Carbon-Catalyzed Methane Pyrolysis in Fluidized-Bed Reactors: Analytical Investigation of Polyaromatic Hydrocarbon Formation and Two-Phase Reactor Modeling

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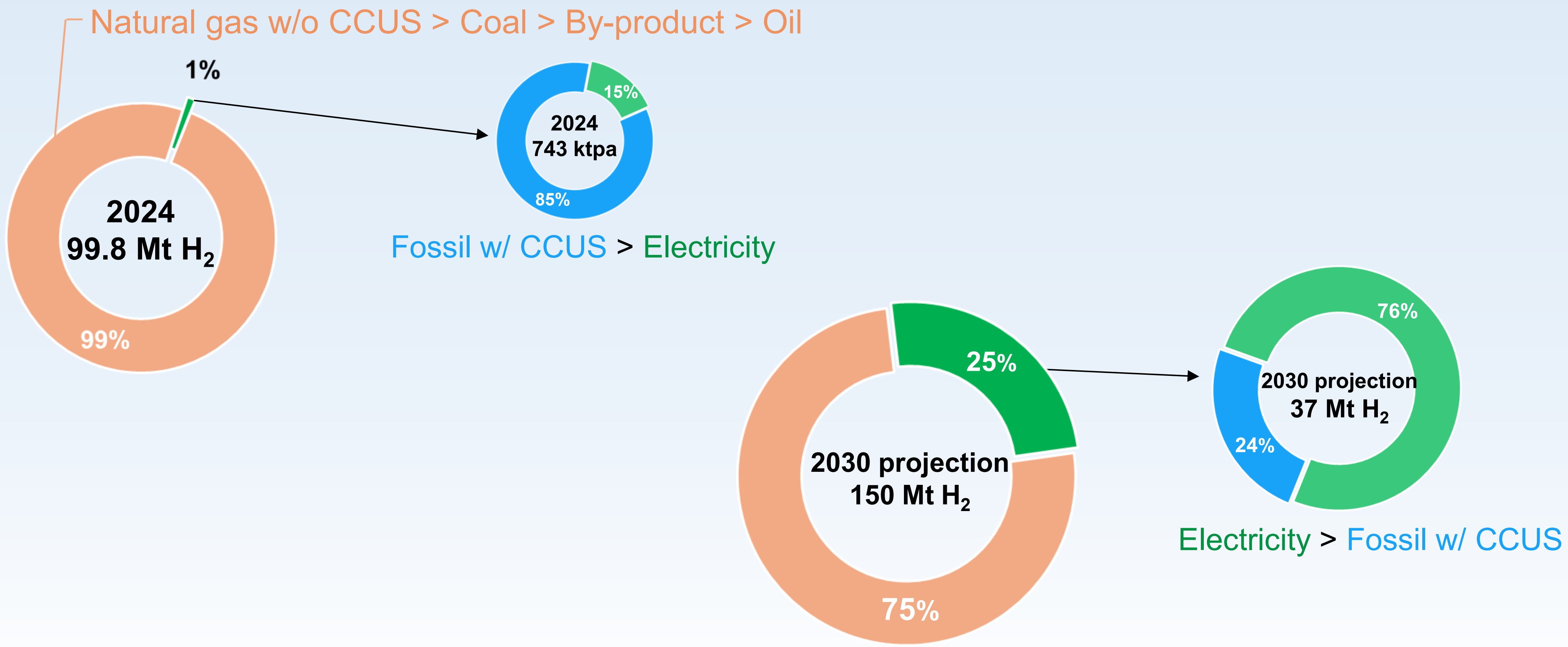
(IEA (2025), Global Hydrogen Review 2025)

Hydrogen economy

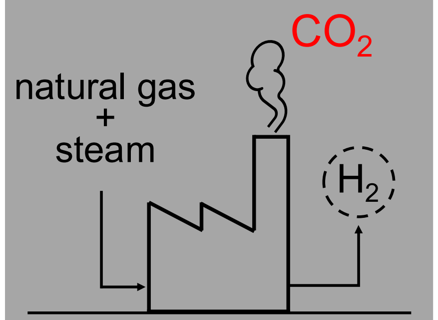


Low-emission H_2 can avoid **950 Mtpa** CO_2 emission in industry and refining

Methane Pyrolysis for H_2 and Solid Carbon

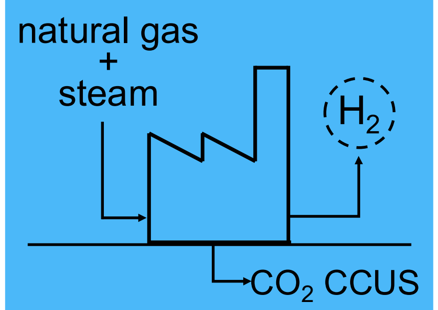
(N. Sánchez-Bastardo et al., Ind. Eng. Chem. Res. 2021, 60)
(A.O. Oni et al., Energy Convers. Manag. 2022, 254)
85% onsite emissions captured
(IEA (2025), Global Hydrogen Review 2025)

GREY HYDROGEN



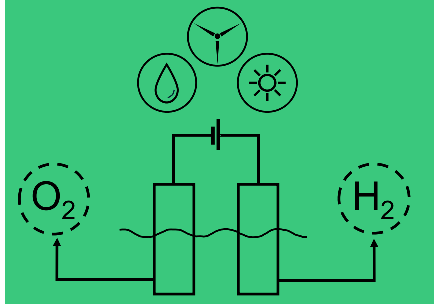
Steam methane reforming or ATR

BLUE HYDROGEN

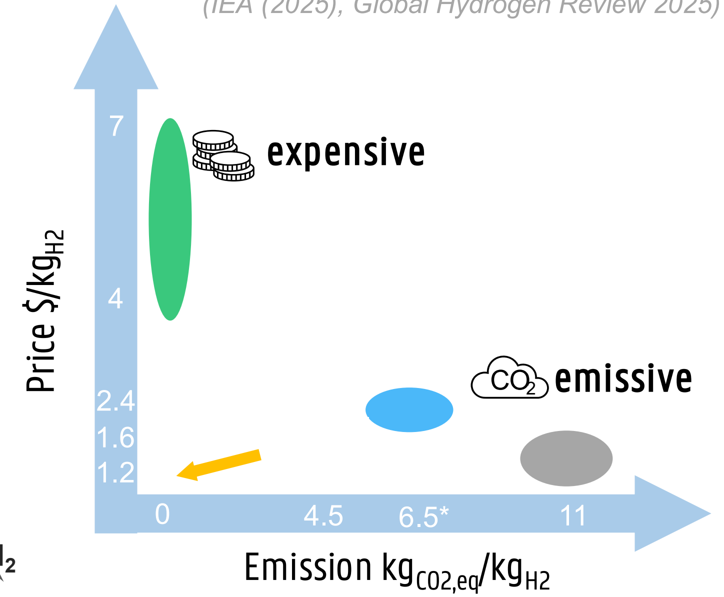


Steam methane reforming or ATR + CCUS

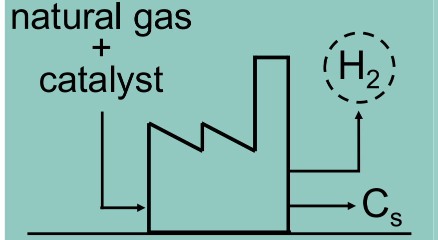
GREEN HYDROGEN



Water electrolysis (AWE, PEM or SOEC)



TURQUOISE HYDROGEN

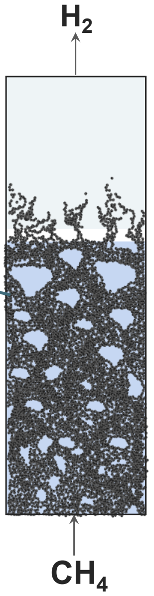


Methane pyrolysis

$$CH_4 \rightleftharpoons 2H_2 + C_{solid}$$

$$\Delta H_{298K} = 37.7 \text{ kJ/mol}_{H2}$$

carbon ↔ metal catalyst

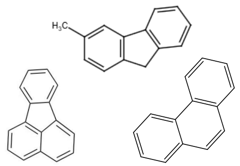


fluidized-bed of catalyst and/or inert particles

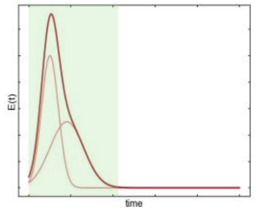
1. avoids aggregation of solids and ΔP↑
2. uniform heating
3. continuous solids handling possible

- potential for electrification

AROMATICS



REACTOR MODEL



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Outline

Introduction methane pyrolysis for turquoise H_2

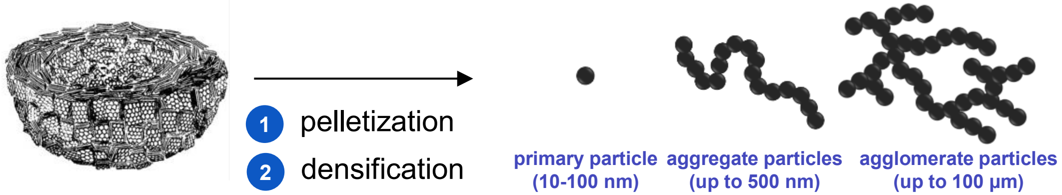
Carbon catalyst and reactor setup

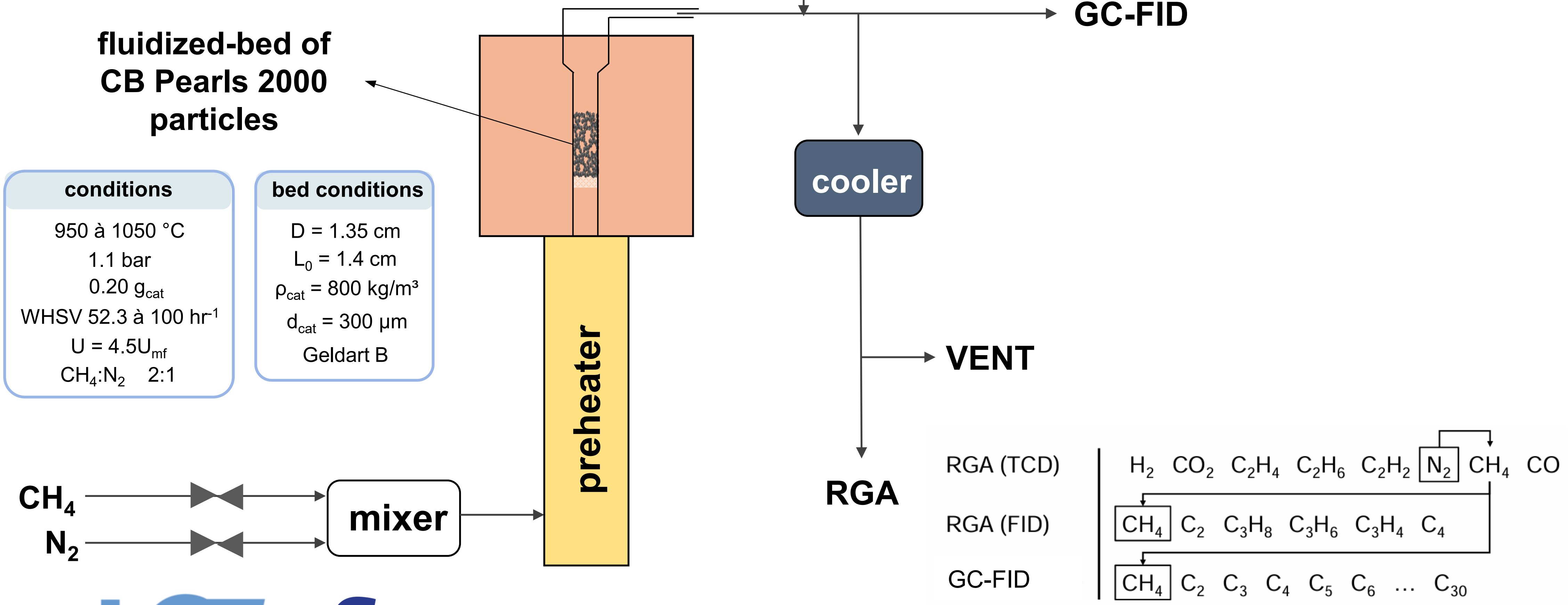
Activity tests and polyarmotic hydrocarbons

Two-phase fluidized-bed reactor model and simulation

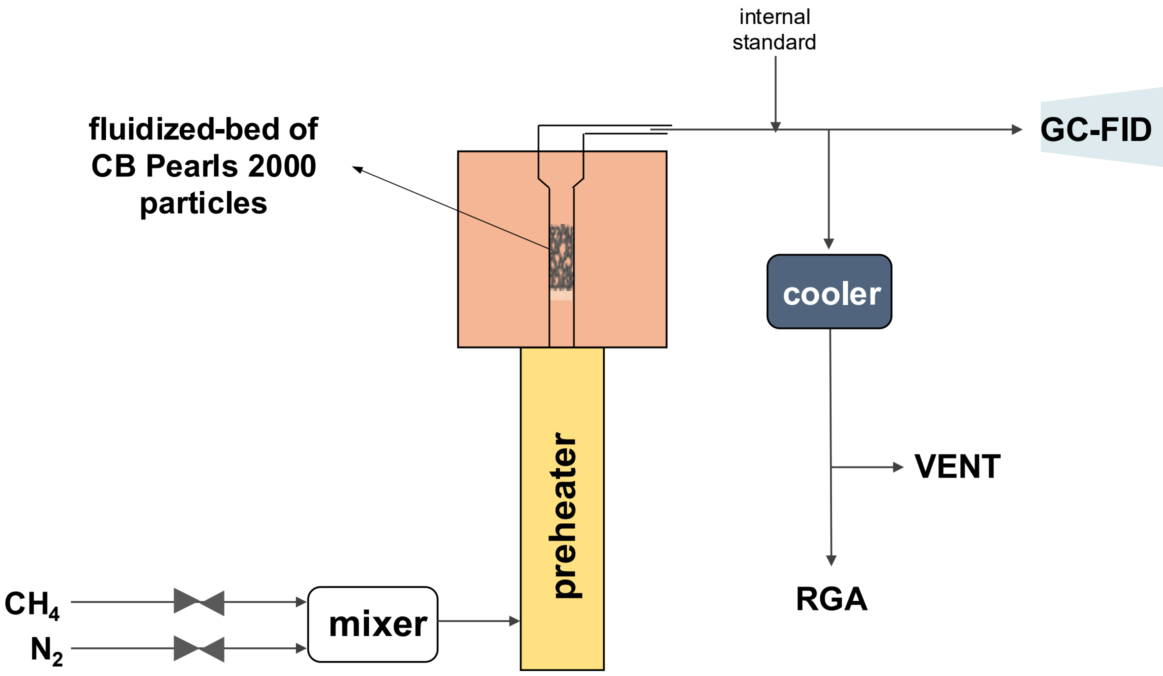
Key takeaways

Catalyst Activity Tests – Methodology





Catalyst Activity Tests – Methodology



IDENTIFICATION OF POLYAROMATIC HYDROCARBONS

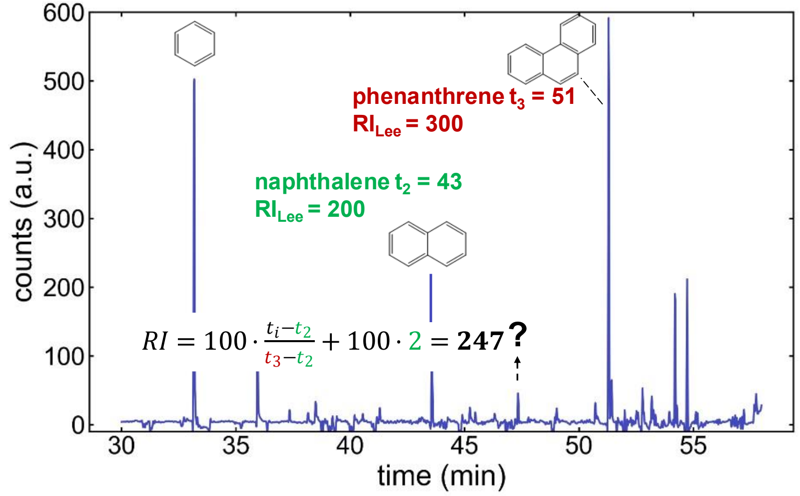
1. Kovats – Van den Dool retention indices
→ ex-situ injection n-alkane mixture

pentane: 500
hexane: 600
…
dodecane: 1200
→ **n is the number of carbons**

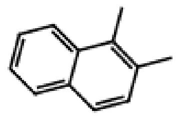
2. Lee aromatic retention indices
→ ex-situ injection benzene, naphthalene, phenanthrene and chrysene

benzene: 100
naphthalene: 200
phenanthrene: 300
chrysene: 400
→ **n is the number of rings**

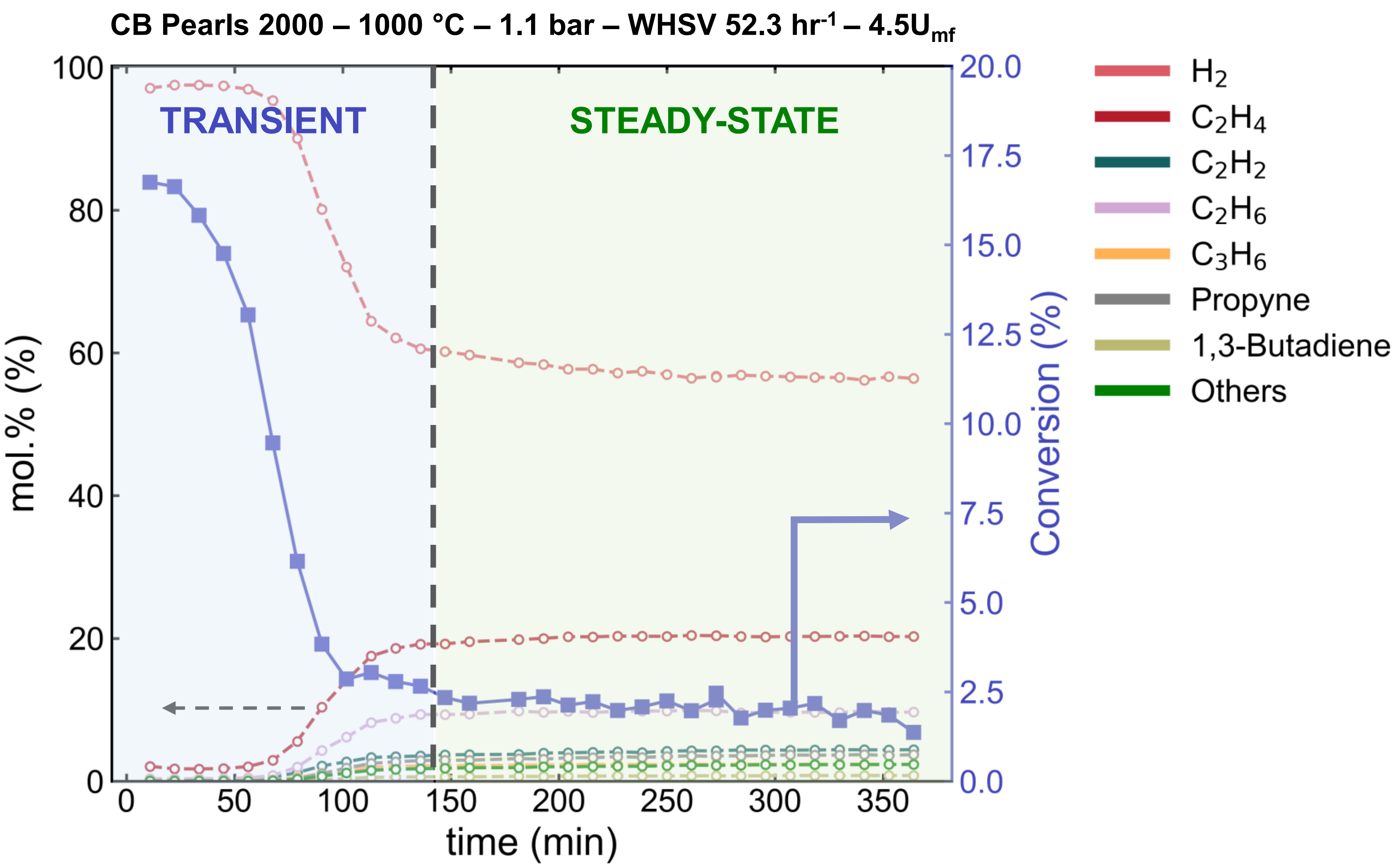
$$RI = 100 \cdot \frac{t_i - t_n}{t_{n+1} - t_n} + 100 \cdot n$$



comparison with
- literature
- Nist

→ 

Catalyst Activity Tests – Results CB Pearls 2000



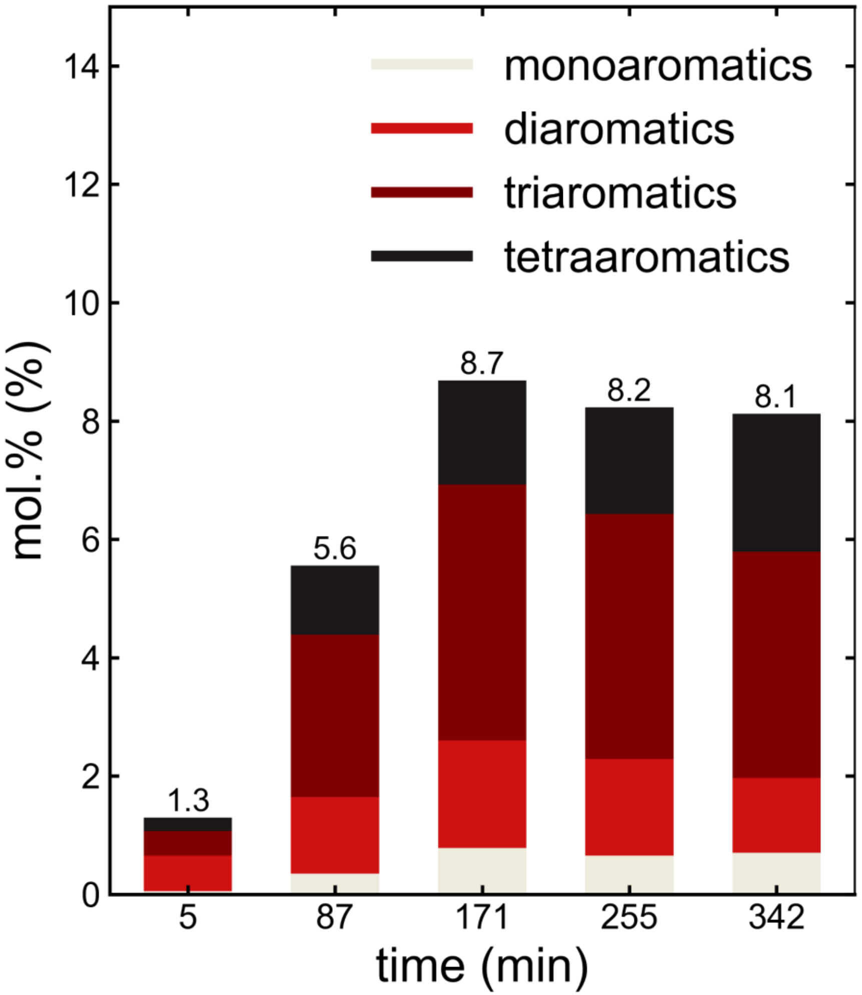
TRANSIENT PHASE

CH_4 conversion 16.7%
H_2 97.1 mol.%

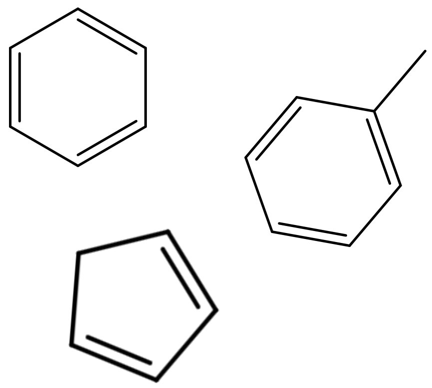
STEADY-STATE PHASE

CH_4 conversion 1.4%
H_2 56.4 mol.%
C_2H_4 20.3 mol.%
C_2H_6 9.7 mol.%
C_2H_2 4.4 mol.%
C_3H_6 2.4 mol.%

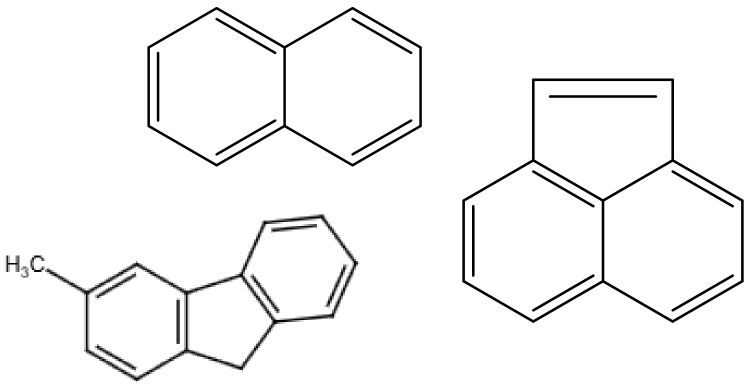
Catalyst Activity Tests – Results CB Pearls 2000



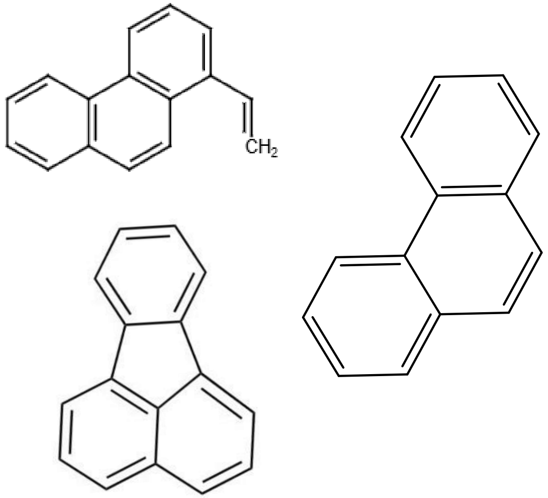
MONOAROMATICS



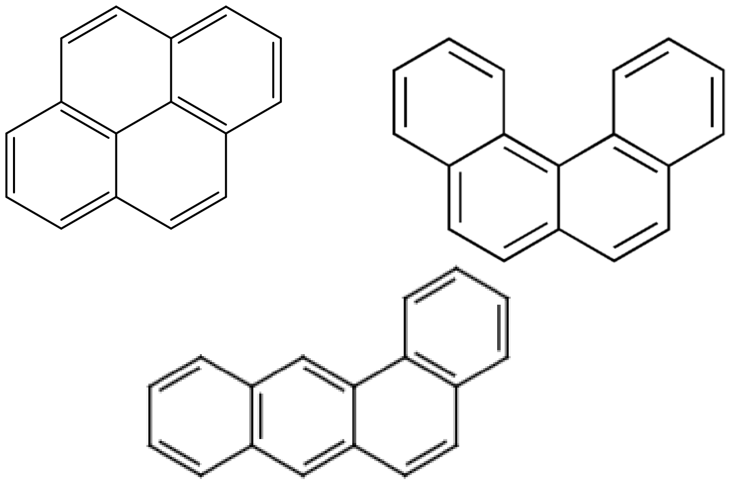
DIAROMATICS



TRIAROMATICS



TETRAAROMATICS



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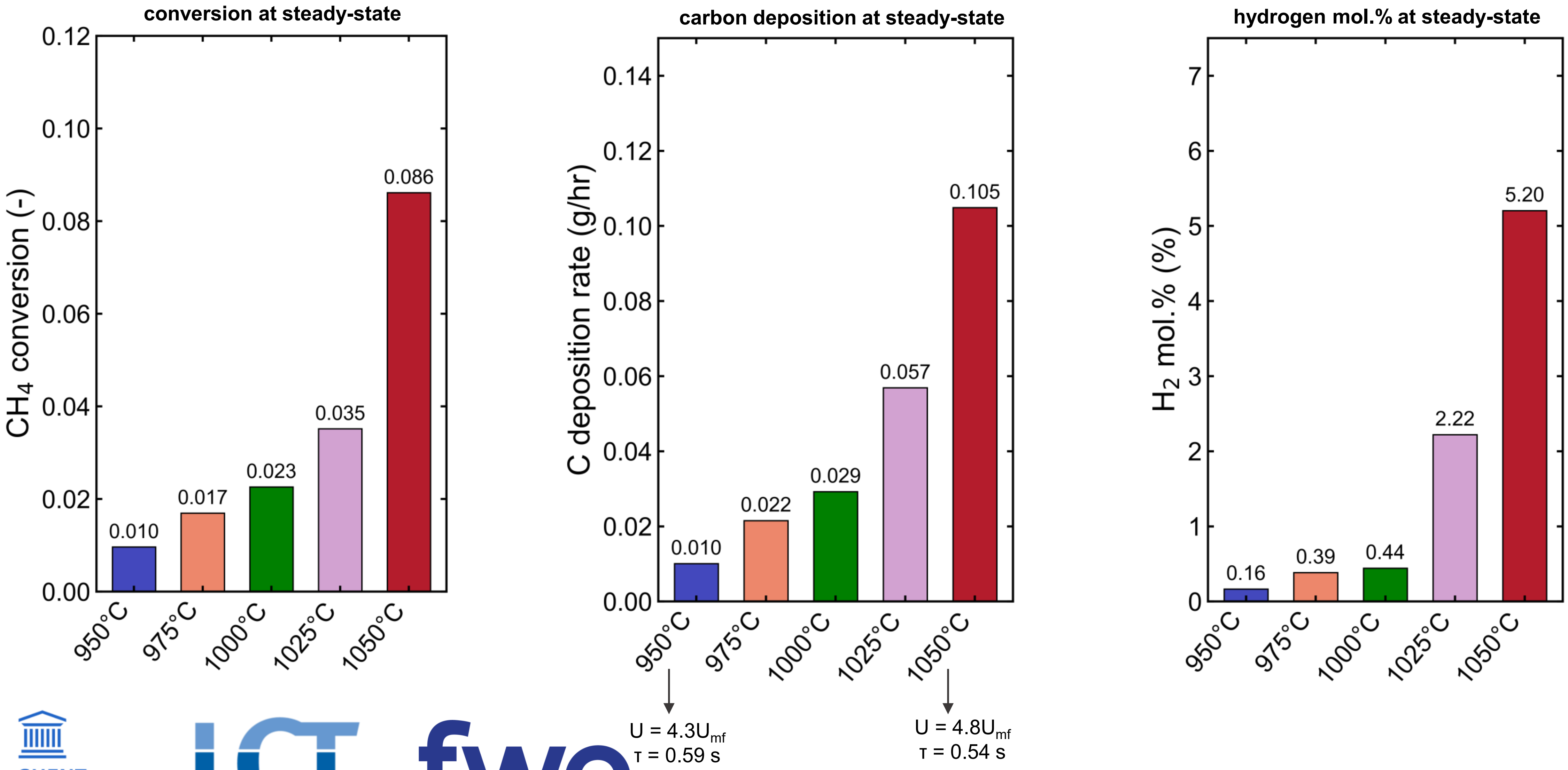
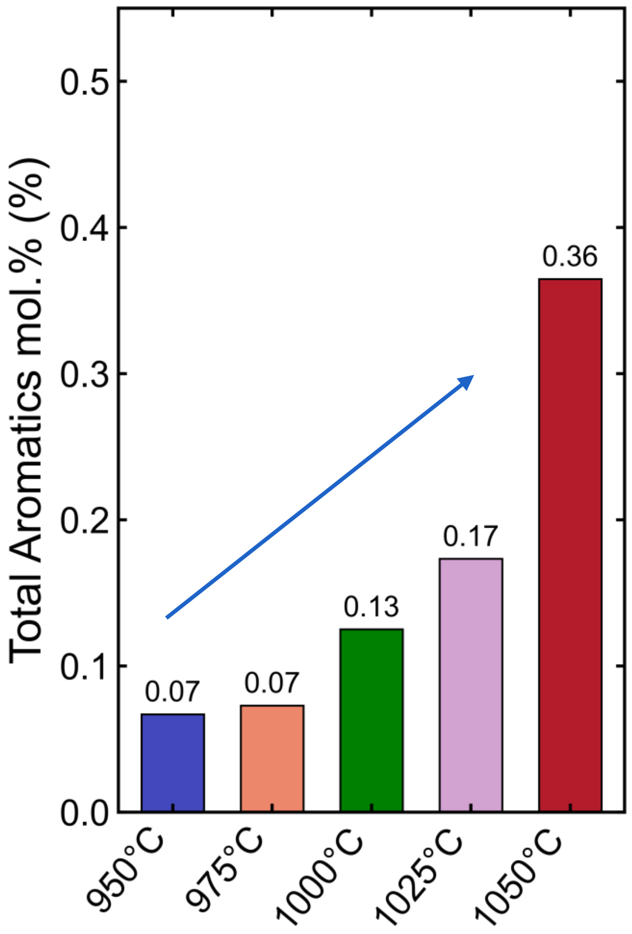
Catalyst Activity Tests – Results CB Pearls 2000



(A. Khrabry et al., Int. J. Hydrogen Energy 2024, 56)

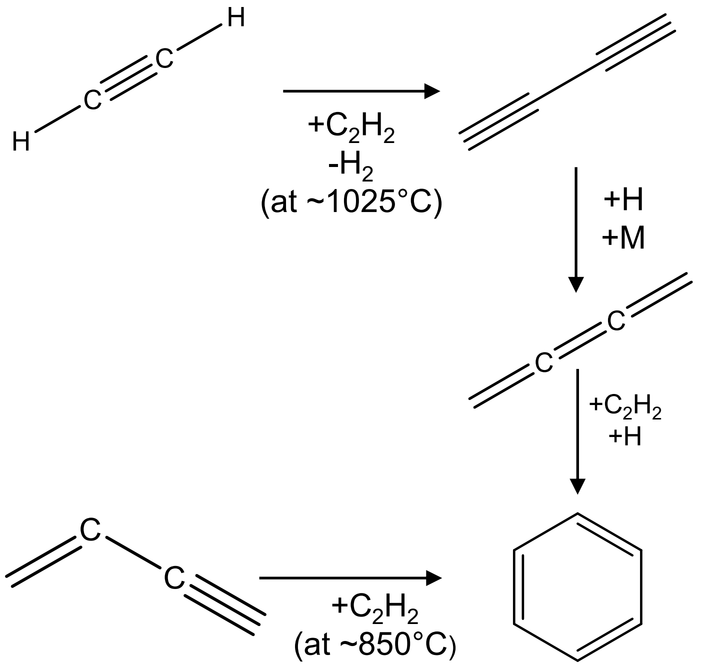
Catalyst Activity Tests – Results CB Pearls 2000

total aromatics mol.% at steady -state

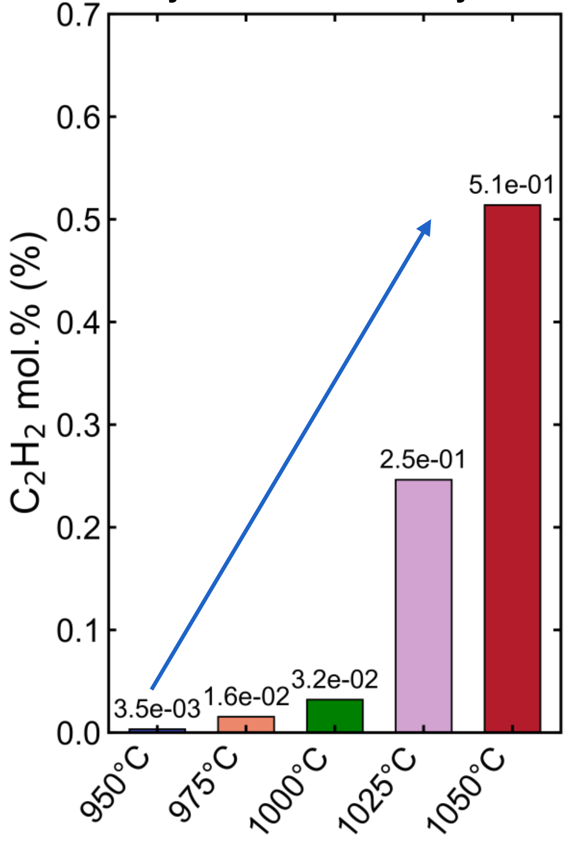


POLYAROMATIC HYDROCARBONS

Increase of Polyaromatic Hydrocarbons concentration in product stream along with increase in acetylene outlet concentration

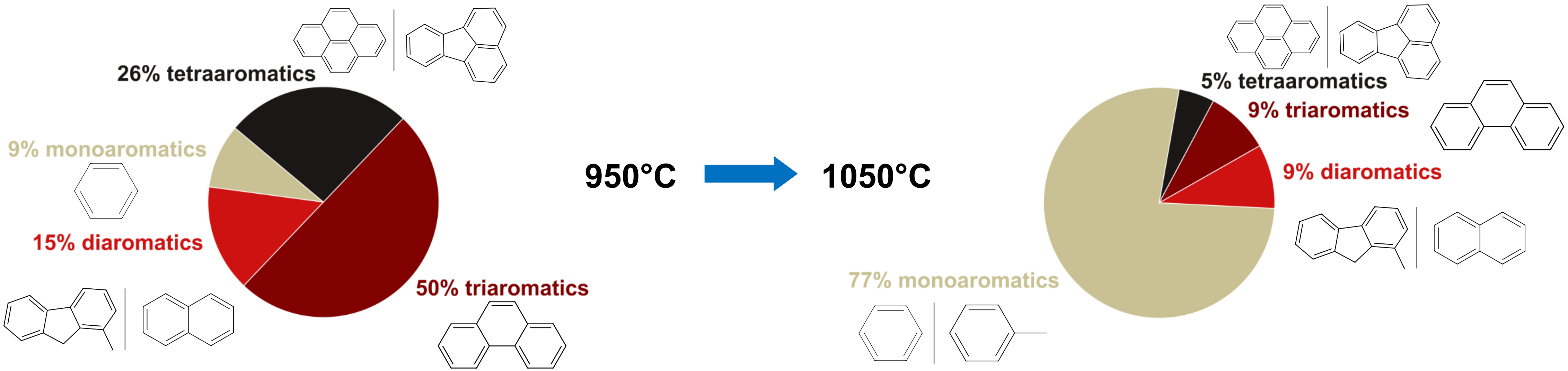


acetylene mol.% at steady-state

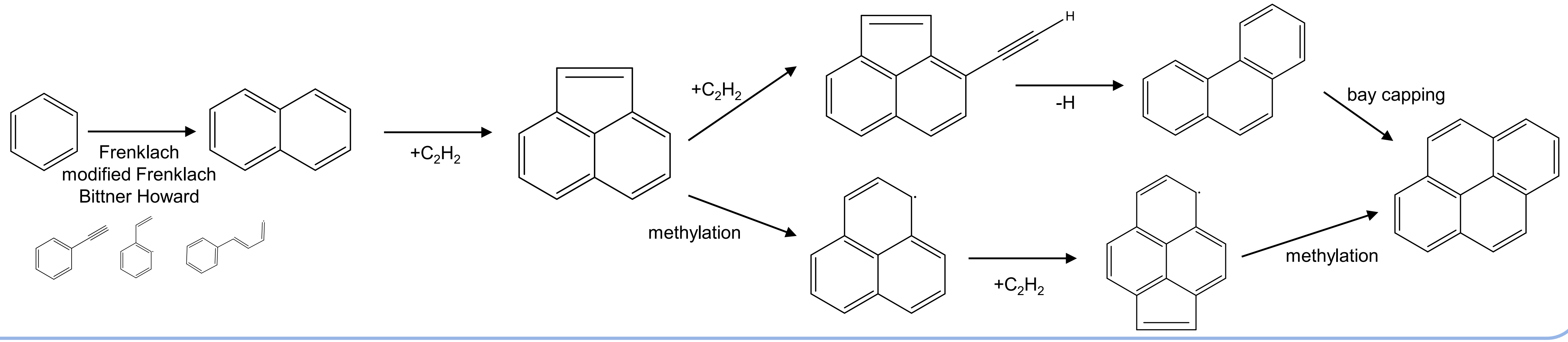


Catalyst Activity Tests – Results CB Pearls 2000

EXPERIMENTS



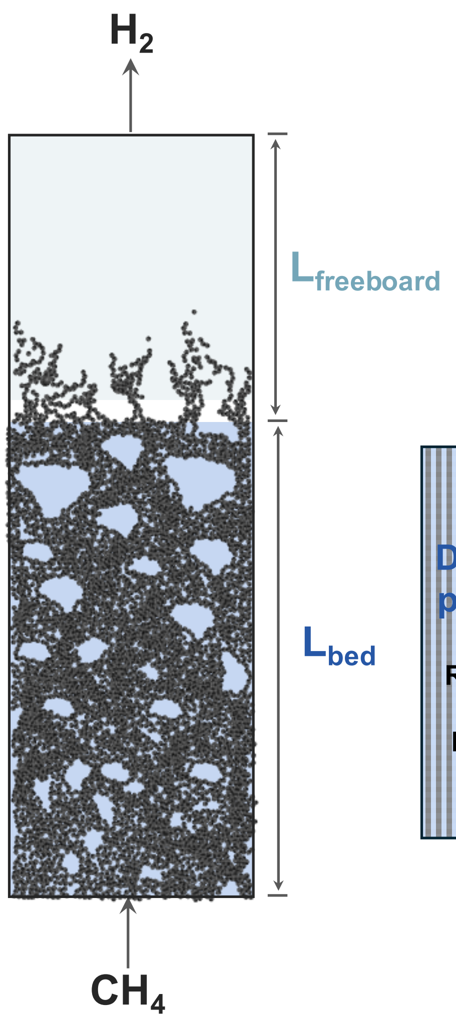
KINETICS THEORY

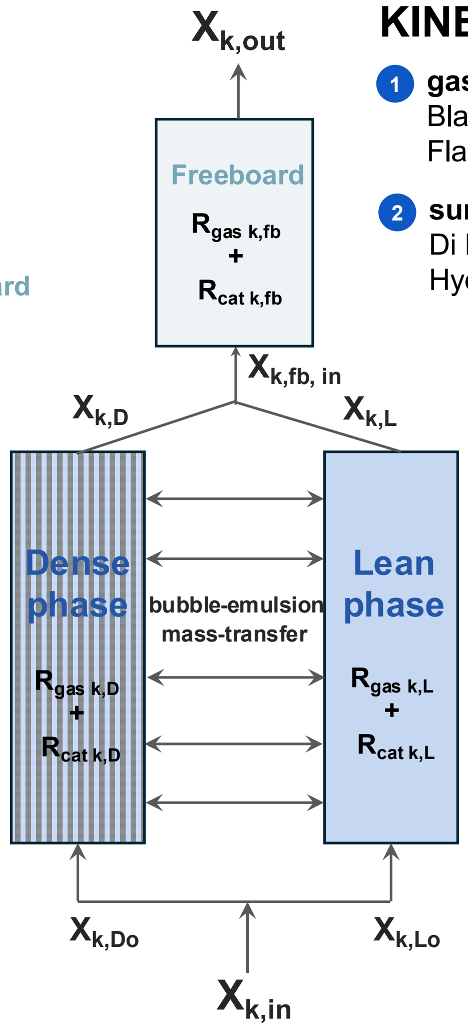


(T. Chu et al., Phys. Chem. Chem. Phys. 2019, 21)
(M. Frenklach et al., Proc. Combust. Inst. 2019, 37)
(M. Frenklach et al., Phys. Chem. Chem. Phys. 2024, 26)

(Abba et al., AIChE J., 2003 49 (7))
(D. Kunii and O. Levenpiel, Fluidization Engineering, 1991)
(N. Mostoufi et al., Ind. Eng. Chem. Res., 2001 40 (23))
(M. Horio and A. Nonaka, AIChE J., 1987 33(11))

Two-Phase Fluidized-Bed Reactor Modeling





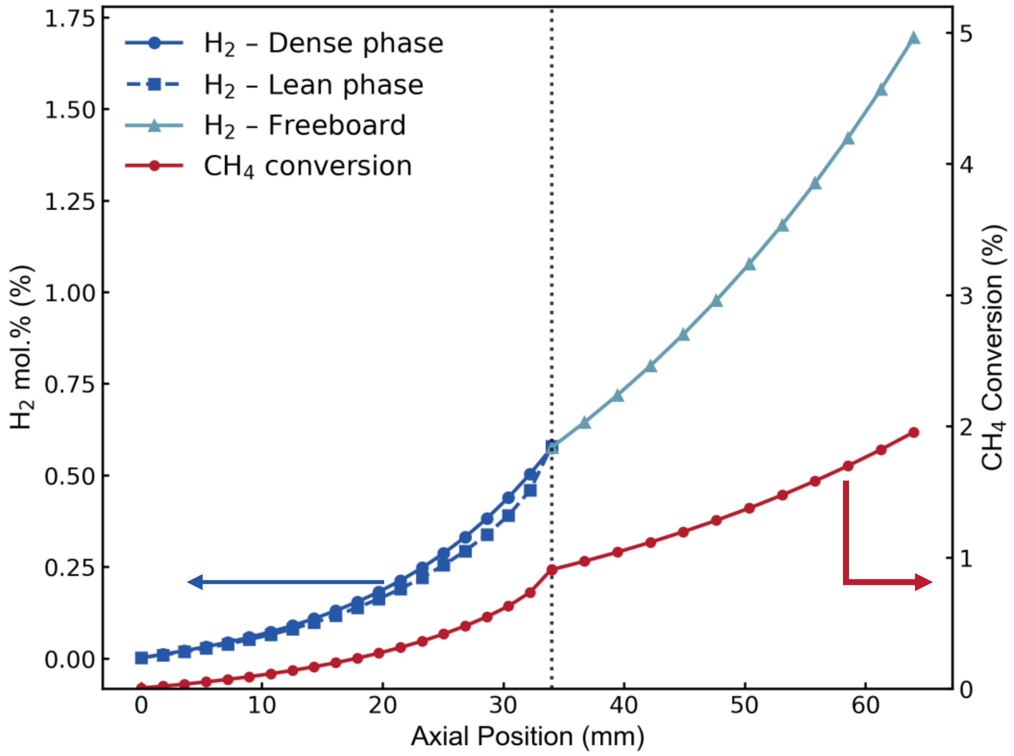
KINETICS

1. **gas-phase Caltech** – G. Blanquart et al., Combust. Flame., 2009 156 (3).
2. **surface-phase HACA** – L. Di Liddo et al., Int. J. Hydrog. Energy., 2024 86.

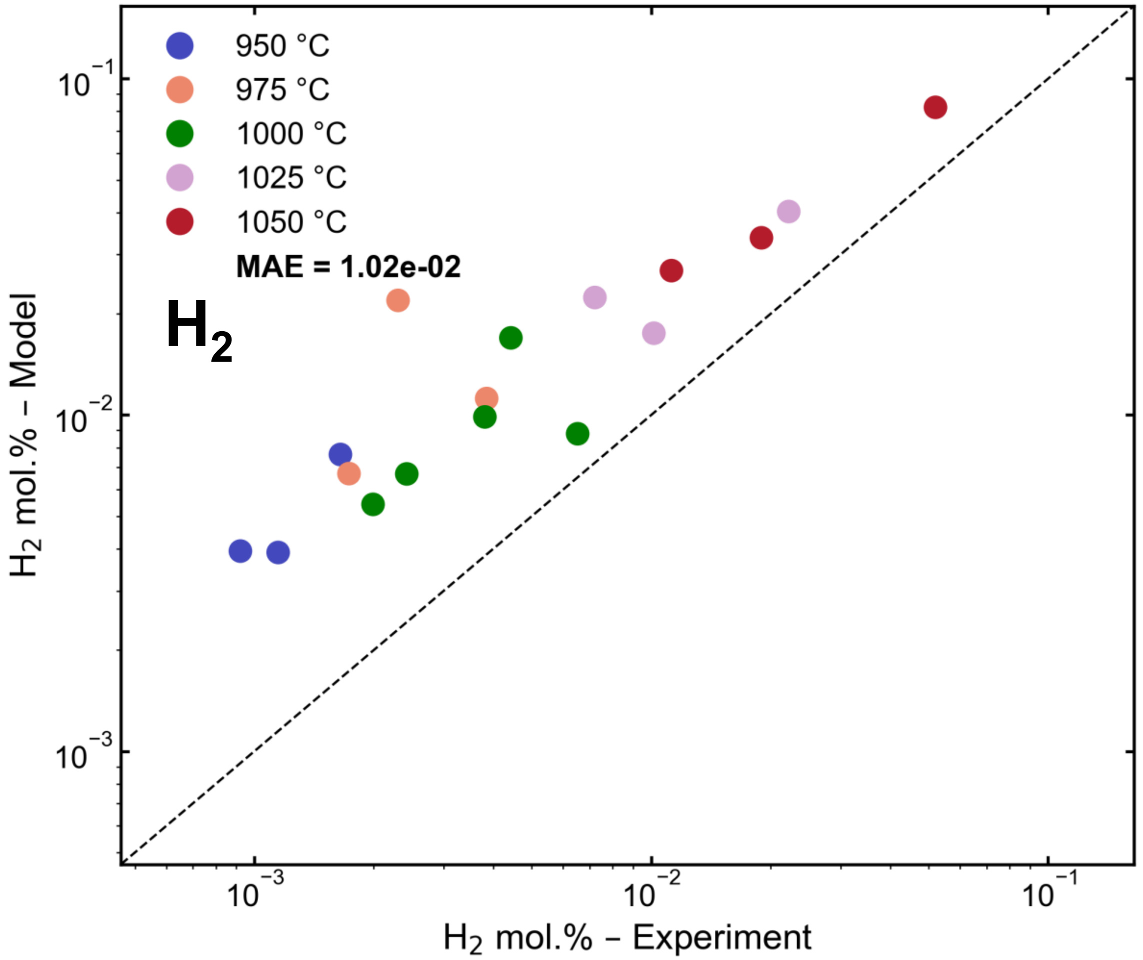
TWO-PHASE FLUIDIZED-BED REACTOR SIMULATION

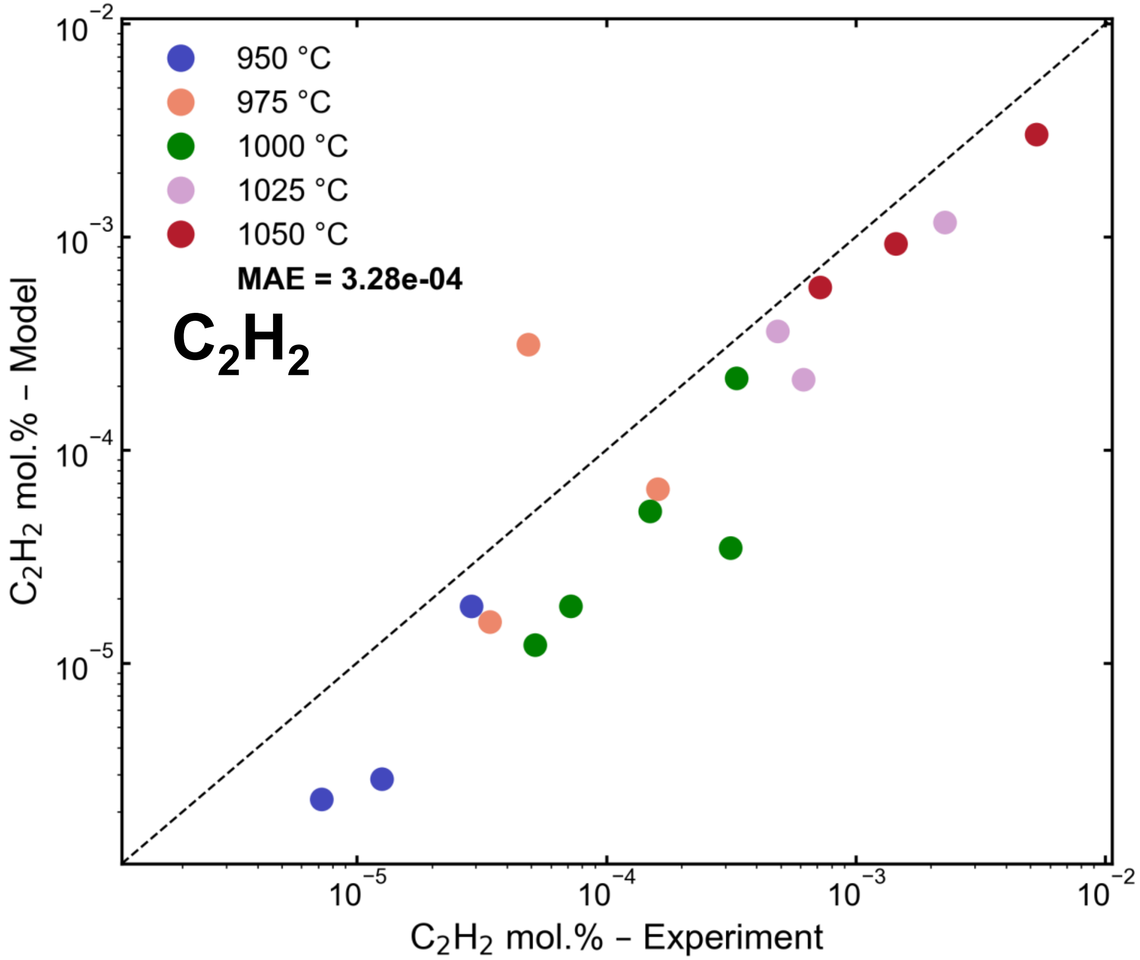
DENSE PHASE	LEAN PHASE
Emulsion	Bubble
Most catalytic reactions	Little catalysis
High axial dispersion	Low axial dispersion

larger catalytic conversion in dense bed-zone



Two-Phase Fluidized-Bed Reactor Simulation





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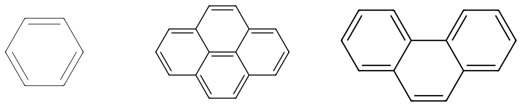
Key takeaways

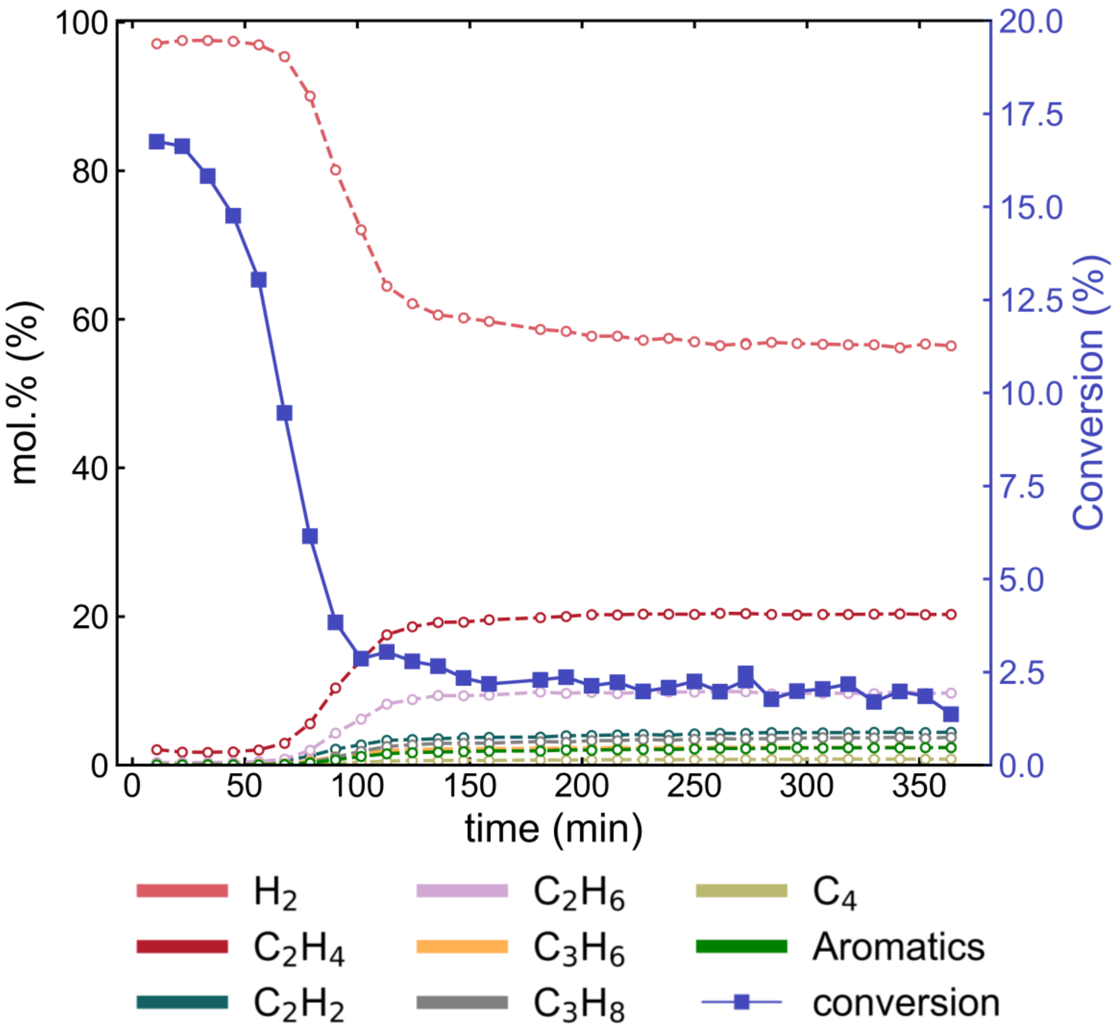
1. Methane pyrolysis for reduced emissions

2. Higher T and residence time → higher H_2 yield

3. Higher T → higher fraction of aromatics
   → benzene, pyrene, phenanthrene largest fraction



4. The kinetic mechanism performs well for hydrogen and C2 species but needs improvement for polyaromatic hydrocarbons



Acknowledgments

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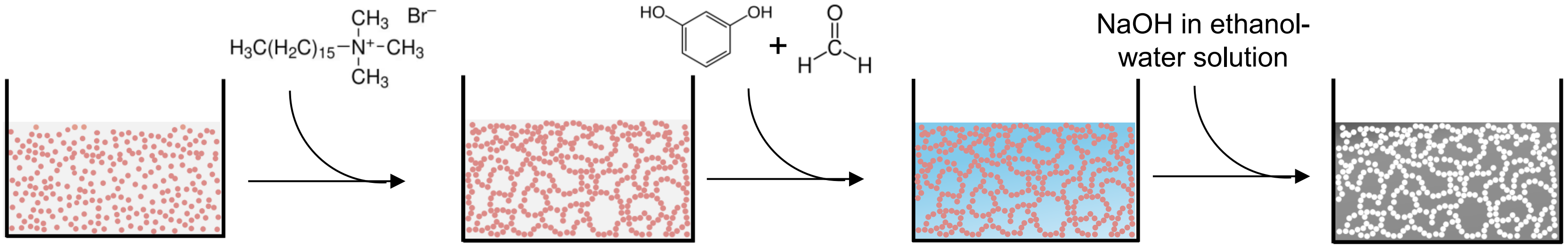
Carbon Catalysts

SMC2

colloidal silica (Ludox HS-40)	stabilized silica	silica-polymer composite	carbon



1. stabilization silica particles with CTAB surfactant (30 minutes at 50°C in mixer)
2. addition resorcinol and formaldehyde under mild suction
3. polymerization: 3 days 85°C with Na_2CO_3 catalyst
4. carbonization
5. leaching silica template
6. filtration + washing

properties

BET-surface (m^2/g)	micro/ mesopore surface ratio	pore volume (cm^3/g)
1234.3	0.08	2.64

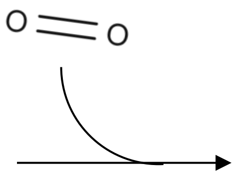
CB Pearls 2000

hydrocarbon feedstock	primary particles	carbon black

gas

aromatics

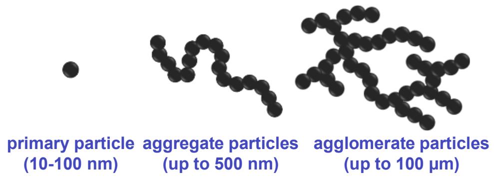
oil



1. partial comustion of hydrocarbons (1200 à 1900 °C)

conventional CB consisting of concentric regions of graphite

2. pelletization
3. densification



CABOT

properties

BET-surface (m^2/g)	micro/ mesopore surface ratio	pore volume (cm^3/g)
1425	0.69	1.27

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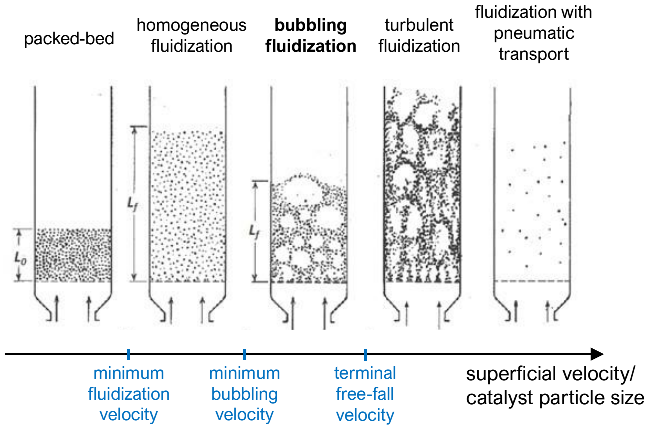
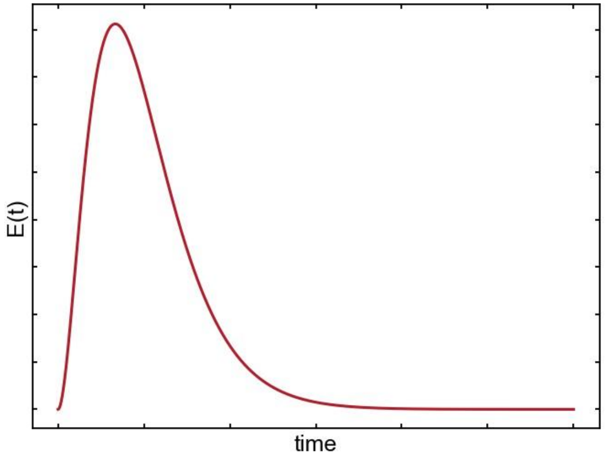
Two-phase fluidized-bed model

(Kunii, Levenspiel, 1991)
(Leva et al, 1959)
(Abba et al, 2003)

REALITY

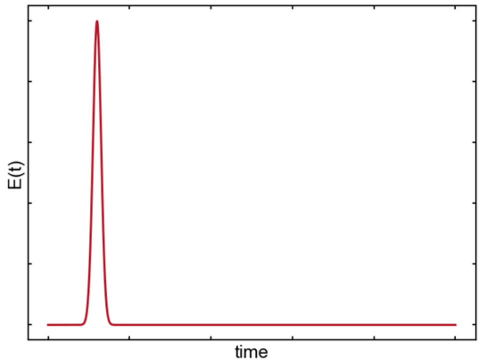


Residence time distribution fluidized-bed

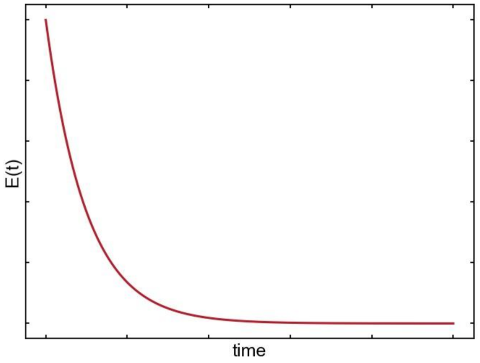


MODEL

Residence time distribution plug-flow



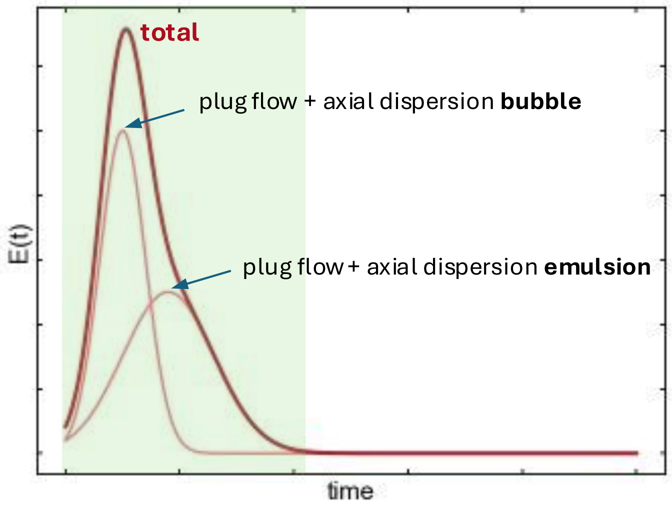
Residence time distribution CSTR

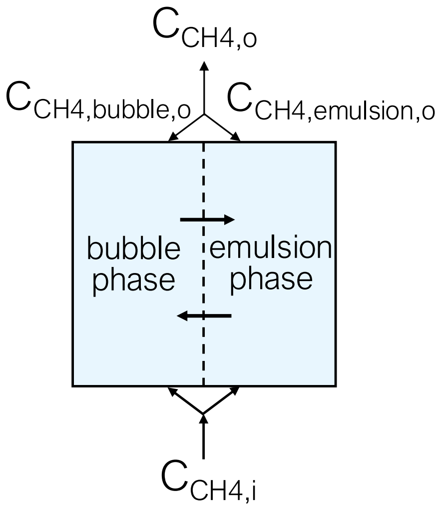


Not correct to model as one CSTR or one plug flow (with axial dispersion)

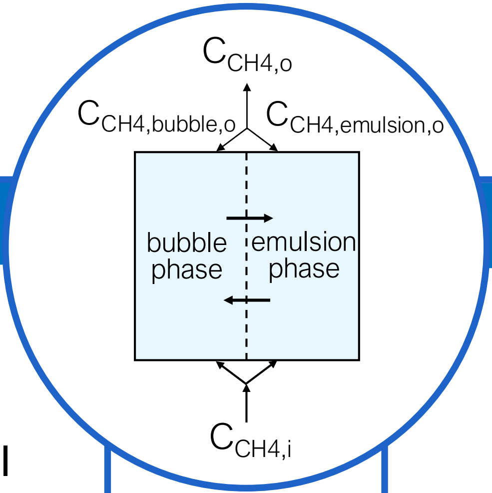
two phases required

Residence time distribution model



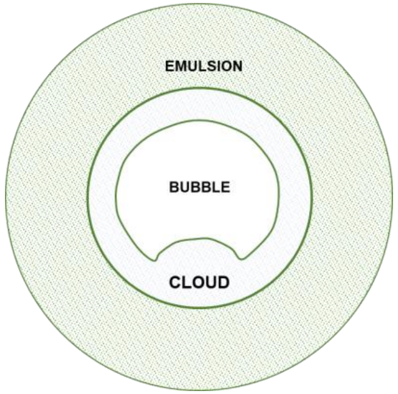


Two-phase fluidized-bed model



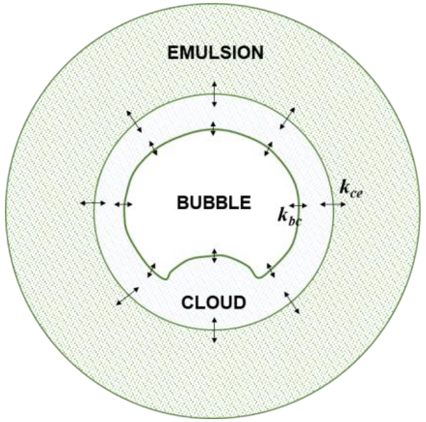
BUBBLE PHASE

- Gas in excess for U_{mf} flows as bubbles through the bed
- Bubble phase essentially in plug flow (small effective diffusivity)
- zones around the bubble
  - bubble
  - wake under bubble
  - cloud (exchange zone)



EMULSION PHASE

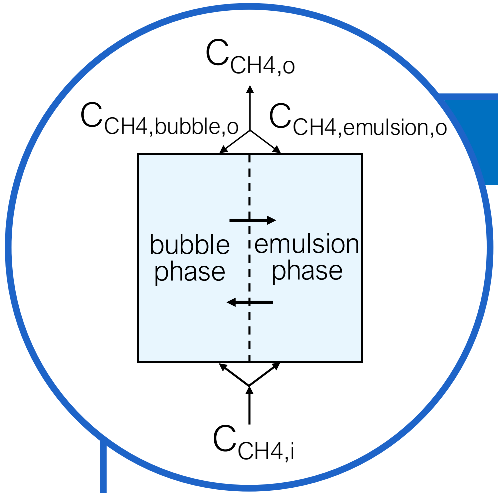
- Emulsion phase exists quasi minimum fluidization conditions
- Emulsion phase in plug flow with effective diffusivity for mixing
- Interchange of gas with the bubble phase



$$\frac{1}{k_{be}} = \frac{1}{k_{bc}} + \frac{1}{k_{ce}}$$

(Kunii, Levenspiel, 1991)
(Mostoufi et al, 2001)
(Abba et al, 2003)

Two-phase fluidized-bed model



TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

- mean concentration of species A

bubble fraction; gas velocity bubble/emulsion

$$C_A = \frac{\Psi u_b}{U} C_{Ab} + \frac{(1-\Psi) u_e}{U} C_{Ae}$$

- mass balance emulsion:

$$u_e \frac{dC_{Ae}}{dz} = K_{be} a_I \epsilon_b \frac{\Psi}{1-\Psi} (C_{Ab} - C_{Ae}) + \rho_e R_{Ae} + D_{ze} \frac{d^2 C_{Ae}}{dz^2}$$

change of component A in emulsion; emulsion-bubble mass transfer; production rate in emulsion; effective axial diffusion for mixing

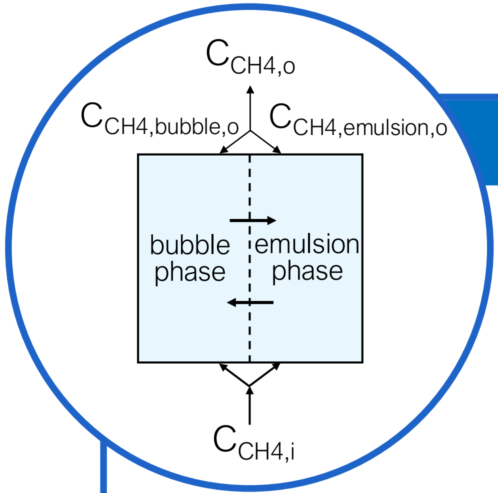
- mass balance bubble:

$$u_b \frac{dC_{Ab}}{dz} = -K_{be} a_I \epsilon_b (C_{Ab} - C_{Ae}) + \rho_b R_{Ab} + D_{zb} \frac{d^2 C_{Ab}}{dz^2}$$

change of component A in bubble; emulsion-bubble mass transfer; production rate in bubble; effective axial diffusion for mixing

(Kunii, Levenspiel, 1991)
(Mostoufi et al, 2001)
(Abba et al, 2003)

Two-phase fluidized-bed model

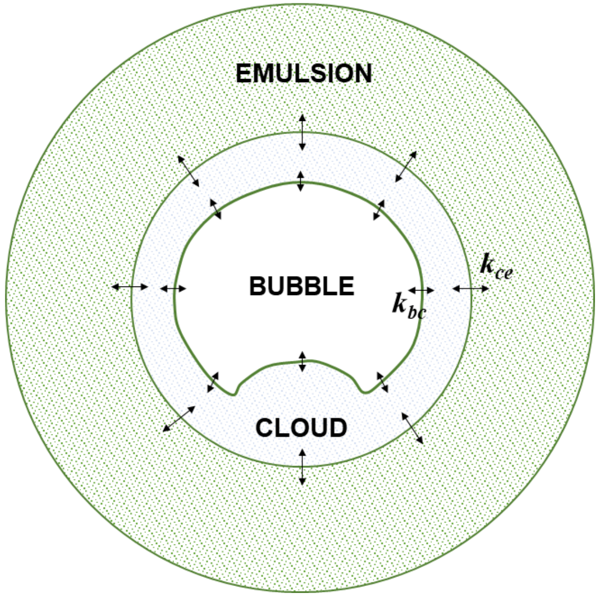


TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

- Bubble to emulsion mass-transfer: $$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}}$$

- Bubble to cloud mass-transfer: $$K_{ce} = 6.77\left(\frac{D_{AB}\epsilon_e\, u_{br}^3}{d_b^3}\right)^{1/2}$$

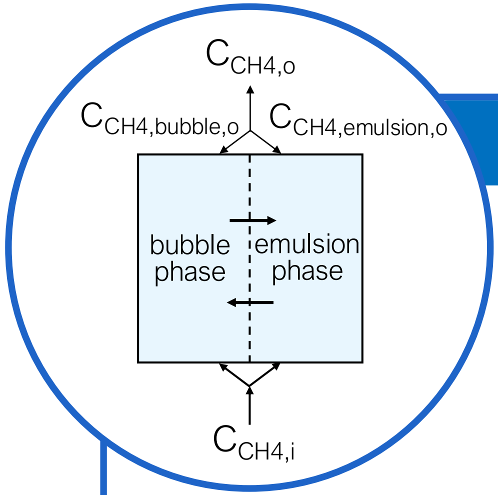
- Cloud to emulsion mass-transfer: $$K_{bc} = 4.5\left(\frac{U_e}{d_b}\right) + 5.85\left(\frac{D_{AB}^{1/2}\, g^{1/4}}{d_b^{5/4}}\right)$$



➡ **correlation based**

(Kunii, Levenspiel, 1991)
(Mostoufi et al, 2001)
(Abba et al, 2003)

Two-phase fluidized-bed model



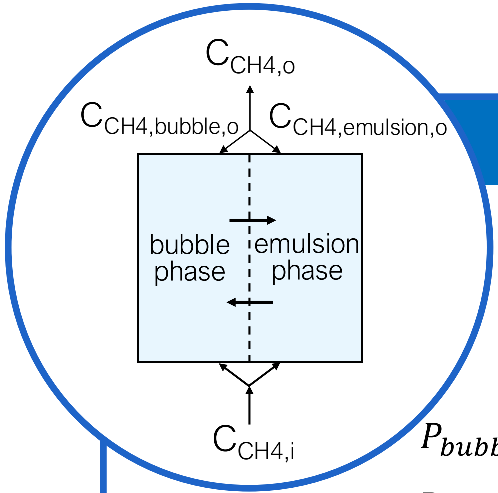
TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

Bed and phase balances:

- phase gas fraction allocation $\epsilon = \Psi\epsilon_b + (1 - \Psi)\epsilon_e$
- phase gas velocity allocation $U = \Psi U_b + (1 - \Psi)U_e$
- phase density allocation $\rho = \Psi\rho_b + (1 - \Psi)\rho_e$
- bubble phase volume allocation $\epsilon_b + \phi_b = 1$
- emulsion phase volume allocation $\epsilon_e + \phi_e = 1$
- bed volume allocation $\epsilon + \phi = 1$
- phase diffusion distribution $D = \Psi D_{ze} + (1 - \Psi)D_{zb}$

(Kunii, Levenspiel, 1991)
(Mostoufi et al, 2001)
(Horio et al, 1989)
(Abba et al, 2003)

Two-phase fluidized-bed model



TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

Probability weighted model parameters allowing for smooth transition between regimes:

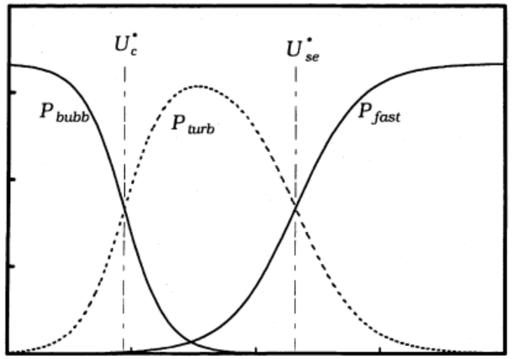
$$\epsilon = \epsilon_{bubbling}P_{bubbling} + \epsilon_{turbulent}P_{turbulent} + \epsilon_{fastfluidization}P_{fastfluidization}$$

$$P_{bubbling} = 1 - P(U > U_{turbulent,cr})$$

$$P_{turbulent} = P(U > U_{turbulent,cr})$$

$$P_{fast} = P(U > U_{fast,cr})$$

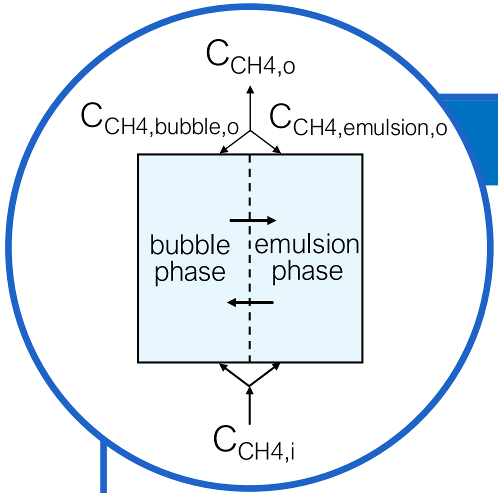
$$P_{turbulent} = 1 - P_{bubbling} - P_{fast}$$



Variable	Bubbling regime	Turbulent regime	Fast Fluidization
$\boldsymbol{\epsilon}$	$\frac{1-(1-\epsilon_{mf})}{\left(1+\frac{U-U_{mf}}{0.711\sqrt{gd_b}}\right)}$	$\frac{U+1}{U+2}$	$\left(1+\frac{G_{so}\Psi_{slip}}{\rho_p U}\right)^{-1}$
$\boldsymbol{K_{be}}$	$\left(\frac{1}{k_{bc}}+\frac{1}{k_{ce}}\right)^{-1}$	$1.631Sc^{0.37}U$	$\left(\frac{4D_{mix}\overline{\epsilon_a}U}{\pi L_t}\right)^{1/2}\frac{2}{r_C}$
$\boldsymbol{\Psi}$	$\frac{\epsilon-\epsilon_{mf}}{\epsilon_b-\epsilon_{mf}}$	$\frac{\epsilon-\epsilon_{mf}}{\epsilon_b-\epsilon_{mf}}$	r_C^2/R^2
$\boldsymbol{D_{ze}}$	D_{mix}	$\frac{UL_d}{Pe_{z1}}$	$0.184\overline{\epsilon_C}^{(-4.445)}$
$\boldsymbol{D_{zb}}$	$\frac{UL_d}{Pe_{z1}}$	$\frac{UL_d}{Pe_{z1}}$	$\frac{UL_t}{Pe_{z2}}$
$\boldsymbol{u_b}$	$MIN\left(\epsilon_b u_{br}, \frac{U-U_{mf}}{\Psi}\right)$	U	U/Ψ_C
$\boldsymbol{\phi_b}$	ϕ_{b0}	$1-\epsilon$	$1-\overline{\epsilon_C}$

(Kunii, Levenspiel, 1991)
(Mostoufi et al, 2001)
(Horio et al, 1989)
(Abba et al, 2003)

Two-phase fluidized-bed model



DYNAMIC TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

- Energy equation:

$$c_p \rho_g \emptyset_r \frac{dT}{dt} = (1-\epsilon)\sum_k (-\Delta_r H)_k \, r_k \emptyset_r + \dot{m} c_p \frac{dT}{dz} - \frac{dQ_{JH}}{dz} - \emptyset_r k_e \frac{d^2T}{dz^2}$$

voltage

$$dQ_{JH} = \frac{V^2 2\pi dz}{s_{bed} \, ln\left(\frac{r_2}{r_1}\right)}$$

bed resistivity

reactor and electrode radius

assumptions:

- bubble and emulsion same temperature
  - heat capacity
  - gas density
  - solid fraction

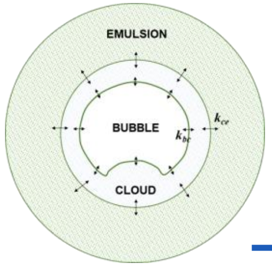
→ averaged and constant over two phases

→ differentiation between two phases possible

- no radial temperature profile

$$K_{bc} = 4.5\left(\frac{U_e \rho_g C_{pg}}{d_b}\right) + 5.85 \frac{\left(k_g \rho_g C_{pg}\right)^{1/2} g^{1/4}}{d_b^{5/4}}$$

$$K_{ce} = 6.77\left(\rho_g C_{pg} k_g\right)^{1/2} \left(\frac{\epsilon_e u_{br}}{d_b^3}\right)^{1/2}$$



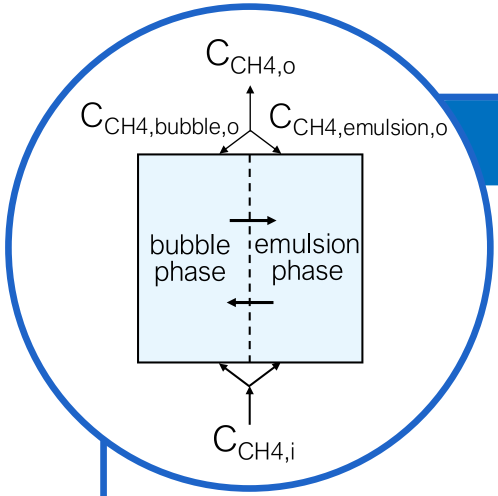
assumptions:

- steady problem
- axisymmetric
- constant resistivity (homogenous medium)
- independent of radial position in reactor

→ **derivation starting from continuity of current and Ohm's law**

(Kunii, Levenspiel, 1991)
(Kiashemshaki et al, 2006)
(Fedorov et al, 2016)

Two-phase fluidized-bed model

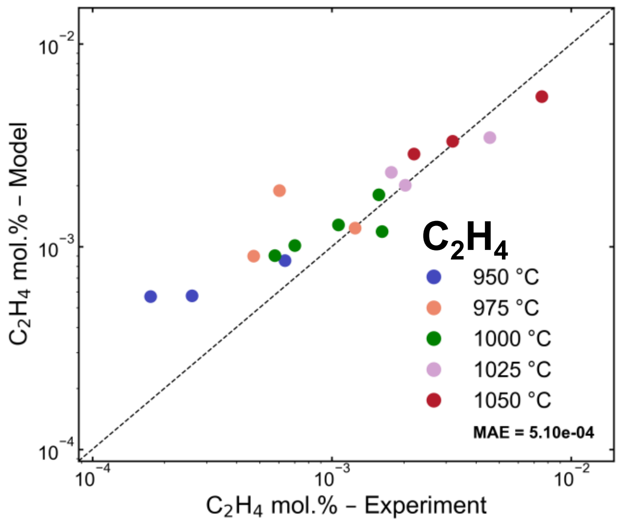


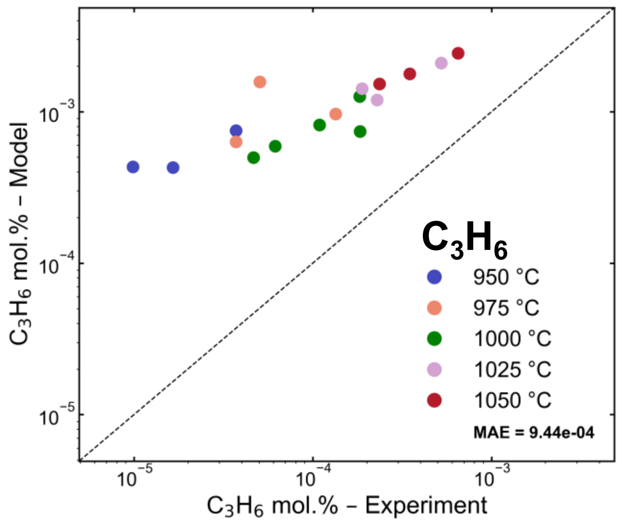
DYNAMIC TWO-PHASE MODEL FOR FLUIDIZED-BED REACTORS

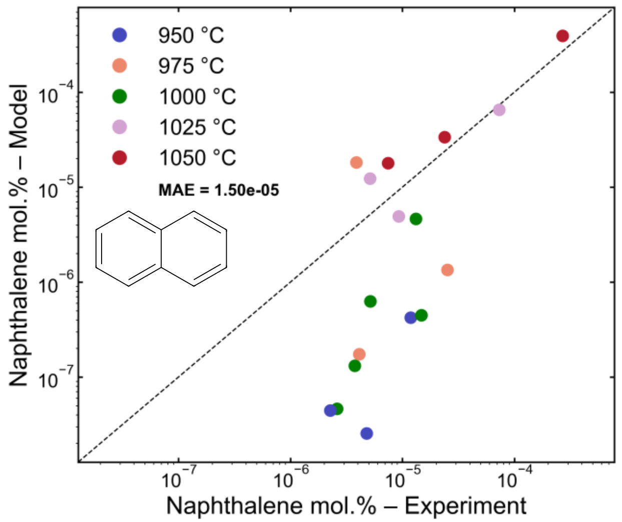
1. mole and energy balances are formulated
2. probability for regime i determined based on the operating conditions and probability density functions of the boundary velocities
3. hydrodynamic parameters are calculated for each regime based on the operating conditions
4. weighting with the pertaining regime probabilities gives the hydrodanimic parameters for the reactor model
5. mole and energy balance are solved to obtain concentrations and temperature in function of the axial coordinate

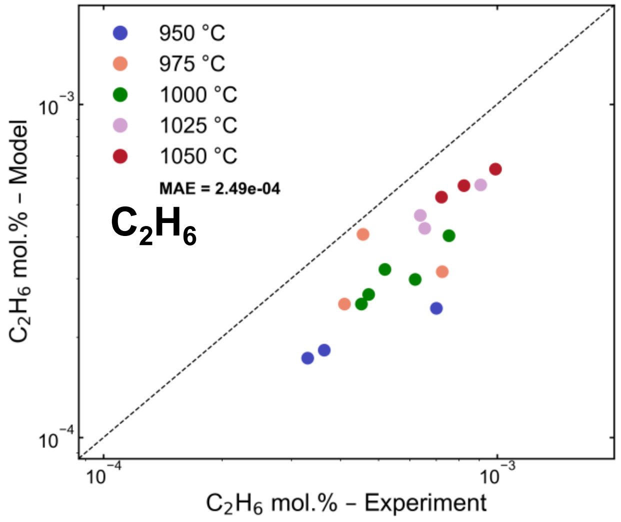
(Abba et al, 2003)

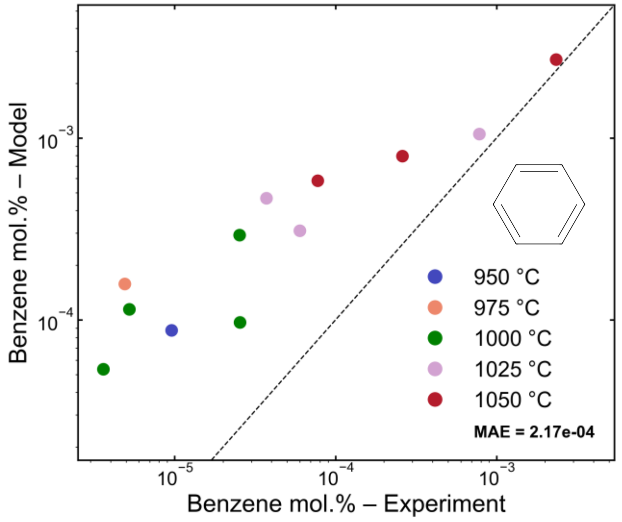
Two-Phase Fluidized-Bed Reactor Simulation

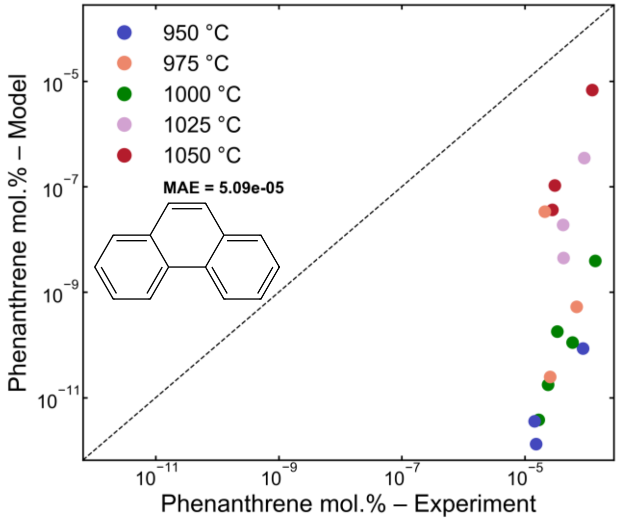












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