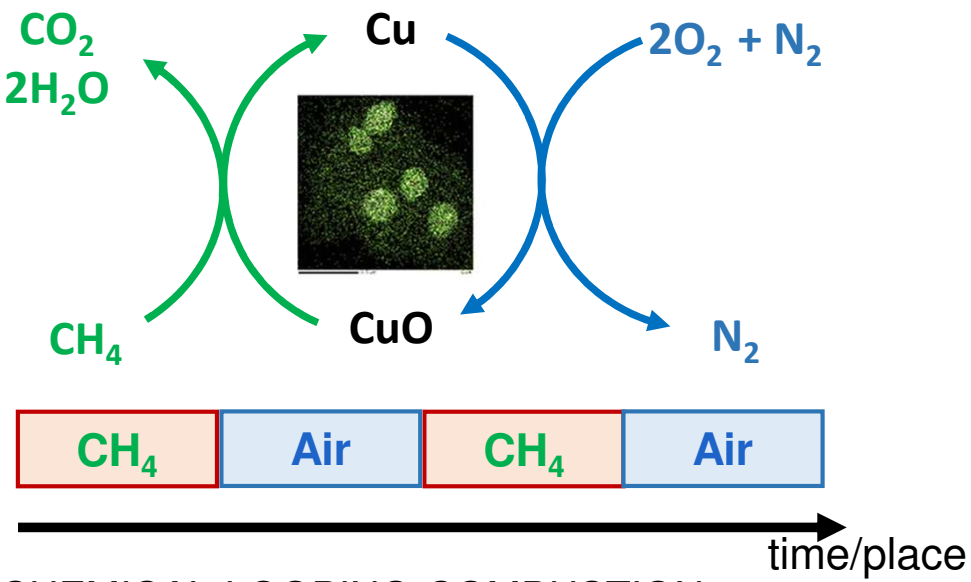
Single set of conditions

Chemical looping process

Different sets of conditions

e.g. Mars - van Krevelen mechanism





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Ishida M. et al.,"Evaluation of a CHEMICAL-LOOPING-COMBUSTION power generation system by graphic exergy analysis" Energy, 12 (1987),147

Chemical Looping allows to:

- ✓ improve selectivity
- ✓ operate safely “within” explosion limits
- ✓ combine reaction and separation
- use cheap materials (CaO, FeO_x, …)
- circumvent equilibrium limitations
- mitigate carbon formation
- optimize heat management
- minimize exergy loss
- …

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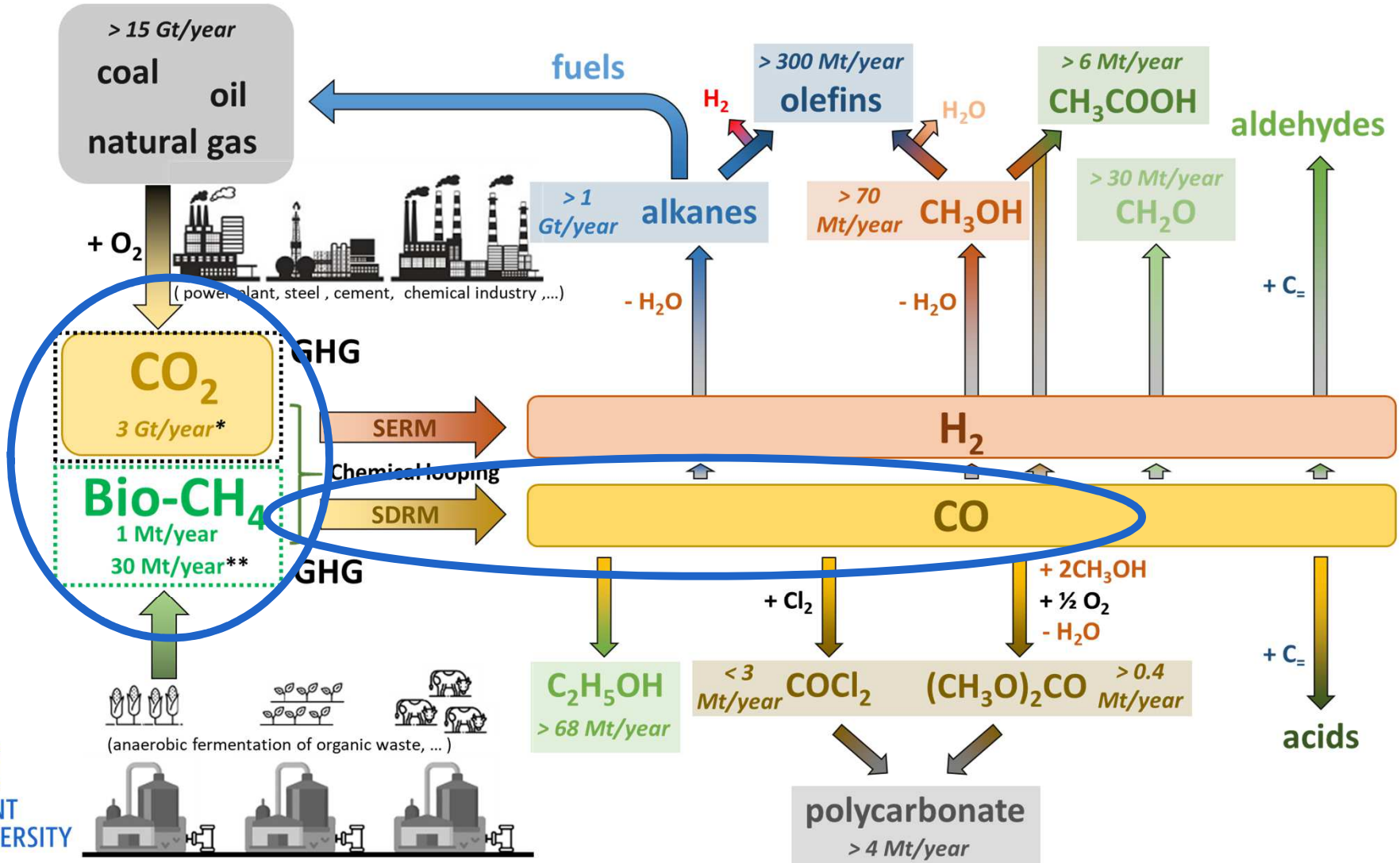
A “Pas de Deux” of methane: CO_2 utilization



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K. Verbeeck, L. Buelens et al., Energy & Environmental Science 11 (2018) 1788-1802 (DOI: 10.1039/C8EE01059E)

Outline

- Introduction
- Super Dry Reforming
- Oxidative coupling
- Conclusions and Perspectives

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Super dry reforming of CH_4

$$3CO_2 + CH_4 \rightarrow 4CO + 2H_2O$$

Water Gas Shift $2CO + 2H_2O \rightarrow 2CO_2 + 2H_2$

Dry reforming $CO_2 + CH_4 \rightarrow 2CO + 2H_2$

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L. Buelens et al., Science 354 (2016) 449

Chemical Looping: super dry reforming of CH_4

$$3CO_2 + CH_4 \rightarrow 4CO + 2H_2O$$

1: $CH_4 + 3CO_2 + Fe_3O_4 + 4CaO \rightleftarrows 2H_2O + 3Fe + 4CaCO_3$

$\Delta_r H^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)	$\Delta_r G^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)
-103	-32

2: $inert + 4CaCO_3 + 3Fe \rightleftarrows 4CaO + Fe_3O_4 + 4CO + inert$

$\Delta_r H^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)	$\Delta_r G^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)
+212	+24

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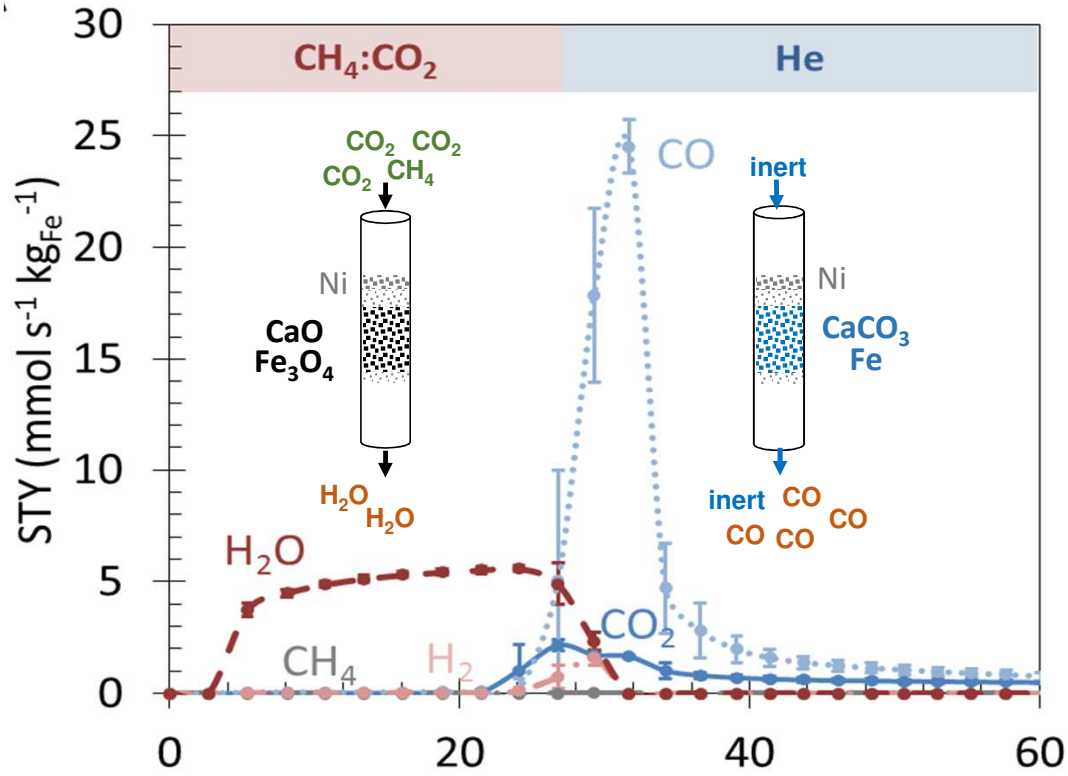
✓ Cheap materials

L. Buelens et al., Science 354 (2016) 449

T = 1023 K

Fixed bed: Permanent periodic regime

T=1023 K; CH_4:CO_2 = 1:3; after 25 cycles



Fe_3O_4: Oxygen carrier/Storage Material (OSM)

CaO : CO_2 sorbent

Ni : reforming catalyst

L. Buelens et al., Science 354 (2016) 449

Super dry reforming of CH_4

→ Step 1: $CH_4 + 3CO_2 + Fe_3O_4 + 4CaO \rightleftarrows 2H_2O + 3Fe + 4CaCO_3$

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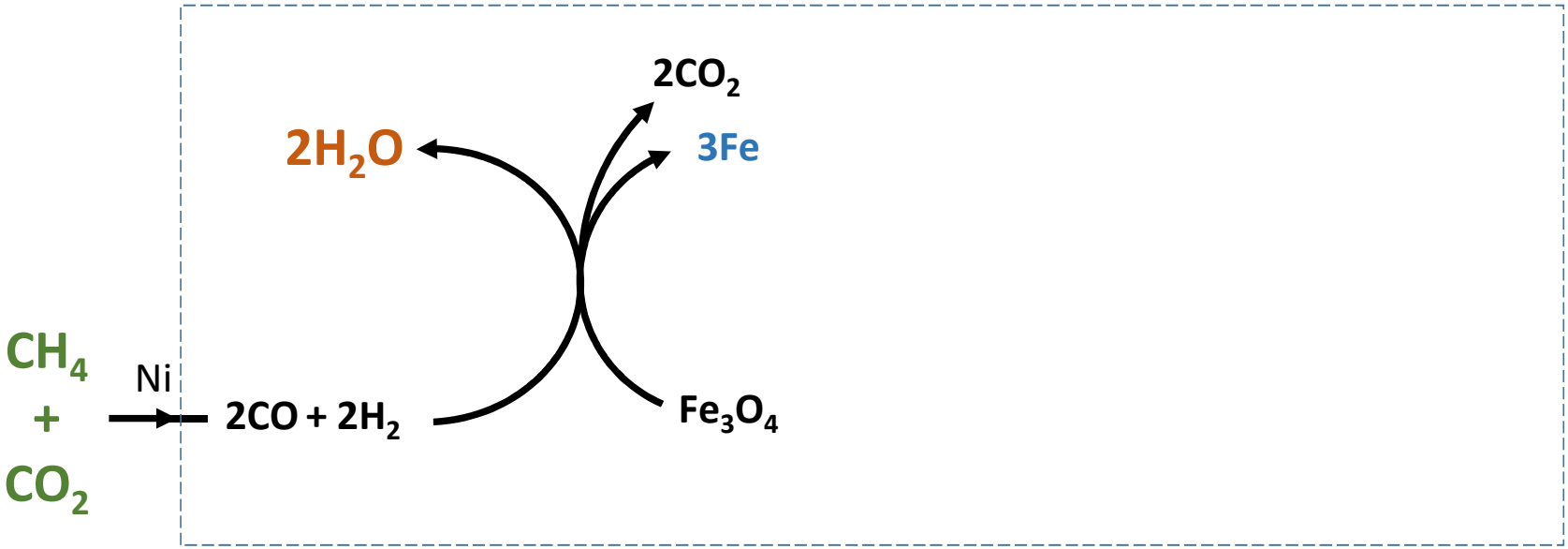

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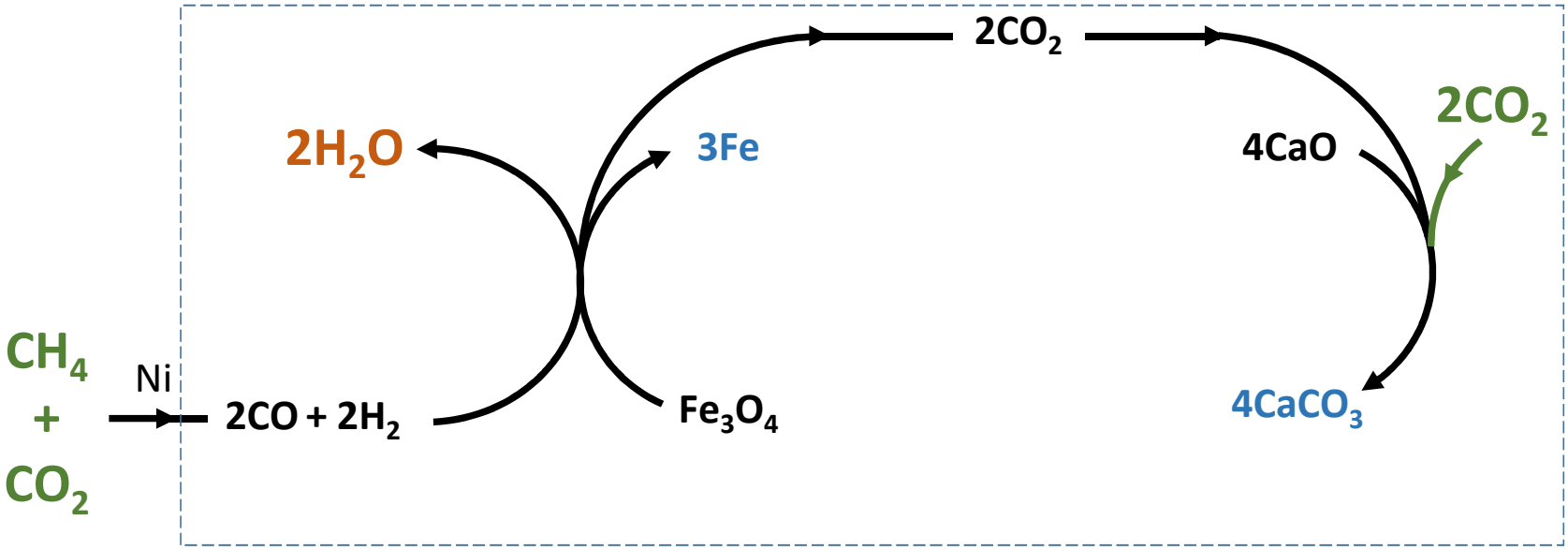

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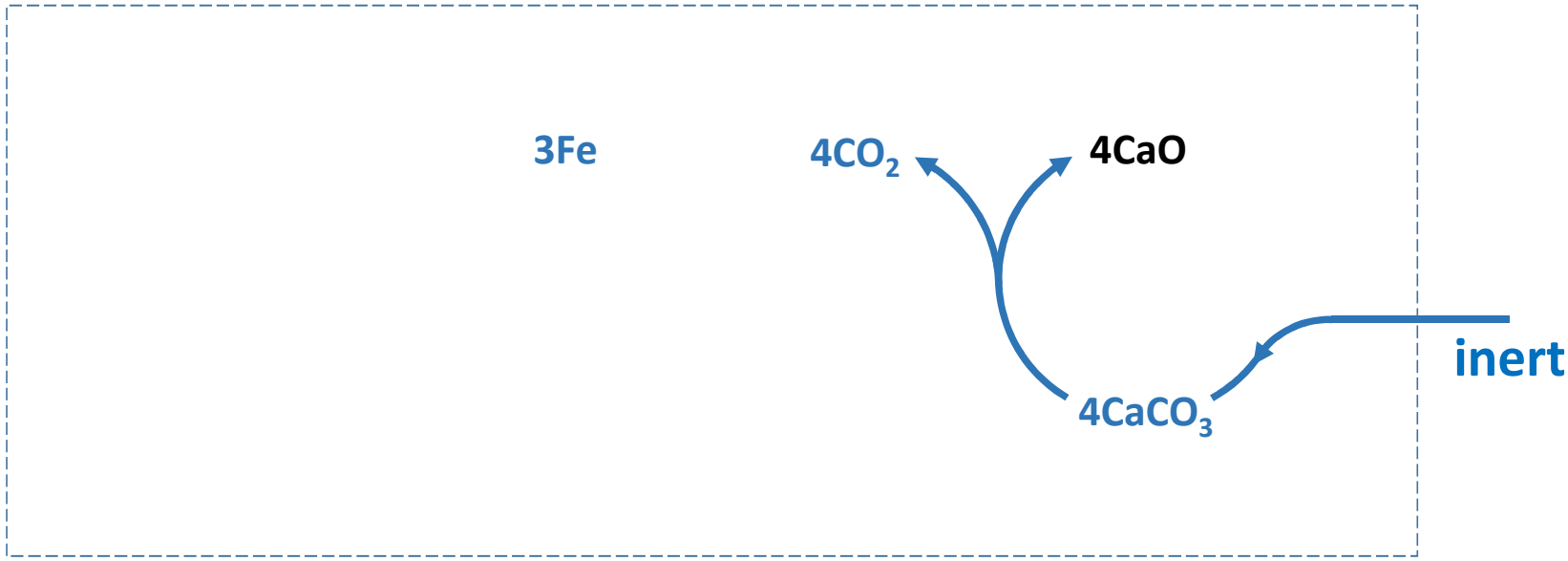
L. Buelens et al., Science 354 (2016) 449

Super dry reforming of CH_4

→ Step 1: $CH_4 + 3CO_2 + Fe_3O_4 + 4CaO \rightleftarrows 2H_2O + 3Fe + 4CaCO_3$

→ Step 2: inert + $4CaCO_3 + 3Fe \rightleftarrows 4CaO + Fe_3O_4 + 4CO$ + inert

$\Delta_r H^\circ_{1023K}$ ($kJ\ mol^{-1}_{CO_2}$)	$\Delta_r G^\circ_{1023K}$ ($kJ\ mol^{-1}_{CO_2}$)
-103	-32
+212	+24



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L. Buelens et al., Science 354 (2016) 449

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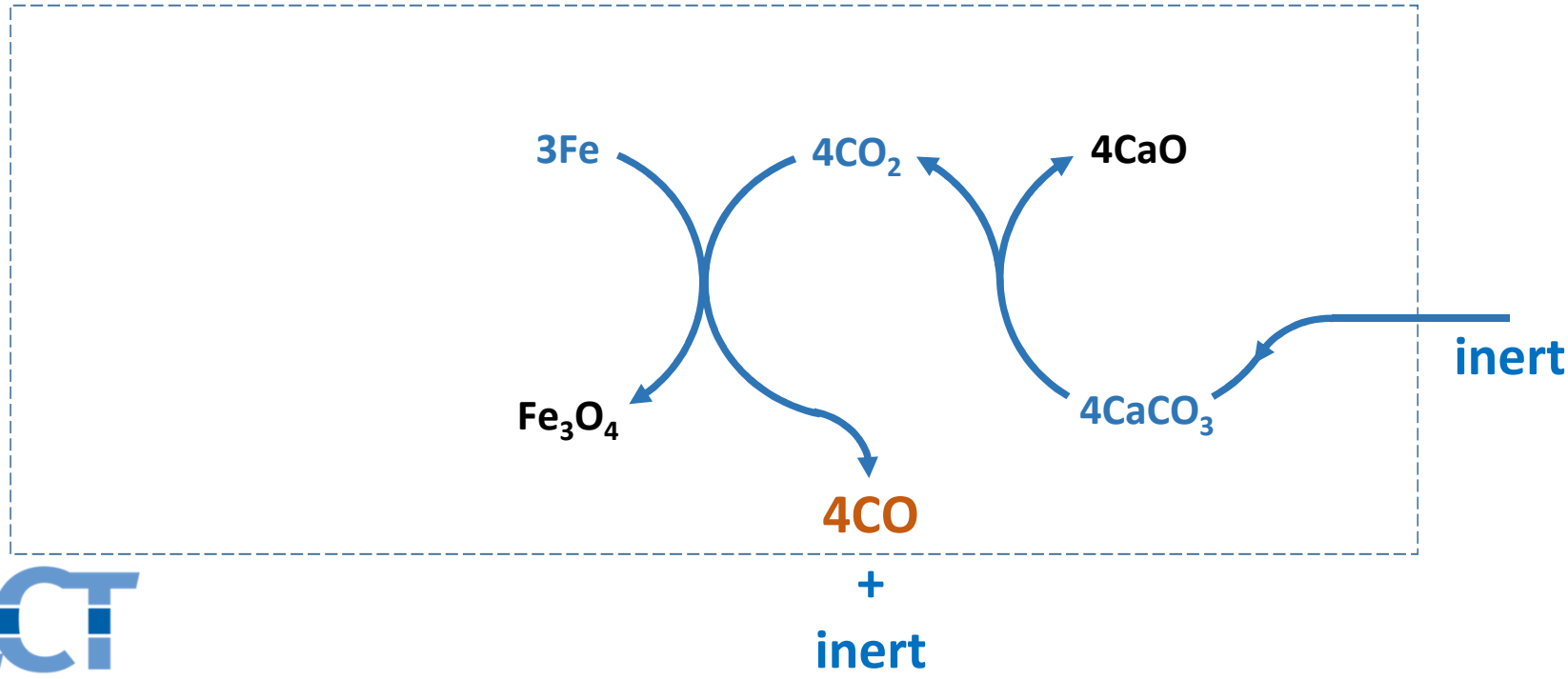

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L. Buelens et al., Science 354 (2016) 449

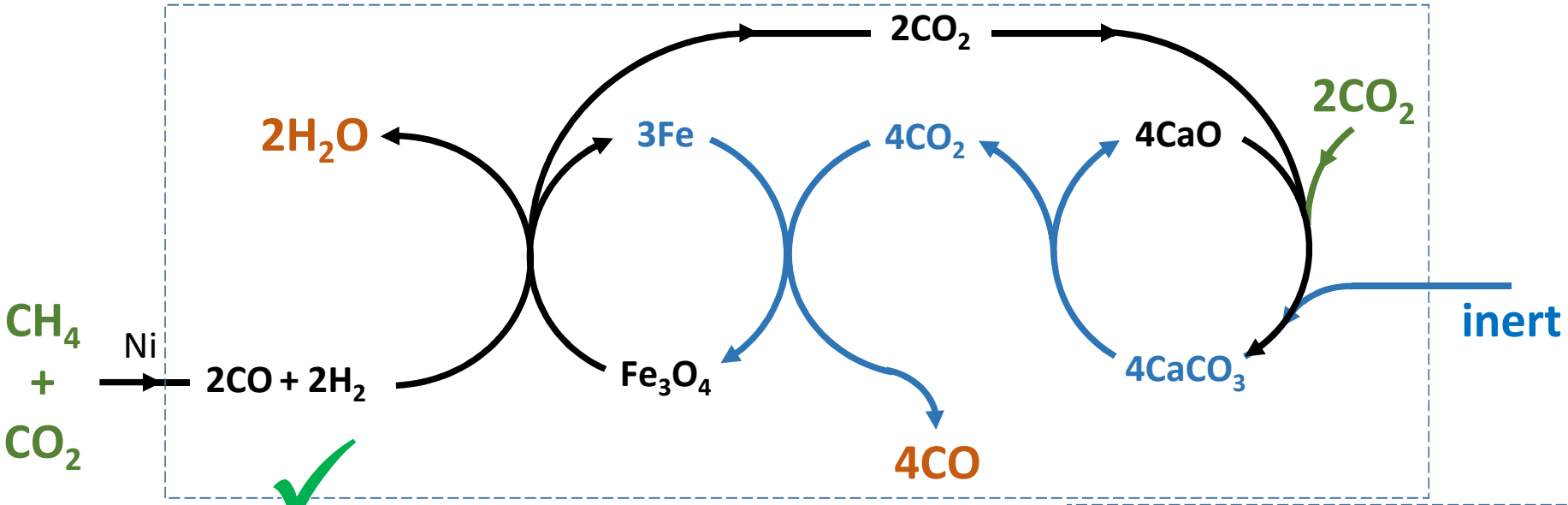
Super dry reforming of CH_4

→ Step 1: $CH_4 + 3CO_2 + Fe_3O_4 + 4CaO \rightleftarrows 2H_2O + 3Fe + 4CaCO_3$

→ Step 2: inert + $4CaCO_3$ + 3Fe ⇄ 4CaO + Fe_3O_4 + 4CO + inert

$CH_4 + 3CO_2$ + inert ⇄ $4CO + 2H_2O$ + inert

$\Delta_r H^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)	$\Delta_r G^\circ_{1023K}$ (kJ $mol^{-1}_{CO_2}$)
-103	-32.4
+212	+23.8
+109	-8.6



Circumvent equilibrium limitations + inert

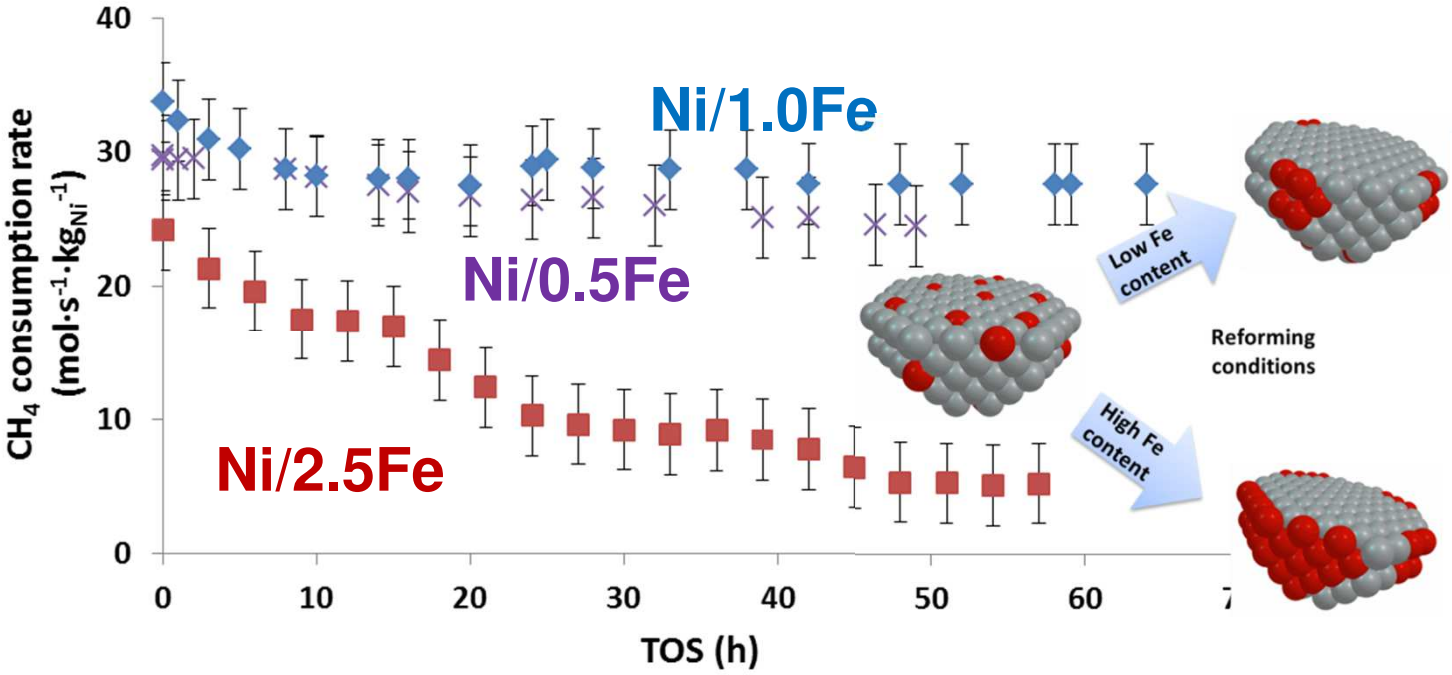
RWGS: $2H_2 + 2CO_2 \rightleftarrows 2H_2O + 2CO$

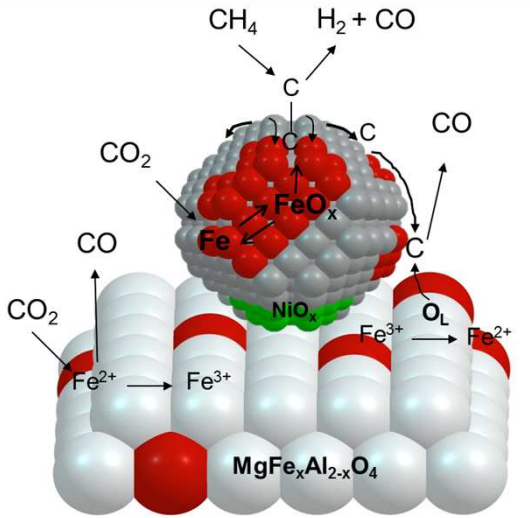
L. Buelens et al., Science 354 (2016) 449

Catalyst: $Ni/MgFe_xAl_{2-x}O_4$ versus $Ni\text{-}Fe/MgAl_2O_4$

$T=1023$ K, $W_{Ni}/F^0_{CH4} = 0.023\text{-}0.025\ kg_{Ni}\ s\ mol^{-1}_{CH4}$

Fe from support	TOS [h]	Deposited carbon [$mol_C\ kg_{cat}^{-1}$]
Ni/0Fe	12	$1.1 \cdot 10^3$
Ni/0.5Fe	49	Under detection limit

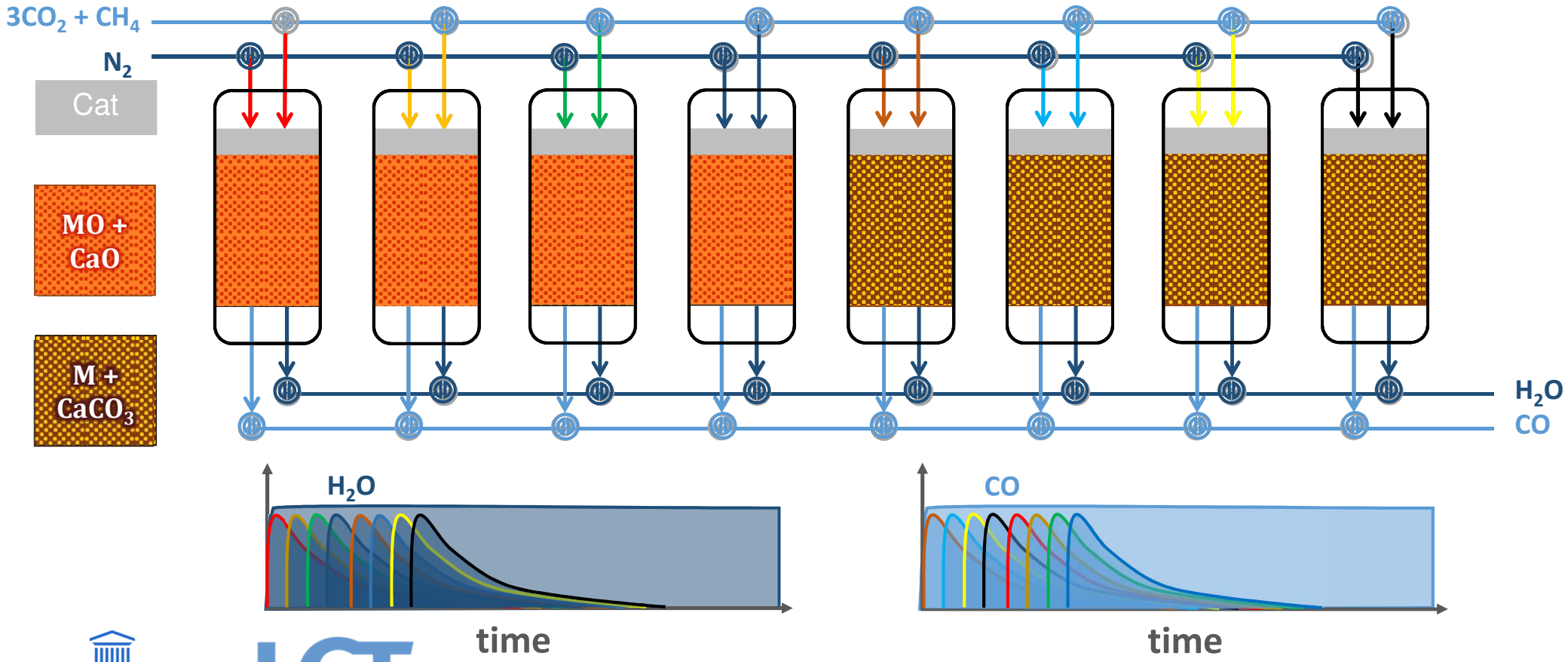




✓ Mitigate carbon formation

S.A. Theofanidis et al., ACS Catalysis 8 (2018) 5983

Permanent periodic regime: simulated moving bed



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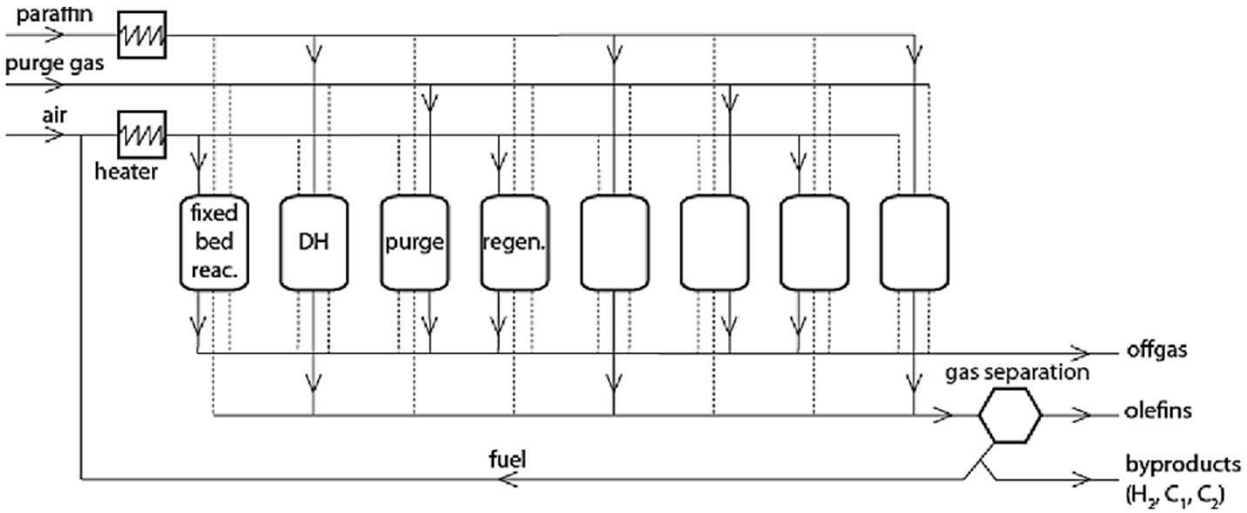
Industrial processes with similar technology

CATOFIN dehydrogenation unit



Cr_2O_3/Alumina

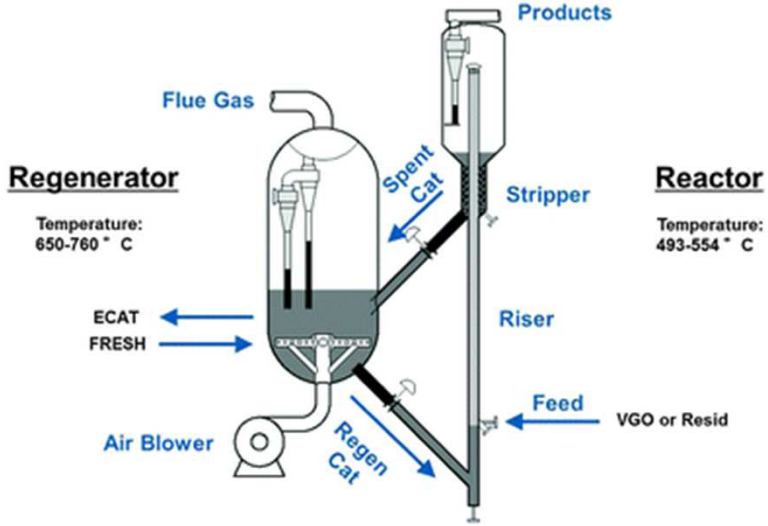
T: 575 °C

P: 0.2 - 0.5 bar

Period: hour

Sattler J.J.H.B. et al., Chem. Rev. 2014, 114, 10613

Fluid catalytic cracking (FCC)



Zeolite

T: 500 - 800 °C

Period: minute

Super Dry Reforming of CH_4

3 CO_2 per CH_4 at a CO space-time yield of 1-10 mol/m^3/s

"The Science of the Possible: windows on reality"
P.B. Weisz, CHEMTECH, July 1982, 425

Overall endothermic: how to reach and maintain 1023K?

Autothermal Dry Reforming

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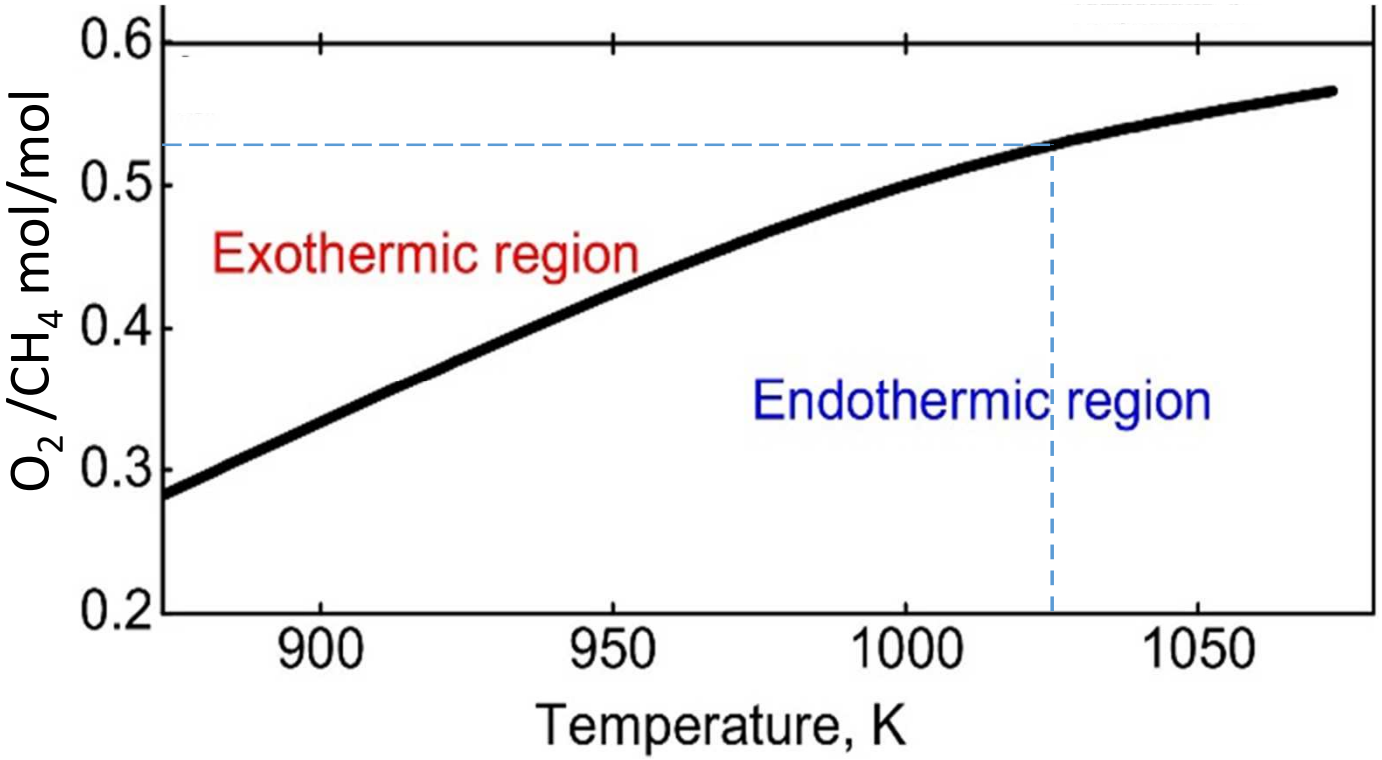
Chemical Looping with “combustion” of some methane

$CH_4 + 3CO_2 \rightleftarrows 4CO + 2H_2O$ $\Delta H^0_{1023} = 327\ kJ/mol_{CH4}$

$CH_4 + xCO_2 + (3 - x)/2O_2 \rightleftarrows (1 + x)CO + 2H_2O$ $\Delta H^0_{1023} = 0\ kJ/mol_{CH4}$

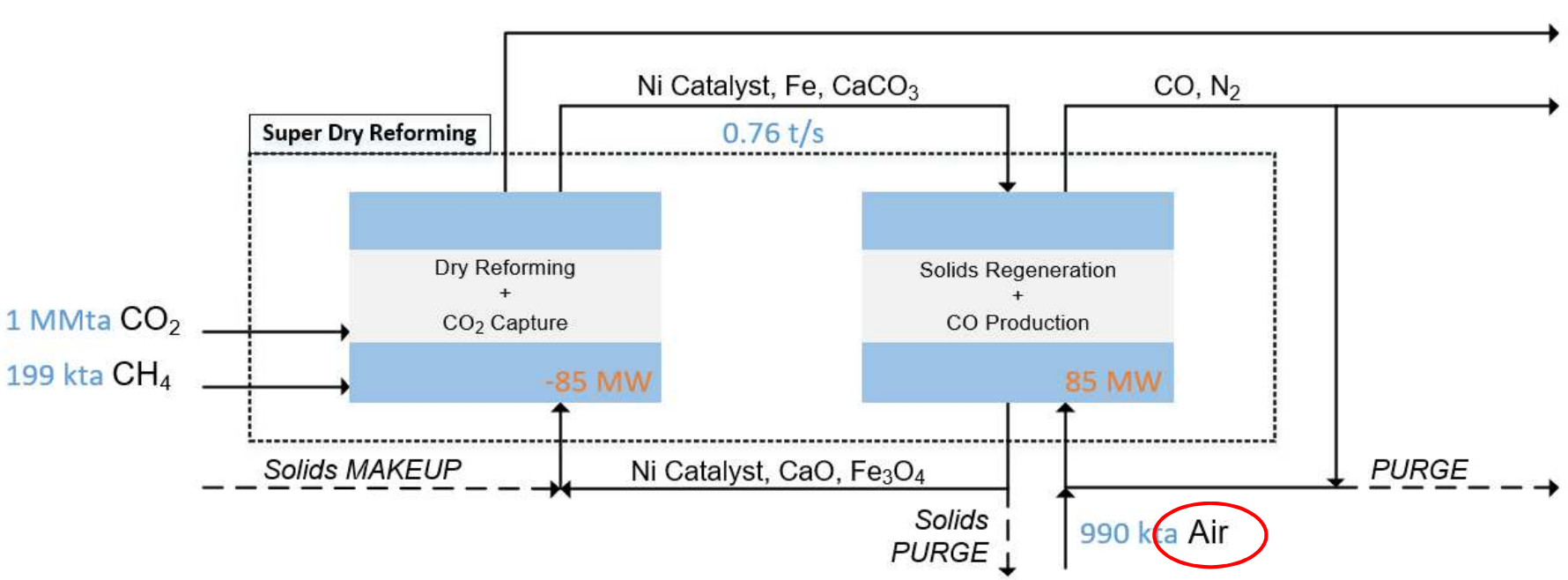
@ T=1023K

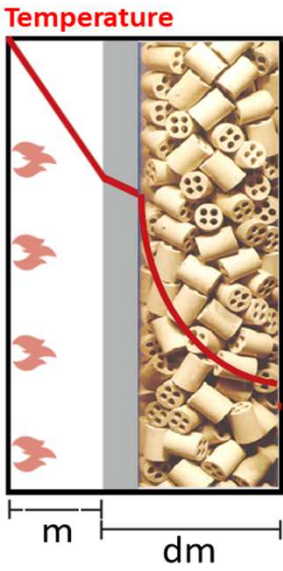
x ≈ 2



J.W. Hu et al. Journal of CO2 utilization, 16 (2016) 8-16; Appl. Cat. B, 231 (2018) 123-136

Autothermal dry reforming: flowsheet (circulating solids)





10 molCO/m3/s ➔ 100 Ton solids

✓ Optimize heat management

✓ Minimize exergy loss

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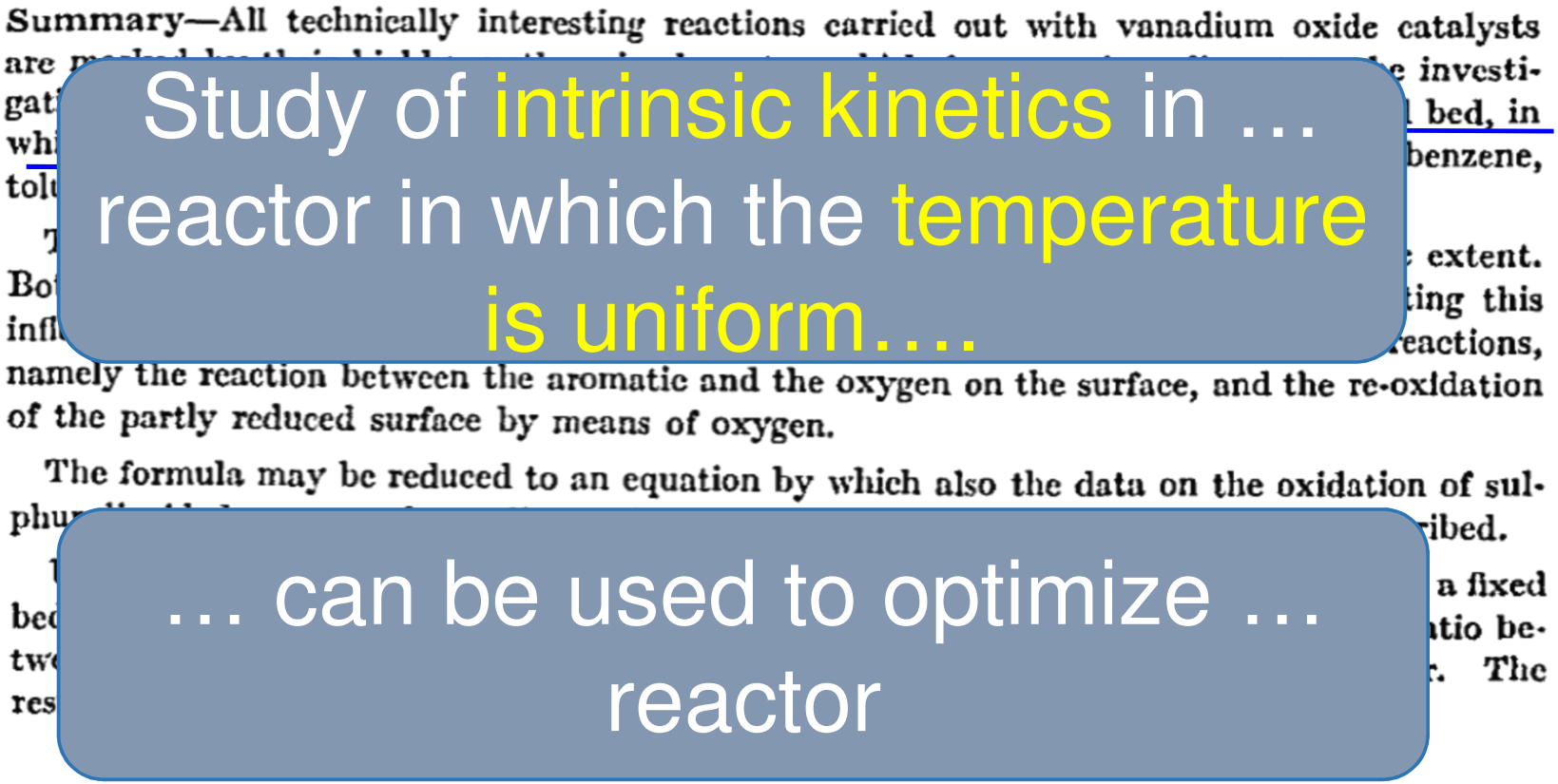
Chemical Engineering and Catalysis



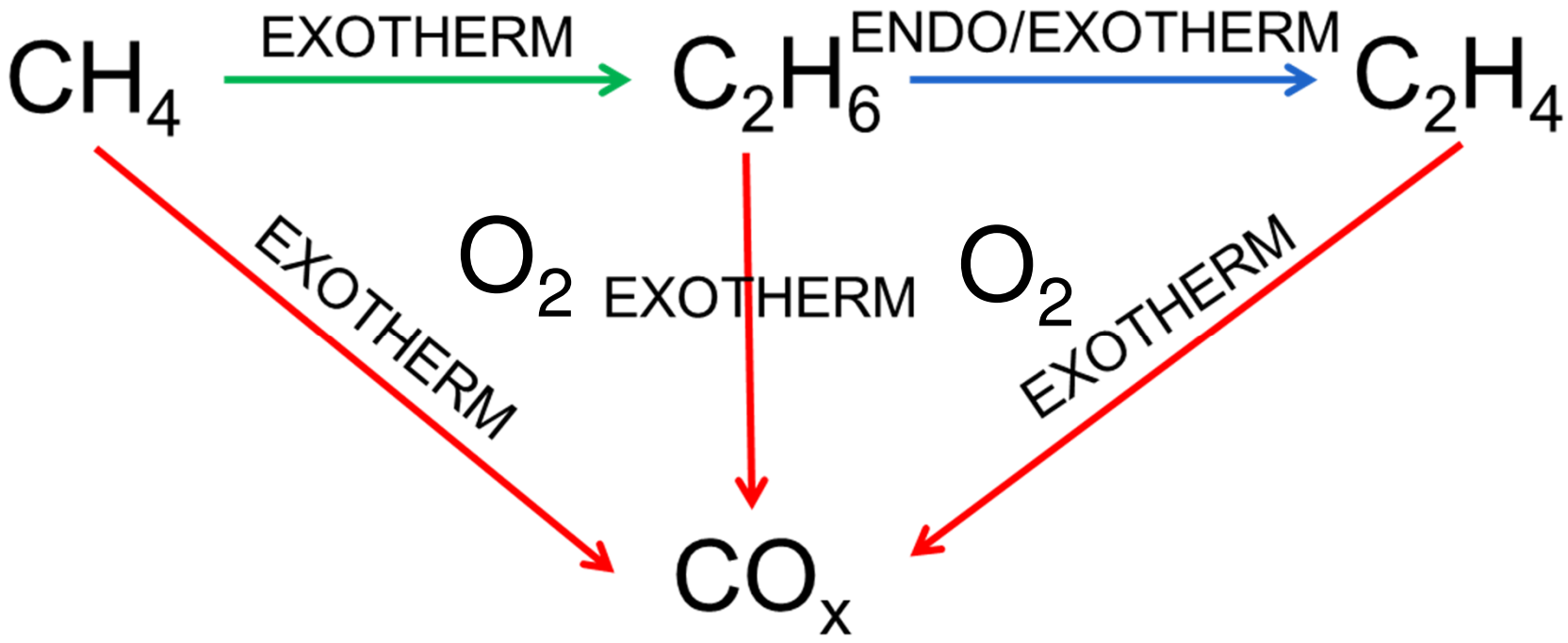
Summary—All technically interesting reactions carried out with vanadium oxide catalysts are [illegible] investi-
gat[illegible] bed, in
wh[illegible] benzene,
tol[illegible]
[illegible] extent.
Bo[illegible] ting this
infl[illegible] reactions,
namely the reaction between the aromatic and the oxygen on the surface, and the re-oxidation of the partly reduced surface by means of oxygen.

The formula may be reduced to an equation by which also the data on the oxidation of sul-
phu[illegible] ribed.
[illegible] a fixed
be[illegible] tio be-
tw[illegible] r. The
res[illegible]

Study of intrinsic kinetics in … reactor in which the temperature is uniform….

… can be used to optimize … reactor

A “Pas de Deux” of methane: oxidative coupling



Gas-Phase Reaction Network

Primary initiation

$CH_4 + O_2 \leftrightarrow CH_3\bullet + HO_2\bullet$

$CH_3\bullet$ generation

$CH_4 + H\bullet \leftrightarrow CH_3\bullet + H_2$

$CH_4 + O\bullet \leftrightarrow CH_3\bullet + OH\bullet$

$CH_4 + OH\bullet \leftrightarrow CH_3\bullet + H_2O$

$CH_4 + HO_2\bullet \leftrightarrow CH_3\bullet + H_2O_2$

$CH_3\bullet$ coupling

$CH_3\bullet + CH_3\bullet + M \leftrightarrow C_2H_6 + M$

$CH_3\bullet$ oxidation

$CH_3\bullet + O_2 \leftrightarrow CH_3O\bullet + O\bullet$

$CH_3\bullet + HO_2\bullet \leftrightarrow CH_3O\bullet + OH\bullet$

$CH_3\bullet + O_2 \leftrightarrow CH_2O + OH\bullet$

Dehydrogenation of ethane

$C_2H_6 + H\bullet \leftrightarrow C_2H_5\bullet + H_2$

$C_2H_6 + OH\bullet \leftrightarrow C_2H_5\bullet + H_2O$

$C_2H_6 + CH_3\bullet \leftrightarrow C_2H_5\bullet + CH_4$

$C_2H_6 + O\bullet \leftrightarrow C_2H_5\bullet + OH\bullet$

$C_2H_5\bullet + M \leftrightarrow C_2H_4 + H\bullet + M$

$C_2H_5\bullet + O_2 \leftrightarrow C_2H_4 + HO_2\bullet$

Hydrogen–oxygen reactions

$O_2 + H\bullet + M \leftrightarrow HO_2\bullet + M$

$H_2O_2 + M \leftrightarrow OH\bullet + OH\bullet + M$

Decomposition of C_2H_4

$C_2H_4 + O\bullet \leftrightarrow CH_3\bullet + CHO$

$C_2H_4 + OH\bullet \leftrightarrow CH_3\bullet + CH_2O$

Oxidation of $CH_3O\bullet$ and CH_2O

$CH_3O\bullet + M \leftrightarrow CH_2O + H\bullet + M$

$CH_2O + OH\bullet \leftrightarrow CHO\bullet + H_2O$

$CH_2O + HO_2\bullet \leftrightarrow CHO\bullet + H_2O_2$

$CH_2O + CH_3\bullet \leftrightarrow CHO\bullet + CH_4$

$CHO\bullet + M \leftrightarrow CO + H\bullet + M$

$CHO\bullet + O_2 \leftrightarrow CO + HO_2\bullet$

$CO + HO_2\bullet \leftrightarrow CO_2 + OH\bullet$

Dehydrogenation of ethene

$C_2H_4 + O_2 \leftrightarrow C_2H_3\bullet + HO_2\bullet$

$C_2H_4 + H\bullet \leftrightarrow C_2H_3\bullet + H_2$

$C_2H_4 + O\bullet \leftrightarrow C_2H_3\bullet + OH\bullet$

$C_2H_4 + OH\bullet \leftrightarrow C_2H_3\bullet + H_2O$

$C_2H_4 + CH_3\bullet \leftrightarrow C_2H_3\bullet + CH_4$

$C_2H_3\bullet + M \leftrightarrow C_2H_2 + H\bullet + M$

$C_2H_3\bullet + O_2 \leftrightarrow C_2H_2 + HO_2\bullet$

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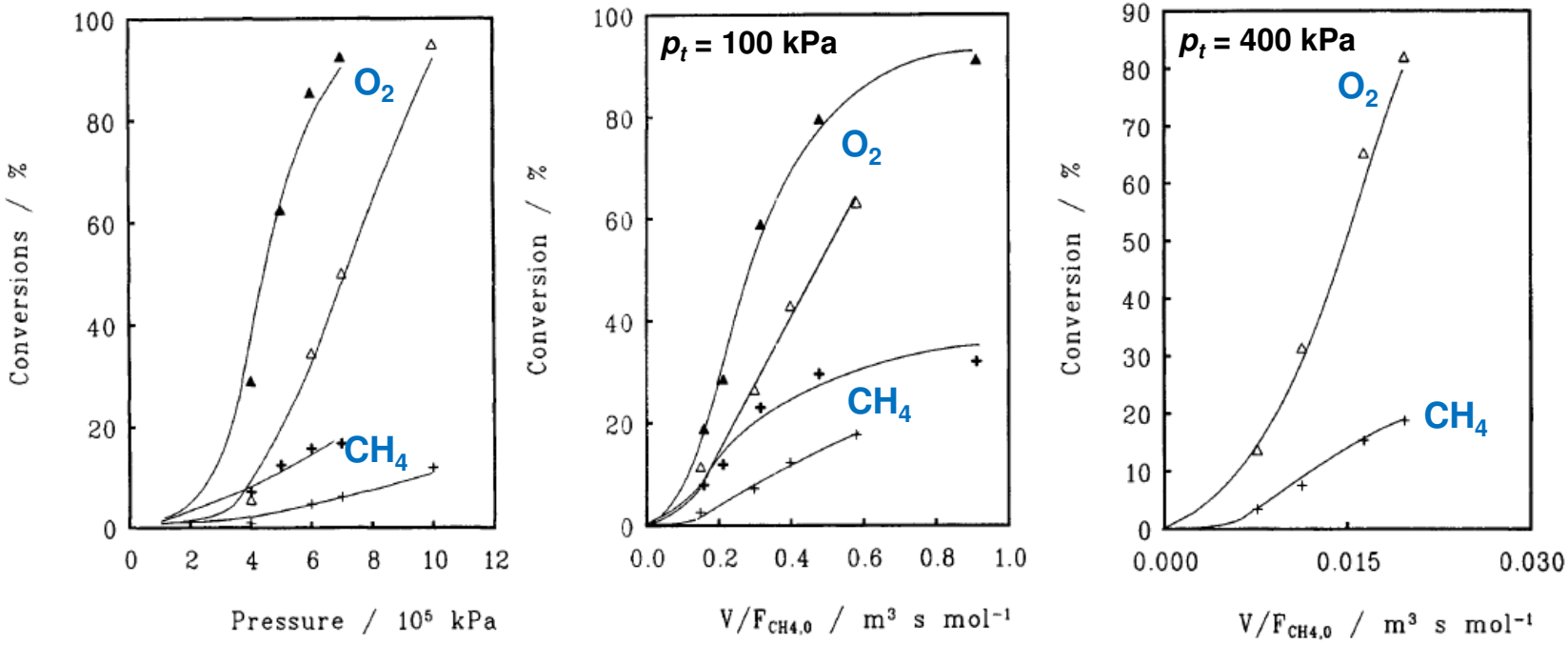
Experimental conditions:

$p_t = p_{atm}$; T = 873–1123 K; CH_4/O_2 I_0 = 4–10; He/CH_4 I_0 = 0–1.25; $V / F_{CH4,0}$ = 0.1–1.9 m^3 s mol^{-1}; ***CH_4 conversion*** = 2–15%, ***O_2 conversion*** = 10–100%

Chen, Qi, et al. Industrial & Engineering Chemistry Research 30.9 (1991): 2088–2097

Effect of pressure on conversion (no catalyst)



a)

Δ O_2 + CH_4, $CH_4/O_2|_0 = 10$

▲O_2 + CH_4, $CH_4/O_2|_0 = 5$

T_{max} = 1090 K, τ = 0.5 s

b)

Δ O_2 + CH_4, $CH_4/O_2|_0 = 10$

▲O_2 + CH_4, $CH_4/O_2|_0 = 5$

T_{max} = 1100 K

c)

Δ O_2 +CH_4, $CH_4/O_2|_0 = 4$

T_{max} = 1078 K

Chen, Qi, et al. AIChE journal 40.3 (1994): 521–535

Surface Reaction Network

HYDROGEN ABSTRACTION BY ELEY–RIDEAL STEPS

$CH_4 + O* \leftrightarrow CH_3^{\bullet} + OH*$

$C_2H_4 + O* \leftrightarrow C_2H_3^{\bullet} + OH*$

$C_2H_6 + O* \leftrightarrow C_2H_5^{\bullet} + OH*$

$C_2H_5^{\bullet} + O* \leftrightarrow C_2H_4 + OH*$

$CH_3O^{\bullet} + O* \leftrightarrow CH_2O + OH*$

$CH_2O + O* \leftrightarrow CHO^{\bullet} + OH*$

$CHO^{\bullet} + O* \leftrightarrow CO + OH*$

$H_2 + O* \leftrightarrow H^{\bullet} + OH*$

$H_2O_2 + O* \leftrightarrow HO_2^{\bullet} + OH*$

$OH^{\bullet} + O* \leftrightarrow O^{\bullet} + OH*$

$H_2O + O* \leftrightarrow OH^{\bullet} + OH*$

$HO_2^{\bullet} + O* \leftrightarrow O_2 + OH*$

HYDROGEN ABSTRACTION BY SURFACE REACTION

$CH_3O* + O* \leftrightarrow CH_2O* + OH*$

$CH_2O* + O* \leftrightarrow HCO* + OH*$

$CHO* + O* \leftrightarrow CO* + OH*$

$C_2H_4O* + O* \leftrightarrow C_2H_3O* + OH*$

RECOMBINATION OF HYDROXYLS

$2OH* \leftrightarrow H_2O* + O*$

CO OXIDATION ON THE SURFACE

$CO* + O* \leftrightarrow CO_2* + *$

C–C CLEAVAGE ON THE SURFACE

$C_2H_3O* + O* \leftrightarrow CH_2O* + HCO*$

ADSORPTION STEPS

$O_2 + 2* \leftrightarrow 2O*$

$CH_3^{\bullet} + O* \leftrightarrow CH_3O*$

Sn/Li/MgO

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LCT DRIVING CHEMICAL TECHNOLOGY

Nibbelke R.H. et al., J. Catal.,(156), 1995, 106-119

Kechagiopoulos, P. N., et al., Ind. Eng. Chem. Res., (53), 2013, 1825–1840

Catalyst and Kinetic Descriptors

- Reaction families:

H abstraction by Eley–Rideal reaction

H abstraction by surface reaction

Recombination of OH

CO oxidation on the surface

C–C cleavage on the surface

- Polanyi relation within a reaction family:

activation energy: $E_{a,i} = E_0 + \alpha \Delta_{r,i} H$

  - kinetic descriptors: α, E_0
  - a reaction family shares the same (E_0,α)

- Reference: abstraction from Methane

$$\mathbf{CH_3 - H + O* \leftrightarrow CH_3 \bullet + OH*}$$

$D_1 = \Delta_{r,1} H$ catalyst descriptor

- Any reaction i in the family: e.g. from Ethane

$$\mathbf{C_2H_5 - H + O* \leftrightarrow C_2H_5 \bullet + OH*}$$

$\Delta_{r,i} H = D_1 + Q_{C2H5-H} - Q_{CH3-H}$

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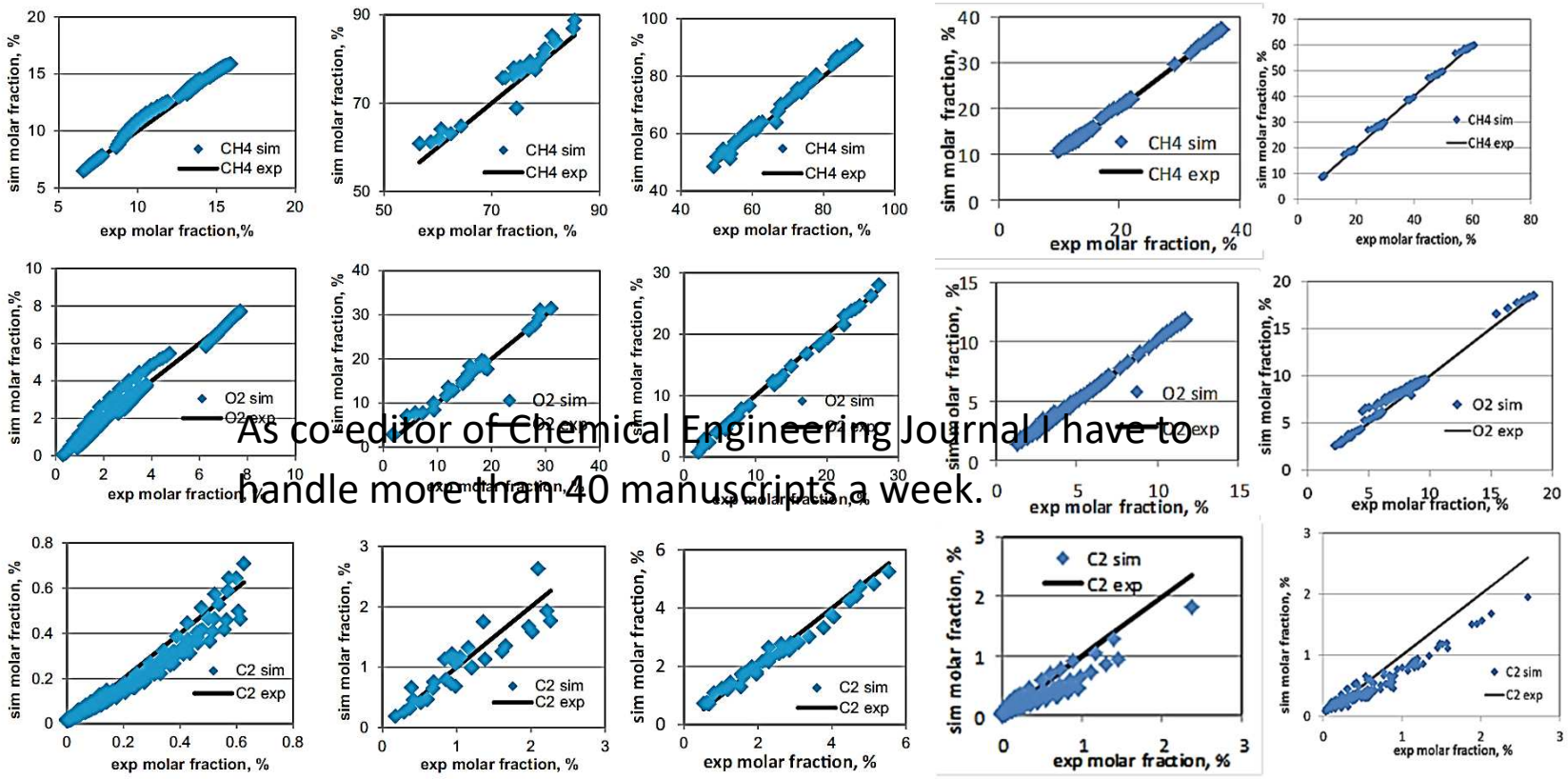
LCT DRIVING CHEMICAL TECHNOLOGY

P.N. Kechagiopoulos et al., Ind. Eng. Chem. Res., (53), 2014, 1825–1840

Gas phase/surface reactions microkinetics



As co-editor of Chemical Engineering Journal I have to handle more than 40 manuscripts a week.

Sr/La_2O_3 **Li/MgO** **Sn–Li/MgO** **LaSr/CaO** **$NaMnW/SiO_2$**

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LCT DRIVING CHEMICAL TECHNOLOGY

Alexiadis, V. I., et al. Applied Catalysis B: Environmental 150 (2014) 496–505

Catalyst descriptors

D1
Reaction enthalpy of H abstraction (kJ/mol_{CH4})

D2
Chemisorption heat O_2 (kJ/mol_{O2})

D3
Sticking probability of CH_3 on O* (-)

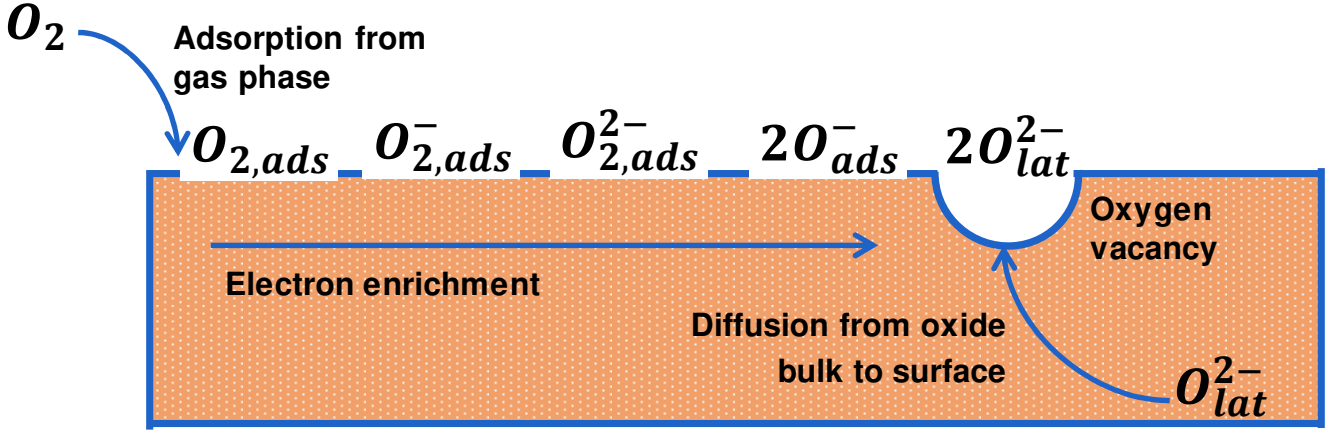
D4
Active sites Density (mol/m^2)

$CH_4 + O* \leftrightarrow CH_3^{\cdot} + OH*$

$O_2 + 2* \leftrightarrow 2O*$

$CH_3^{\bullet} + O* \leftrightarrow CH_3O*$

$Oxygen\ Pool\ Capacity$



Nibbelke R.H. et al., J. Catal. 156), 1995, 106-119

Pirro, L. et al., Catal. Sci. Technol. (9), 2019, 3109-3125

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Catalyst descriptors and catalyst performance

	D_1	D_2	D_3	D_4
Unit	kJ mol^{-1}	kJ mol^{-1}	10^{-4}	10^{-6}mol m^{-2}
Sr/La_2O_3	44.4±0.2	119.5±3.5	6.5 ±0.5	10 ± 1
Li/MgO	91.2±0.2	73.6±2.2	1.1900±0.0002	0.4330 ±0.0009
Sn–Li/MgO	56.6±0.8	60.5±2.6	0.62±0.01	1.33 ±0.03
LaSr/CaO	65.1±1.6	139.6±5.3	1.14±0.03	6.4±1.5
$NaMnW/SiO_2$	81.400±0.002	44.0±1.6	0.10±0.02	0.457±0.005

Value ±95% confidence interval

HIGH ACTIVITY:
low D1, high D3,D4

LOW ACTIVITY:
high D1, low D4

HIGH SELECTIVITY:
low D2,low D3

D_1 – Reaction enthalpy of hydrogen abstraction from CH_4
D_2 – Chemisorption heat of O_2
D_3 – Initial sticking probability of CH_3
D_4 – Density of active sites

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Alexiadis, VI, et al. Applied Catalysis B-Environmental , 199,252-259,2016

Chemical Engineering and Catalysis

- Introduction
- Super Dry Reforming
- Oxidative coupling: heat transfer
- Conclusions and Perspectives

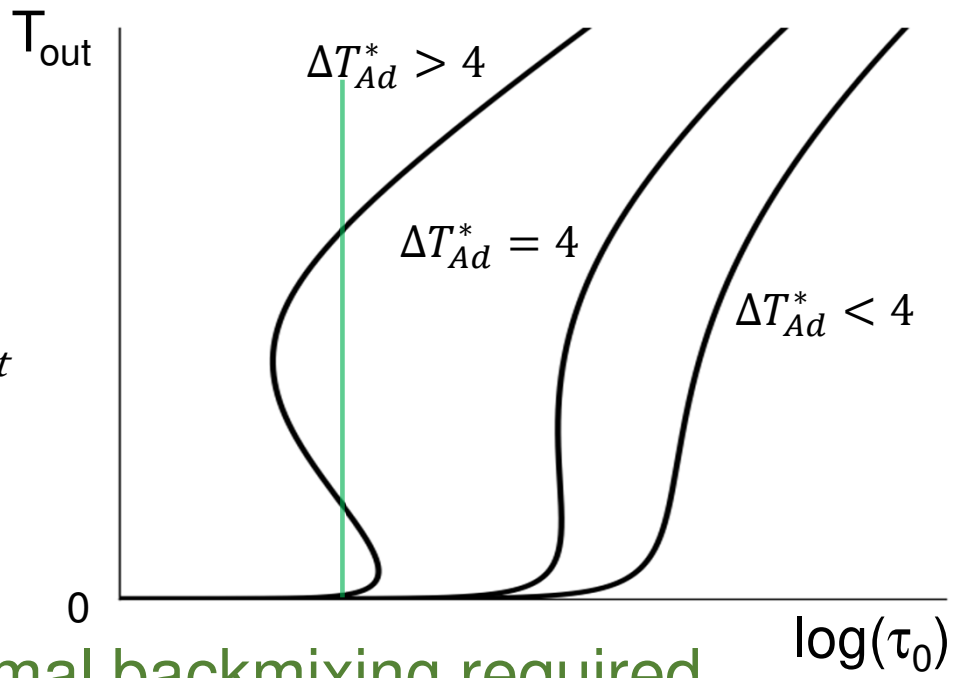
Exothermic reactions: steady-state multiplicity

Unfolding parameter: e.g. dimensionless adiabatic temperature rise ΔT_{Ad}^*

$$\Delta T_{Ad}^* = \frac{E}{RT_0^2}\Delta T_{Ad}$$

State variable:

e.g. *outlet temperature* T_{out} *or conversion* X_A



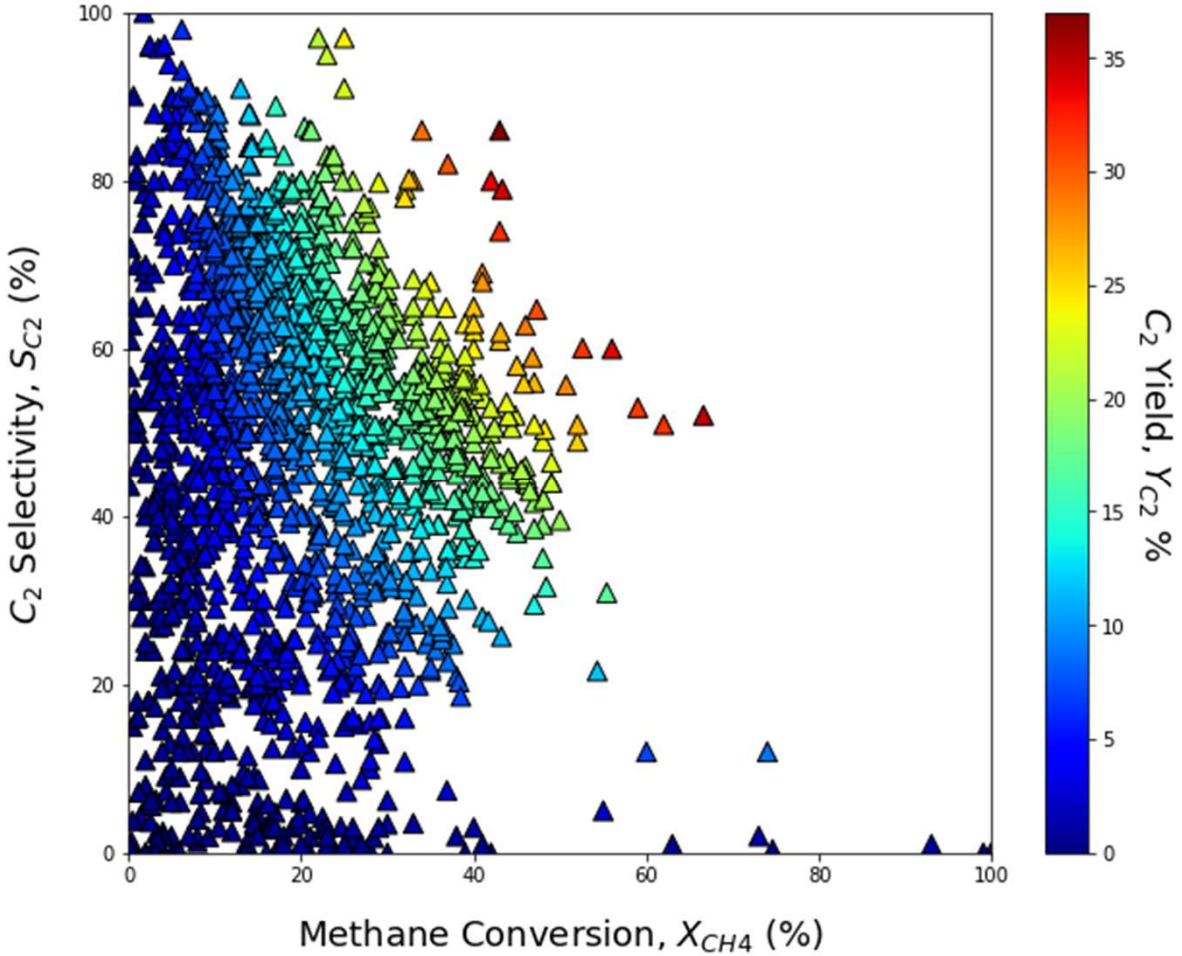
Positive feedback: sufficient thermal backmixing required

Bifurcation parameter: e.g. *inlet temperature* T_{in} *or* $\tau_0 = \frac{V}{F^0_{V(STP),CH_4}}$

Isothermal laboratory data

1802 “**isothermal**” experiments (1981 - 2009)

T= 823 – 1218K, CH_4/O_2= 0.8 - 38.3



based on the data reported by: R. Schmack et al., Nat. Comm., (10), 2019, art. 441.

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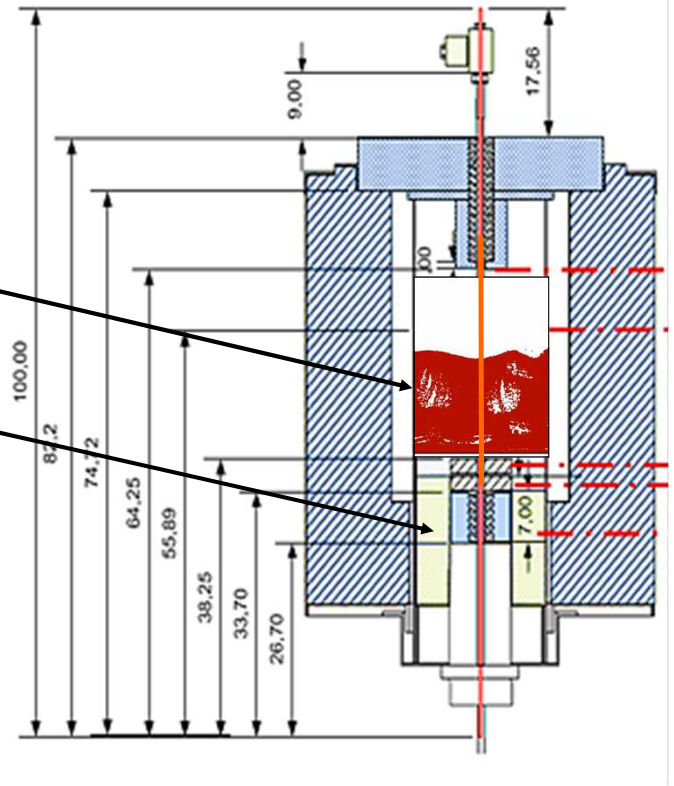
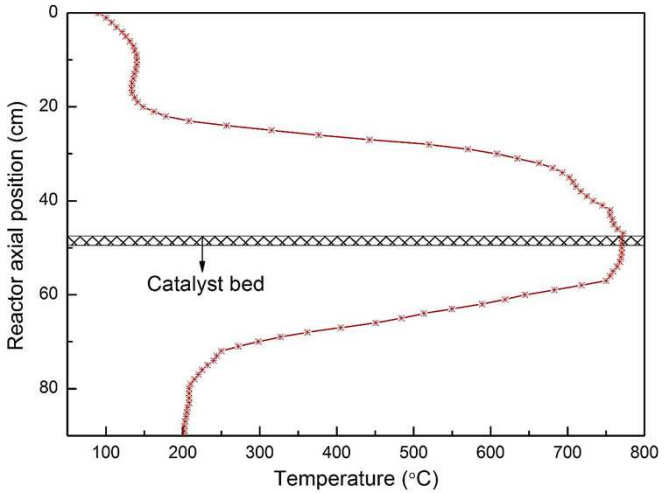
Experimental Set-Up: isothermal conditions

Fluidized sand bath

Air distributor





T profile

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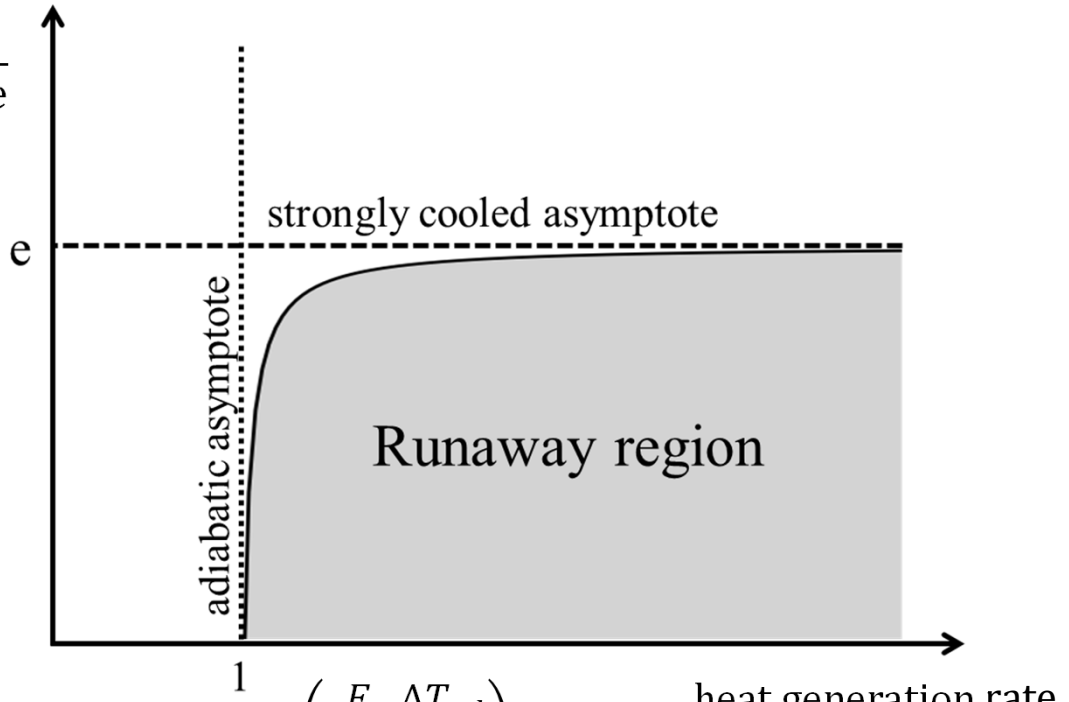
Runaway risk

$$\frac{RT_0{}^2}{E\Delta T_{ad}}\frac{1}{k(T_0)}\frac{U}{\rho_f C_{pf}}\frac{4}{d_t} = \frac{\text{cooling rate}}{\text{heat generation rate}}$$

$> e = 2.72$ for unconditionally safe reactor operation, irrespective of the space time

David West , ISCRE 2018



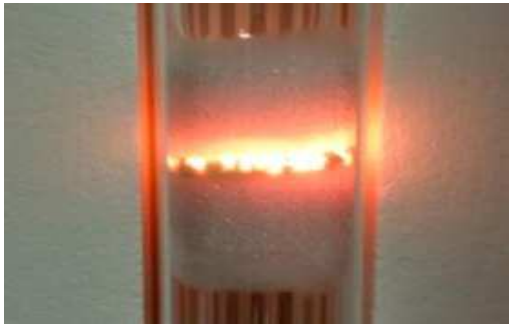
ISOTHERMAL OPERATION NOT OBVIOUS

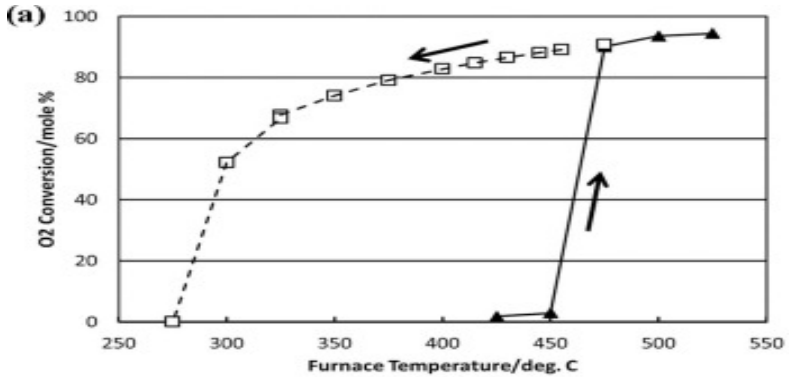
Balakotaiah & Luss, AIChEJ,37(1991), 1780

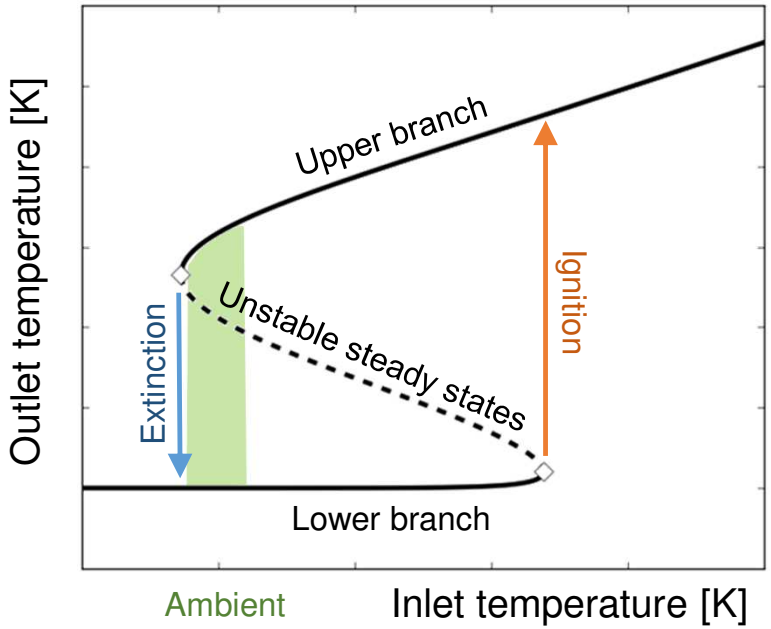
Christoforatou et al.,AIChEJ, 44(1998), 394

Behaviour of cooled reactor: steady-state multiplicity

Ignition/Extinction/Hysteresis







S. Sarsani et al., Chem. Eng. J., (328), 2017, 484-496.

AUTOTHERMAL ADIABATIC OPERATION WITH AMBIENT INLET TEMPERATURE?

Scale-up of cooled reactor:

J.H.B.J. Hoebink et al., Chem. Eng. Sci., (49), 1994, 5453-5463

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Outline

- Introduction
- Super Dry Reforming
- Oxidative coupling: reactor design
- Conclusions and Perspectives

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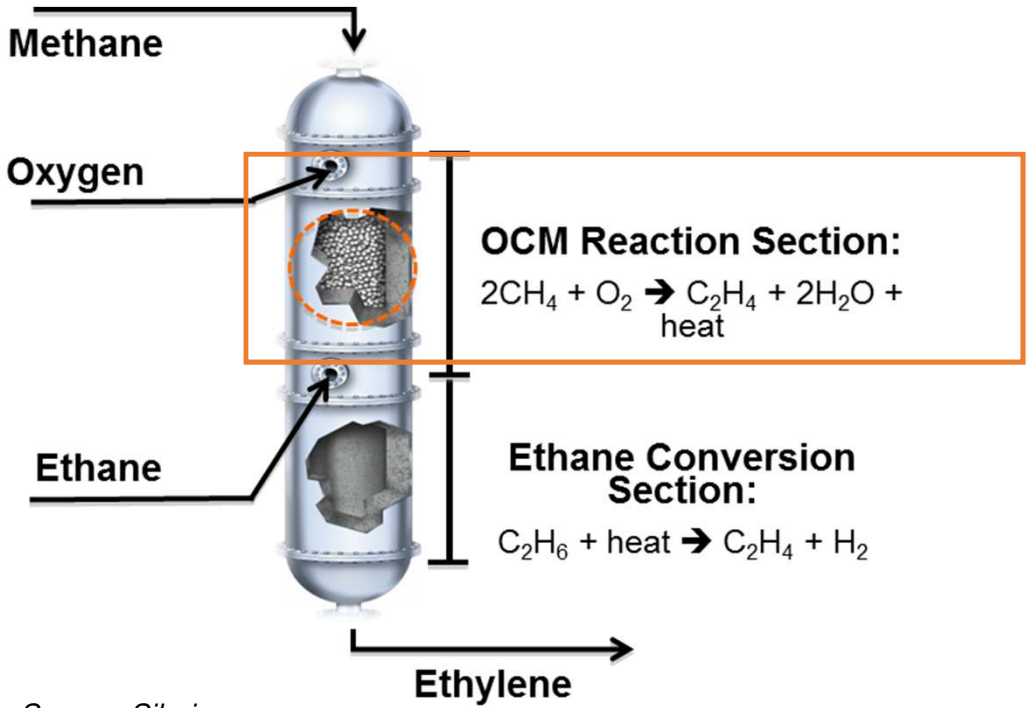
Industrial reactor concepts

Adiabatic fixed bed reactor

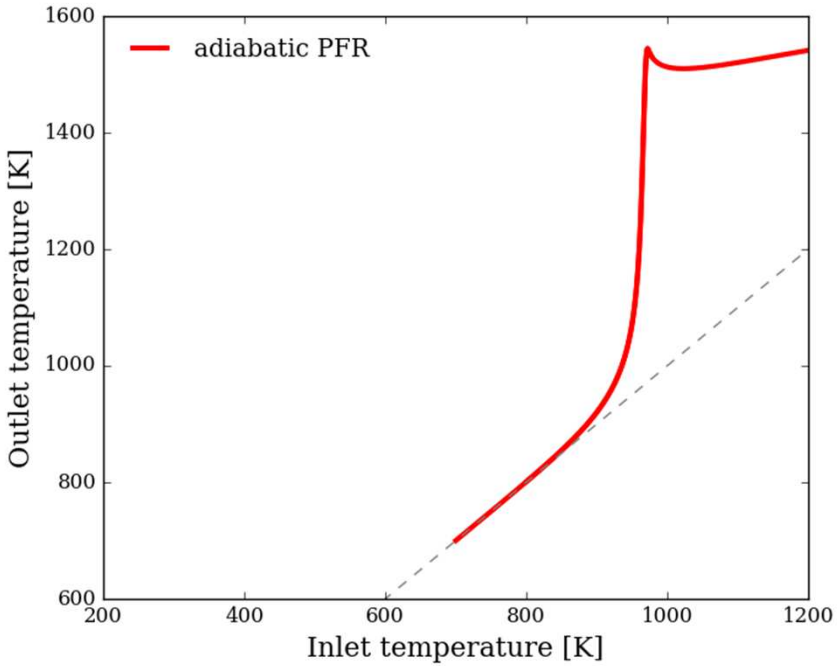


Source: Siluria

Adiabatic plug flow reactor (PFR)

Sr/La_2O_3

$CH_4:O_2 = 6$, $V/F^0_{V(STP),CH4} =$ 0.01 s, $m_{cat}/V = 1000\ kg_{cat}/m^3$



Difficult thermal control

Risk for hot spots and runaway

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L.A. Vandewalle et al., Chem.Eng.Sci., (199), 2019, 635-651.

Ideal reactor types

- Plug flow reactor **(PFR)**

  No species backmixing, no thermal backmixing

- Continuously stirred tank reactor **(CSTR)**

  Perfect species backmixing, perfect thermal backmixing

- Lumped thermal reactor **(LTR)**

  No species backmixing, perfect thermal backmixing

  (Zhe Sun et al. CEJ , 343, 770-788, 2018)

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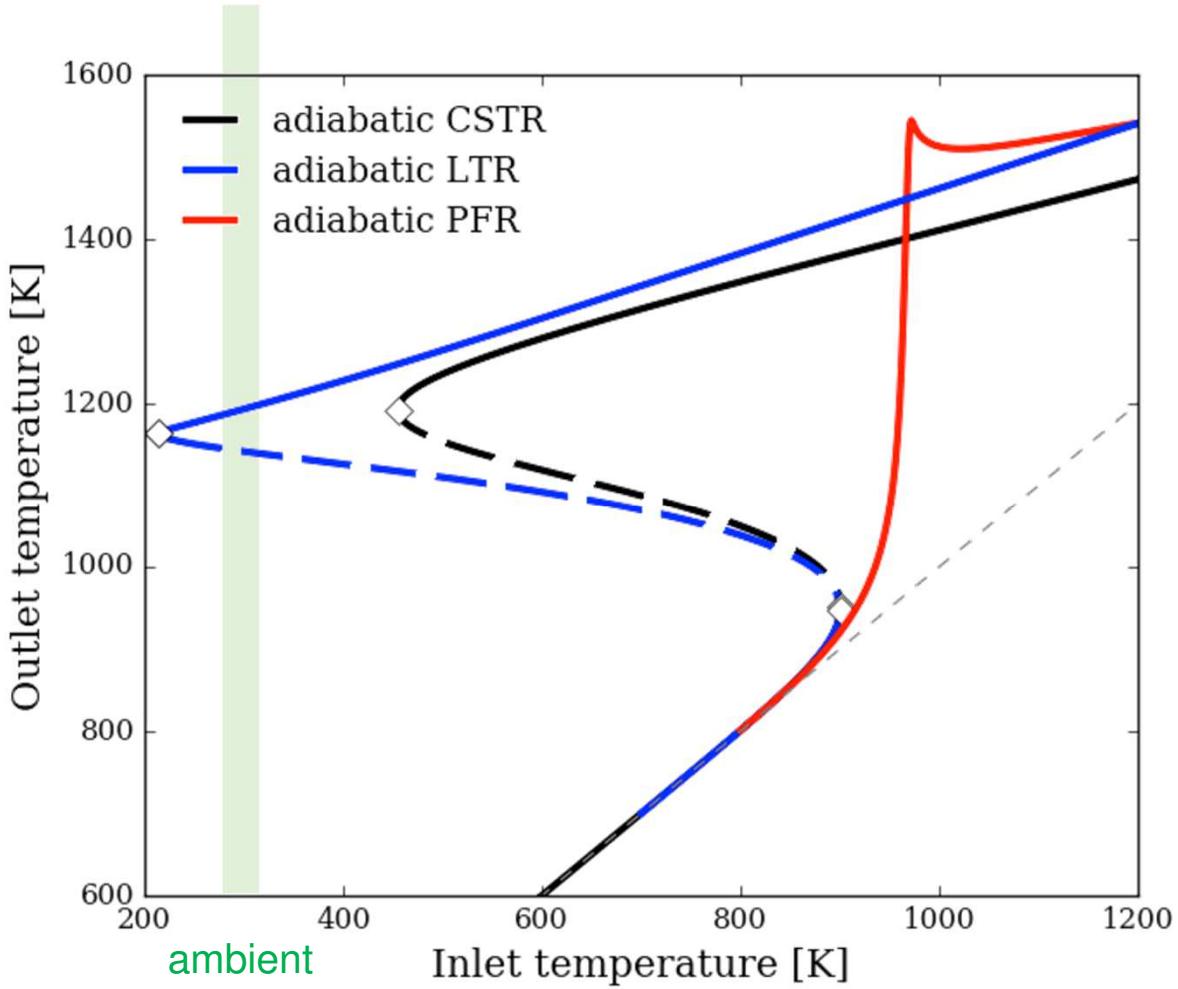
OCM with Sr/La_2O_3 : comparison of reactor types

LTR most promising

- Lowest extinction point (ambient inlet temperature possible)

Operating conditions:
P = 1 bar, CH_4:O_2 = 6,
$V/F^0_{V(STP),CH4}$ = 0.01 s,
m_{cat}/V = 1000 kg_{cat}/m^3



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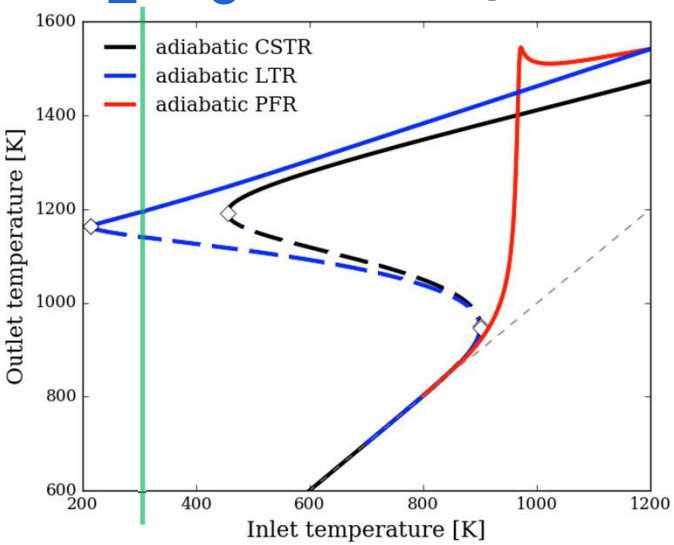
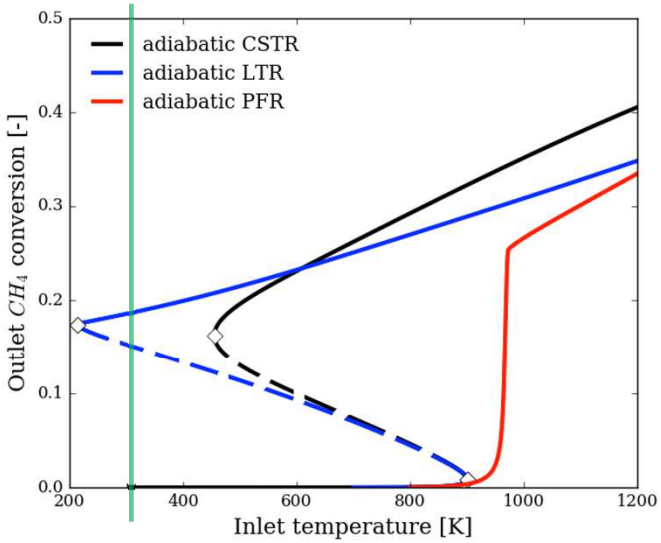
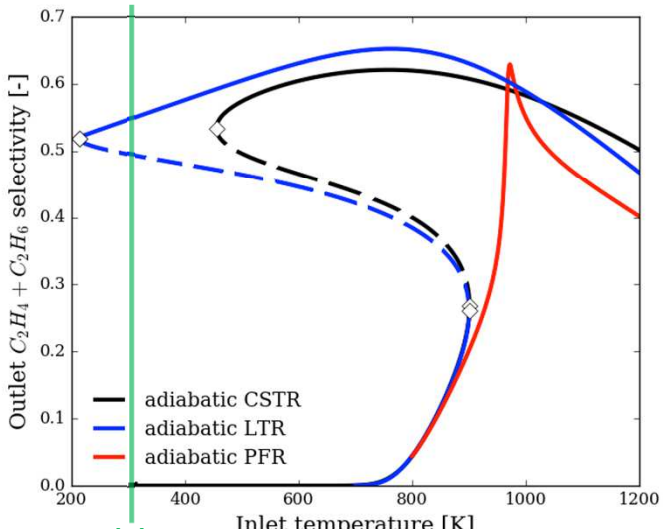
OCM with Sr/La_2O_3 : comparison of reactor types

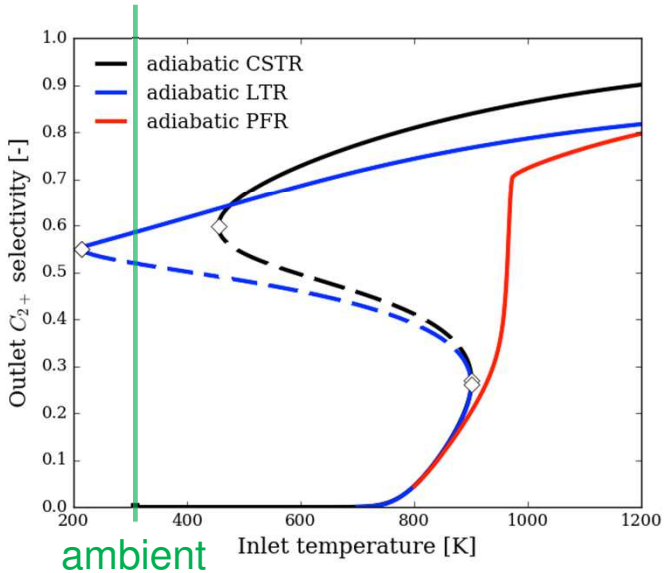
LTR most promising

– Lowest extinction point (ambient inlet temperature possible)









Operating conditions:
P = 1 bar, $CH_4:O_2 = 6$,
$V/F^0_{V(STP),CH4} = 0.01$ s,
$m_{cat}/V = 1000\ kg_{cat}/m^3$

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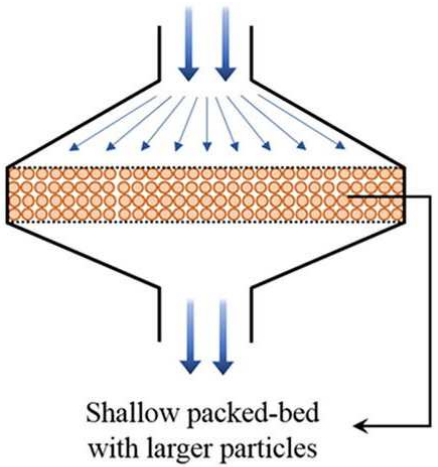
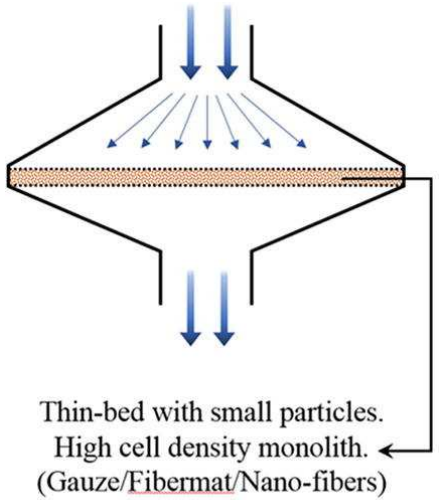
Lumped Thermal Reactors in real life

Key feature: little species but good thermal backmixing

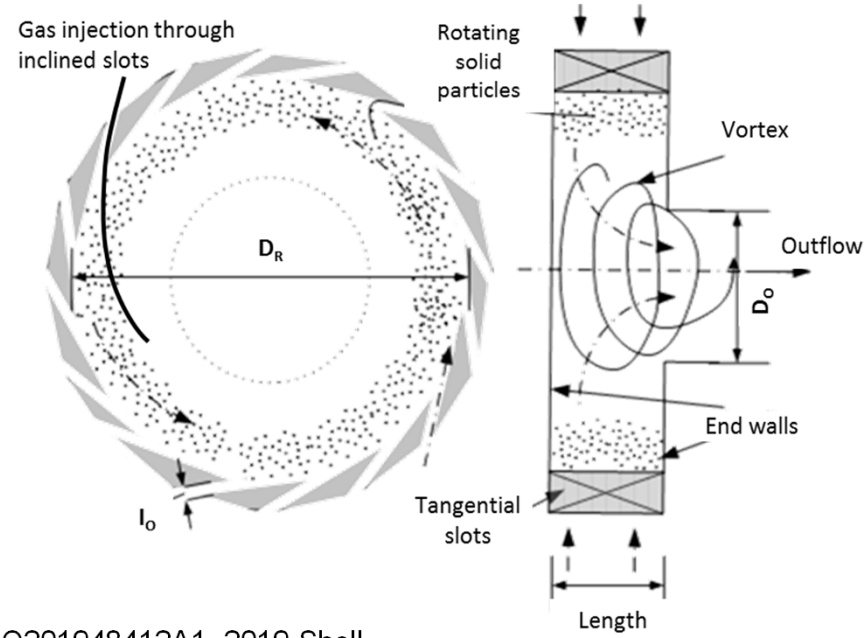
Shallow packed bed



High cell density monoliths



Gas-solid vortex reactor



Balakotaiah, V. et al. Chem. Eng. J. 2019, *374*, 1403–1419

Thin bed cofeed reactors for methane conversion, US4876409A, 1989 ARCO

Process for oxidatively converting methane to higher hydrocarbon products, WO2019048408A1, WO201948412A1, 2019 Shell

Vandewalle, L. A. et al. Chem. Eng. Sci. 2019, *198*, 268-289

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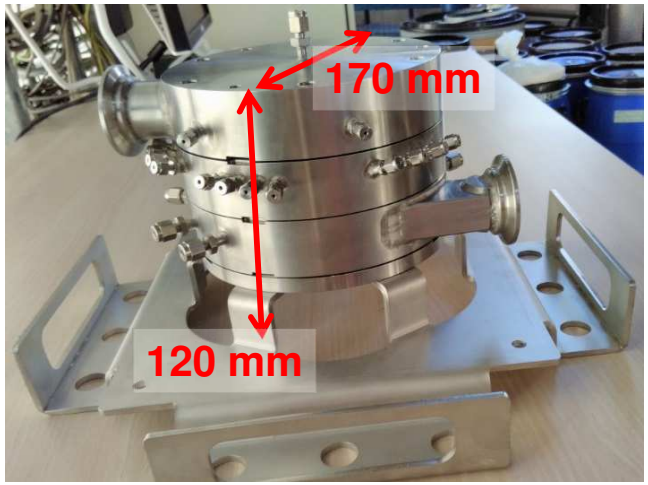
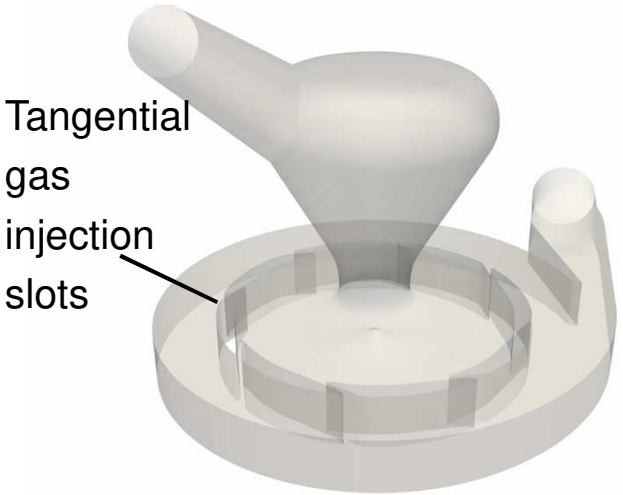
Gas-Solid Vortex Reactor (GSVR)





Rotating bed in
Vortex reactor

- High gas feed flow rates → small gas residence time
- High gas-solid slip velocity → good gas-solid heat and mass transfer

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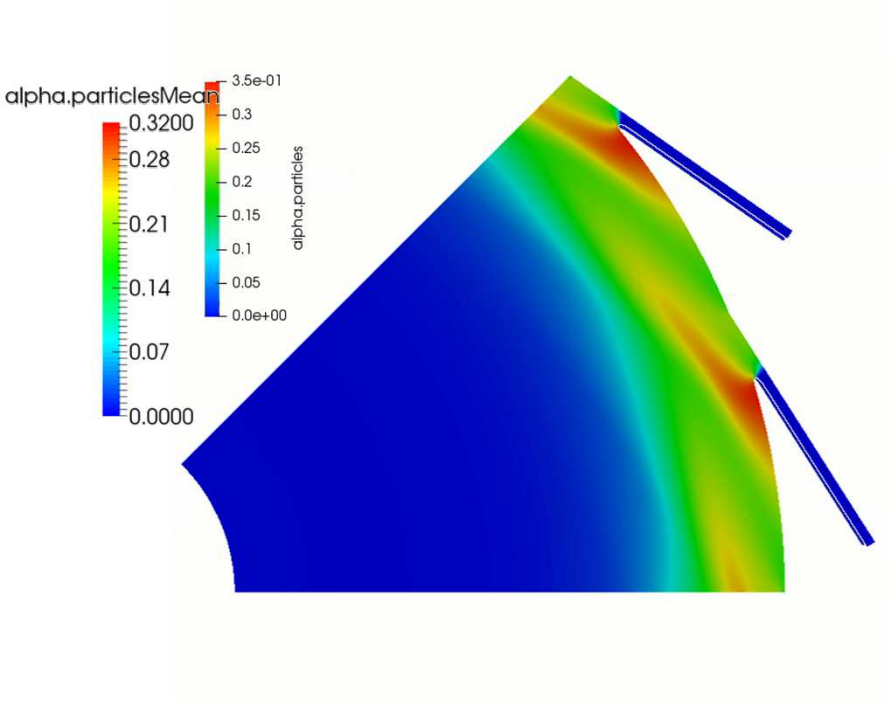
PROCESS INTENSIFICATION

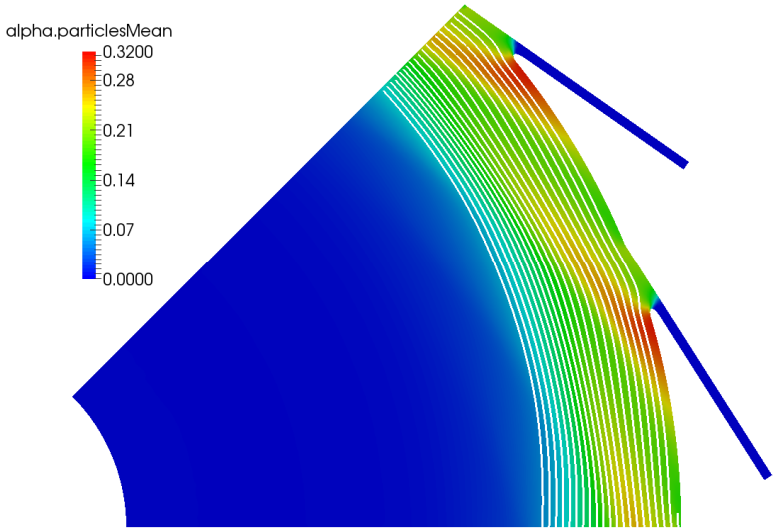
M .N. Pantzali et al., AIChE J., (61), 2015, 4114-4125.

Non-reactive CFD simulations of the GSVR

Gas streamlines on a background of
Time-averaged particle volume fraction



Particle streamlines on a background of
Time-averaged particle volume fraction



16 slots GSVR, 2D simulation
Inlet slot velocity 75 m/s
Particle diameter 500 µm, density 2300 kg/m³

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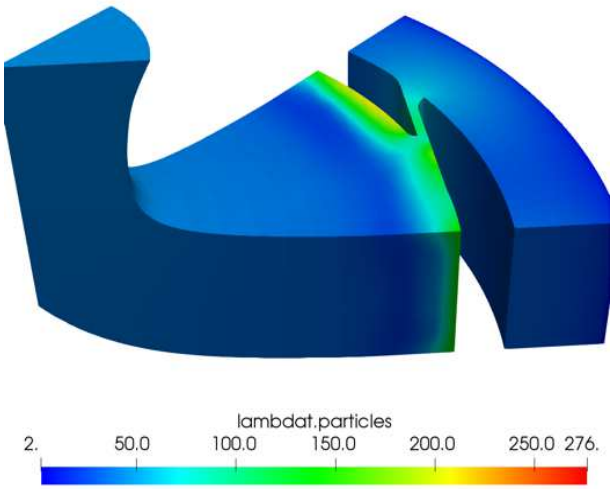
✓ Limited species backmixing

Thermal backmixing: effective thermal conductivity

Evaluation of effective thermal conductivity λ_e from

- Granular temperature θ: Kinetic Theory of Granular Flow (Gidaspow,'94)
- Particle volume fraction ε: from CFD simulations

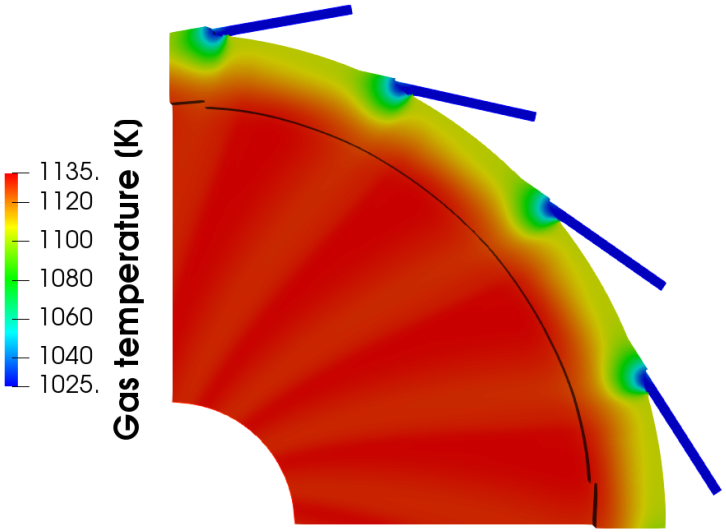


100-150 W/mK : One order of magnitude larger than in a packed bed

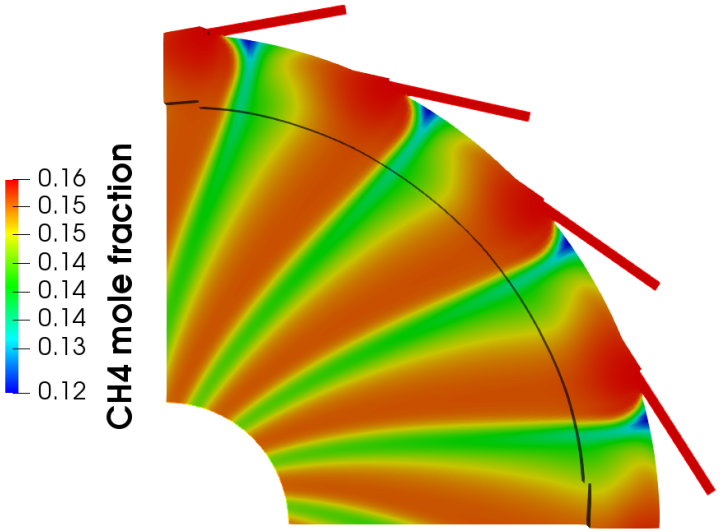
Sufficient thermal backmixing ?

Autothermal adiabatic oxidative coupling in GSVR

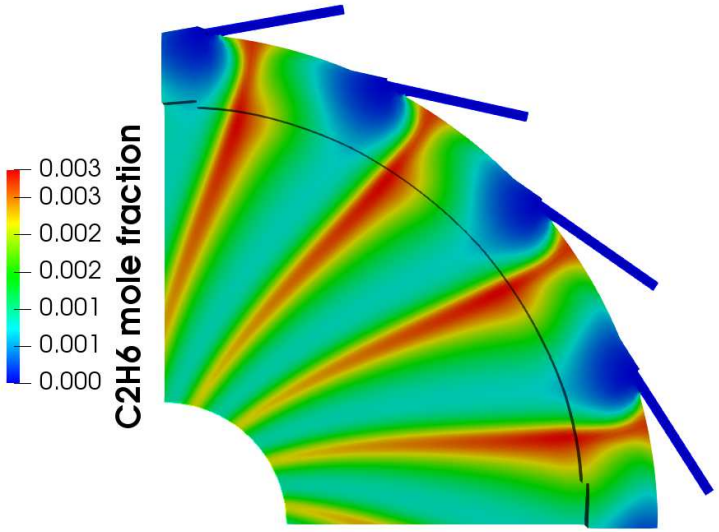
Sr/La_2O_3 catalyst, $CH_4:O_2 = 4$, 80% N_2 dilution, $T_{in} = 1023$ K



Temperature rises ~ 110 K from inlet to outlet

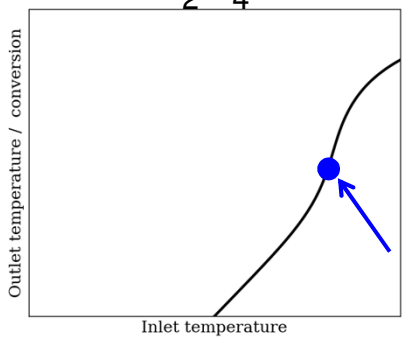


CH_4 conversion ~ 5.2 %



C_2 selectivity ~ 43 %
9 % C_2H_4 + 34 % C_2H_6

(~5-10 K not resulting from reaction)



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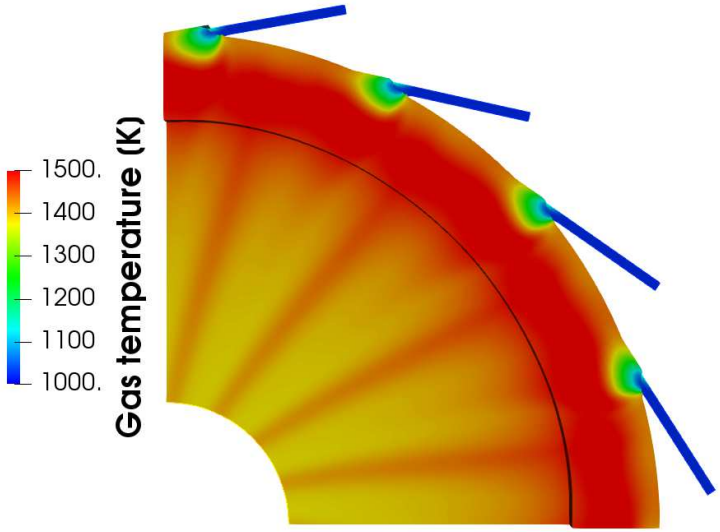
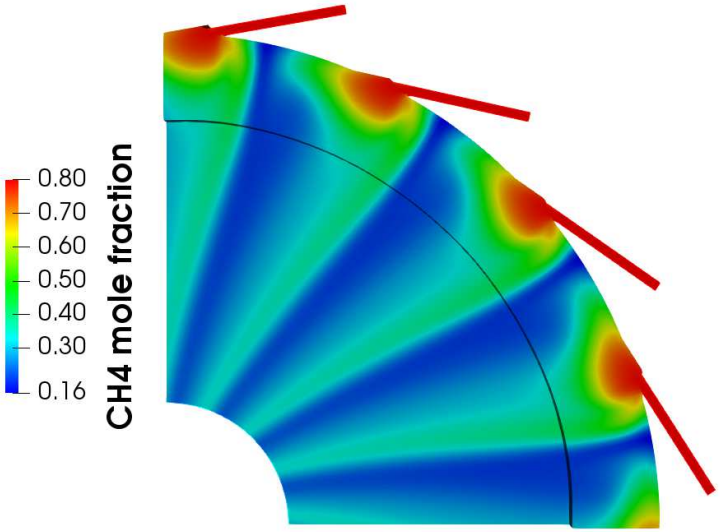
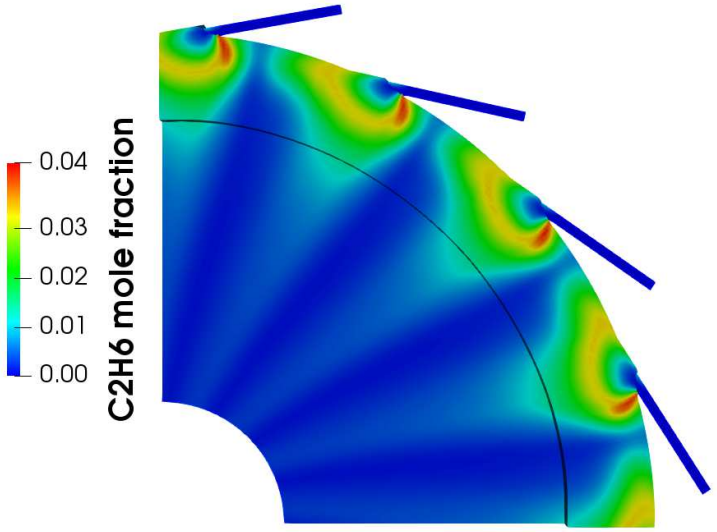
2D simulation, 16 slots, D_R = 8 cm, $U_{g,inj}$ = 85 m s^{-1}
Total catalyst loading ~10 g if L_R/D_R = 0.2, d_s = 500 µm
Catalyst porosity 0.27, A/V = 5e6 m^2/m^3

Autothermal adiabatic oxidative coupling in GSVR

Sr/La_2O_3 catalyst, $CH_4:O_2 = 4$, no N_2 dilution, $T_{in} = 1023$ K



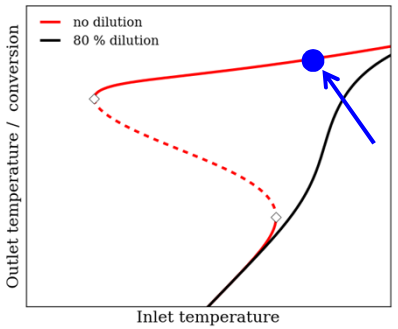




Temperature has increased ~ 250 K from inlet to outlet
Volume-weighted average bed temperature 1495 K

CH_4 conversion ~ 56 %
Local high conversion in 'dead' zone between the slots

C_2 selectivity ~ 31 %
30 % C_2H_4 + 1 % C_2H_6



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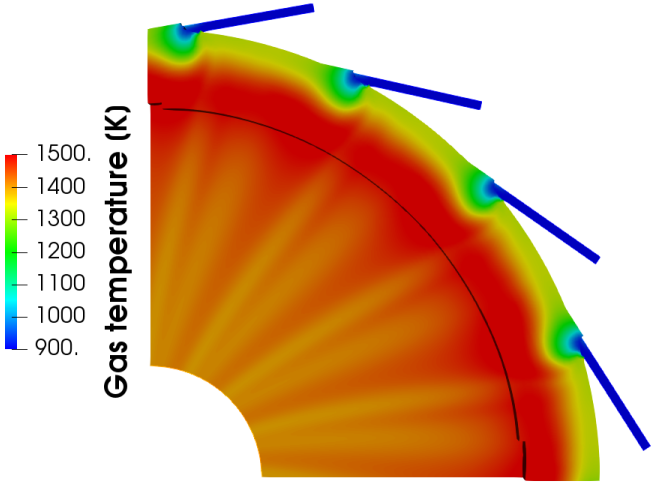
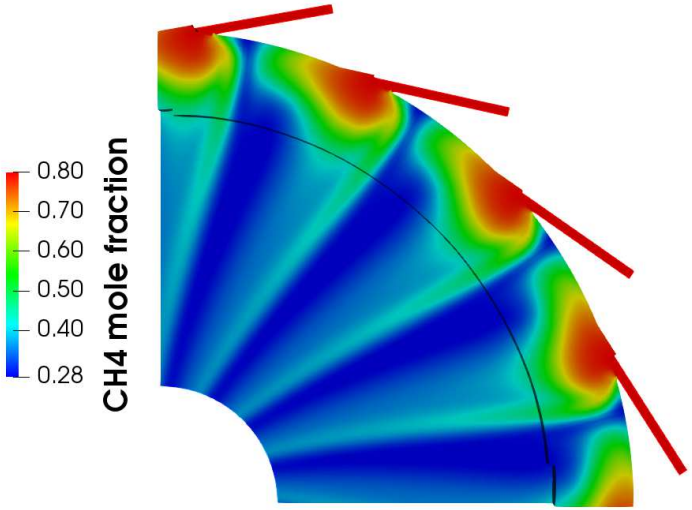
2D simulation, 16 slots, D_R = 8 cm, $U_{g,inj}$ = 85 m s^{-1}
Total catalyst loading ~10 g if L_R/D_R = 0.2, d_s = 500 µm
Catalyst porosity 0.27, A/V = 5e6 m^2/m^3

Autothermal adiabatic oxidative coupling in GSVR

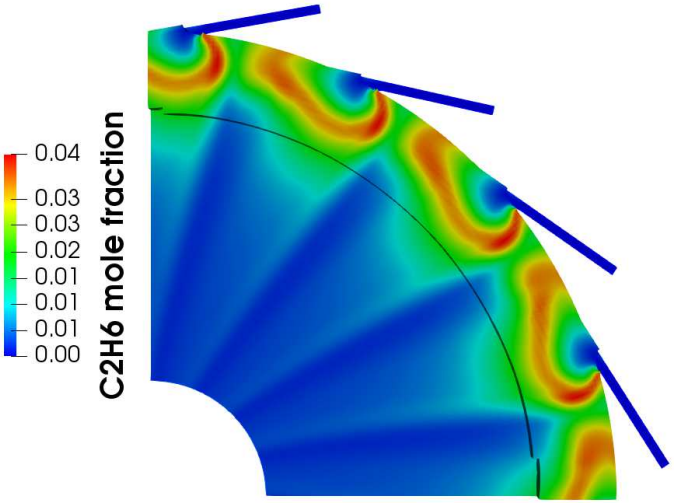
Sr/La_2O_3 catalyst, CH_4:O_2 = 4, no N_2 dilution, T_{in} = 900 K



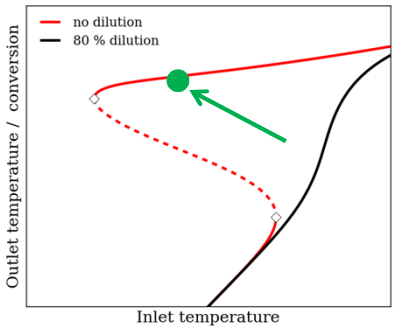
Volume-weighted average bed temperature 1425 K



CH_4 conversion ~ 50 %



C_2 selectivity ~ 38 %
36 % C_2H_4 + 1.5 % C_2H_6



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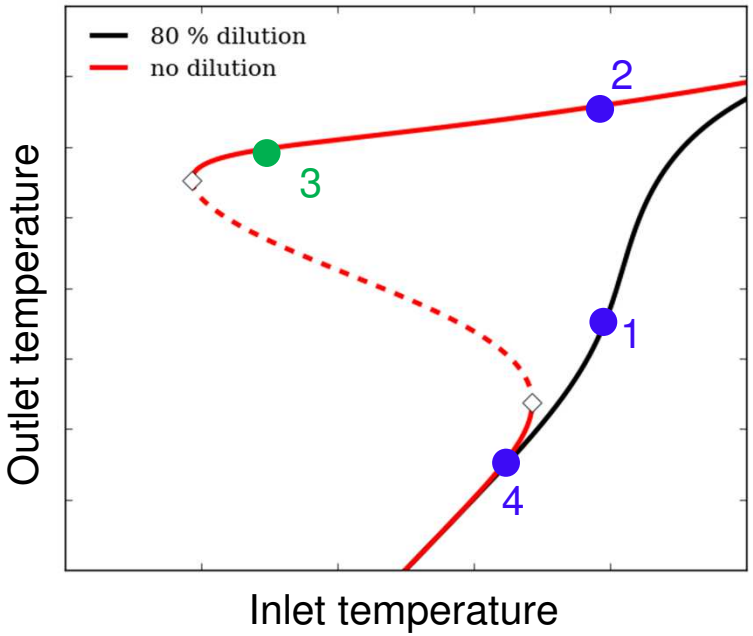
2D simulation, 16 slots, D_R = 8 cm, $U_{g,inj}$ = 85 m s^{-1}
Total catalyst loading ~10 g if L_R/D_R = 0.2, d_s = 500 µm
Catalyst porosity 0.27, A/V = 5e6 m^2/m^3

Autothermal operation in a GSVR

Qualitative bifurcation behavior for GSVR conditions



1. 80% N_2 dilution, T_{in} = 1023 K
2. No N_2 dilution, T_{in} = 1023 K
3. No N_2 dilution, T_{in} =900 K
4. No N_2 dilution, T_{in} = 973 K

   80% N_2 dilution, T_{in} = 973 K

✓ Sufficient thermal backmixing

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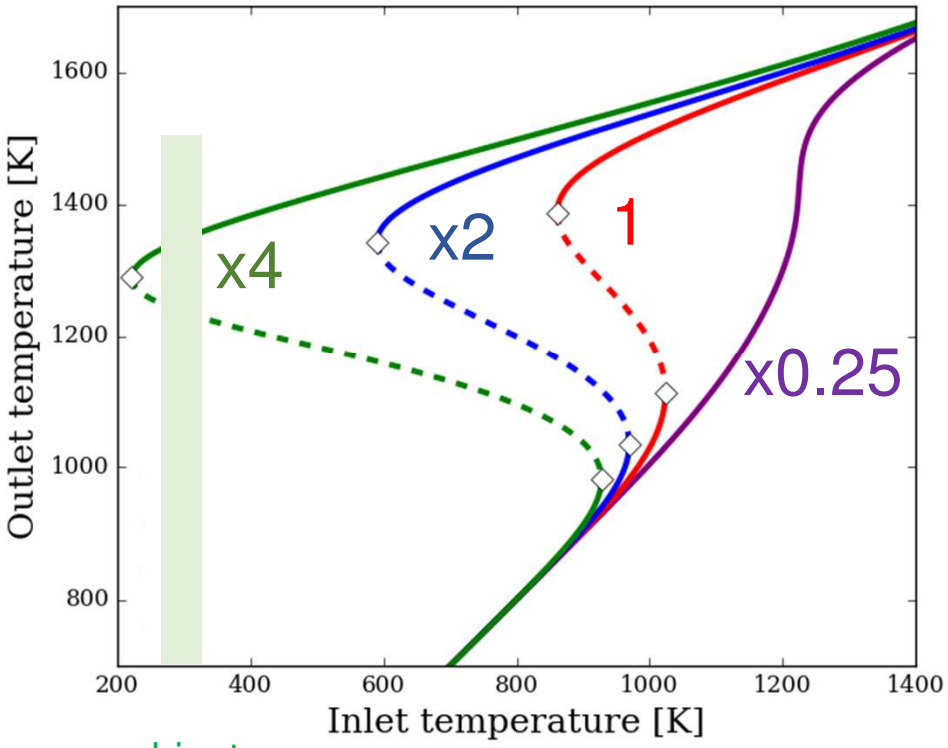
Effect of catalyst activity

A **more active catalyst** should allow to operate with **ambient inlet temperature**



ambient

1: Sr/La_2O_3

Outline

- Introduction
- Super Dry Reforming
- Oxidative coupling
- Conclusions and Perspectives

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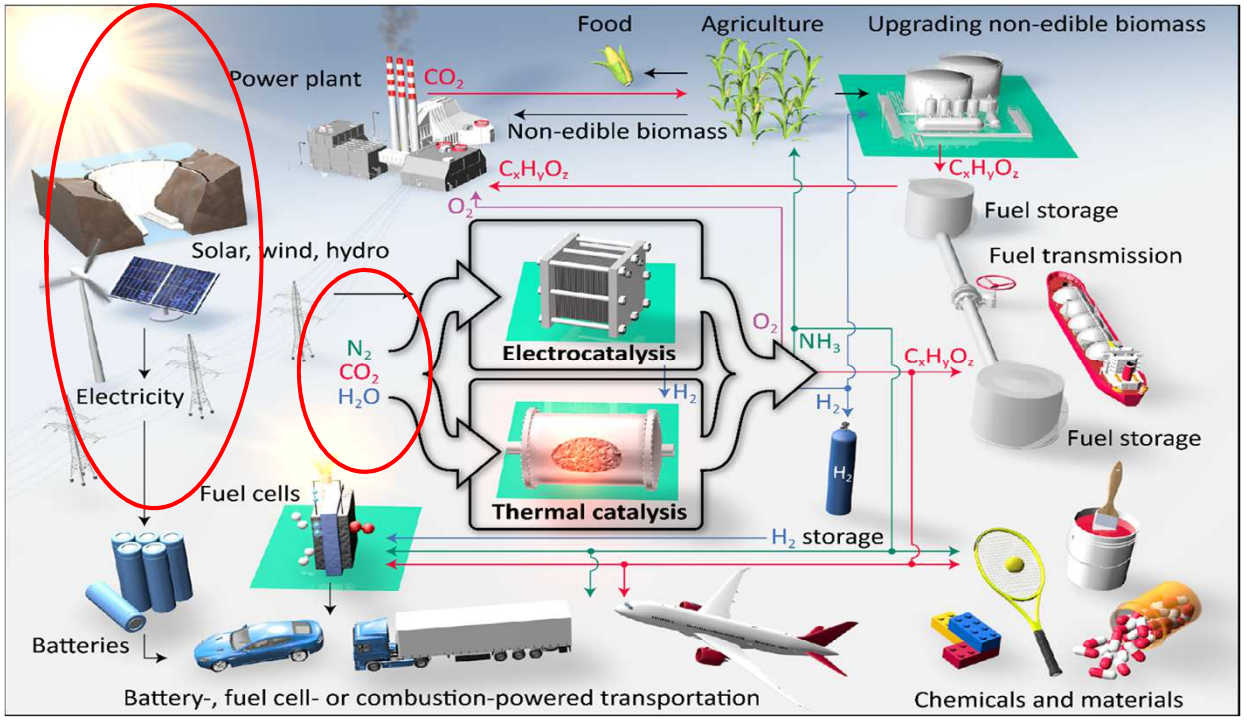
Chemical engineering and catalysis: ENERGY-X



"Research needs towards sustainable production of fuels and chemicals"
White paper by Jens K. Norskov et al. (2019)

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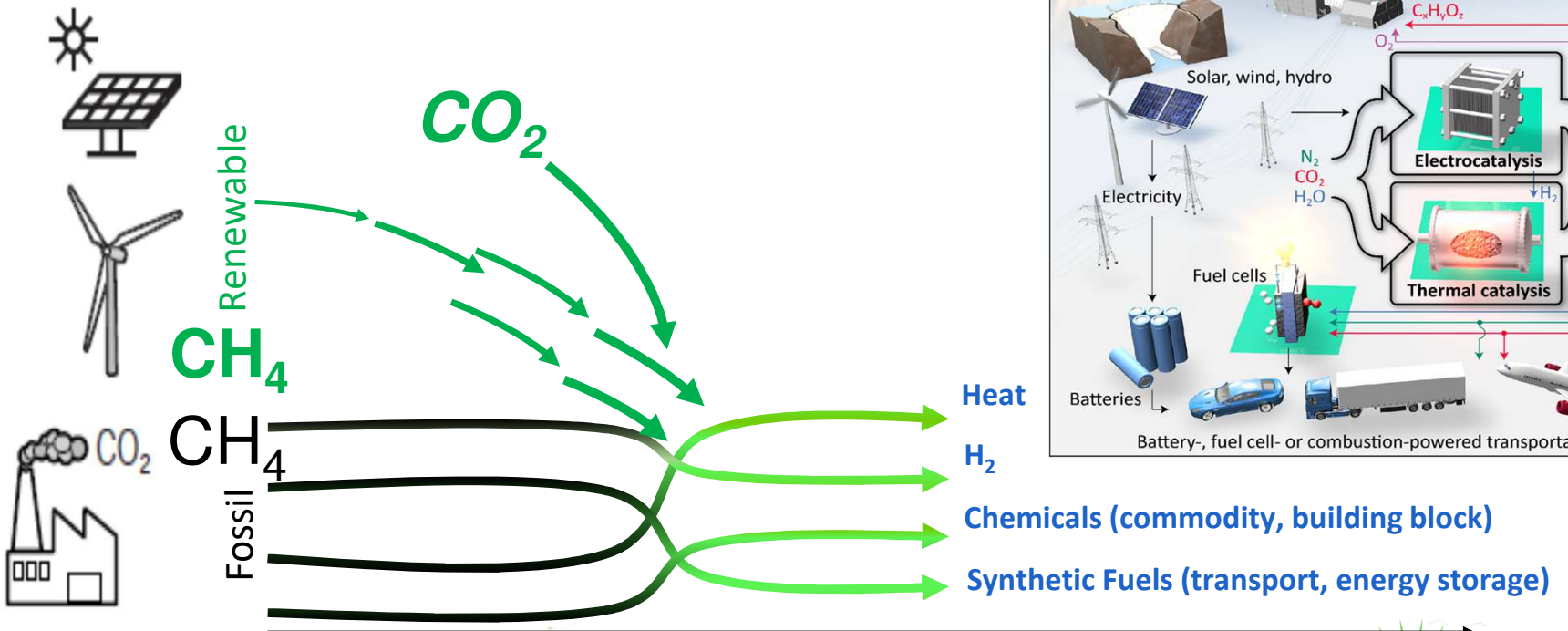
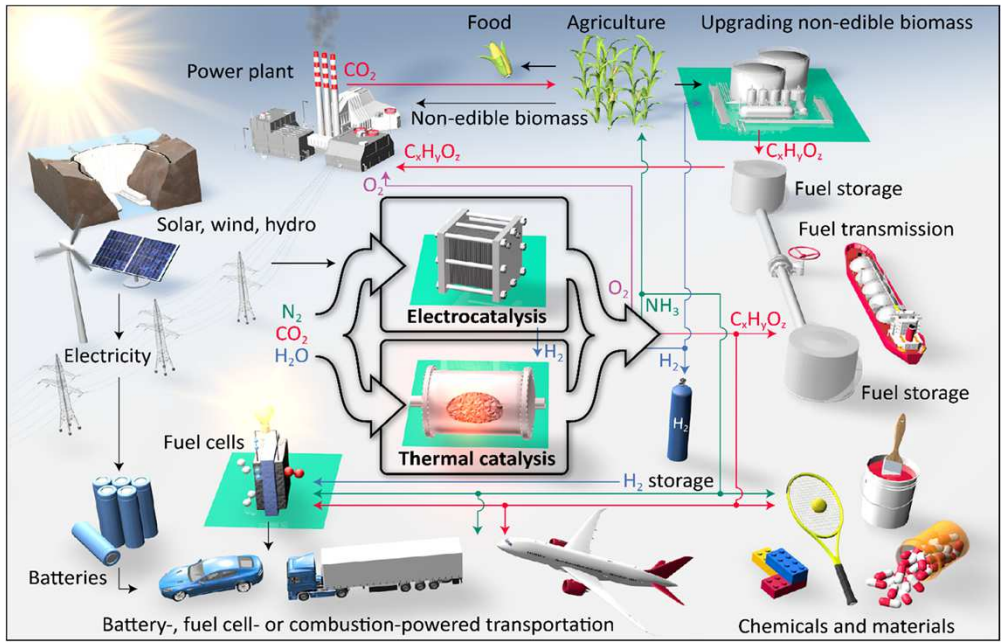
ENERGY X

Chemical engineering and catalysis: ENERGY-X





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K.M. Van Geem et al., Science, 364 (6442) 6442 734 (2019)

ENERGY X

Conclusions and Perspectives

- Combine
  - computational and experimental techniques
  - material and process development
  - chemical engineering and catalysis
    - Transport phenomena on lab and industrial scale
    - Autothermal adiabatic operation of exothermic reactions
- Think out of the box
- Do not bother about “old wine in new bottles”
- Do not neglect stoichiometry, thermodynamics and kinetics

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