Fischer-Tropsch Synthesis revisited
considerations on Reaction-Diffusion and Selectivity in a cobalt catalyst particle

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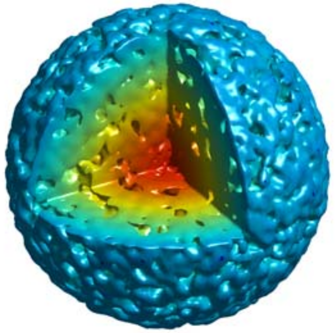


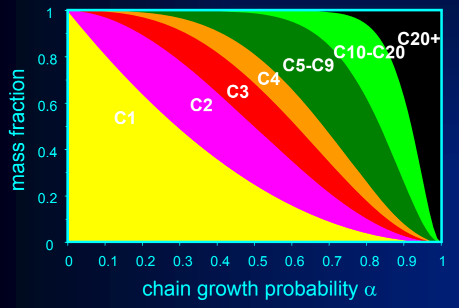
Catalysis Science and Technology
2 (2012) 1221–1233
DOI: 10.1039/c2cy20060k

Eurokin workshop, Delft 15 Feb 2012

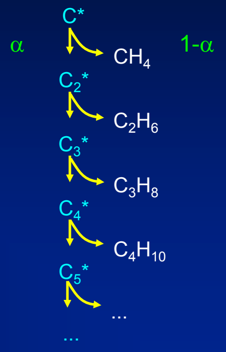
Fischer-Tropsch synthesis

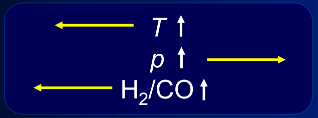
$$CO + 2H_2 \longrightarrow C_nH_{2n+2} + H_2O$$

ΔH = -170 kJ/mol CO



polymeric growth scheme





Kinetics

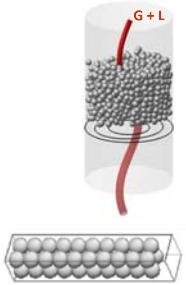
Heat & Mass Transport ?

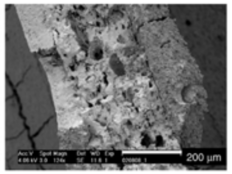
Applications and Relevance

Diffusion limitations in Fischer-Tropsch catalyst

Diffusion length > ~80 μm

- (Egg-shell) catalysts
- Packed bed reactor
- Monolith with coated walls
- Micro-packed beds





Goal: Investigate catalyst performance

- Reaction-diffusion model
- Selectivity model
- Performance as $f(T, P, H_2/CO)$
- Model utilization

The Fischer-Tropsch process

- Basic reaction:

syngas — *Hydrocarbon distribution* — *water*

$$x\,CO + y\,H_2 \xrightarrow{catalyst} z\,(\text{-}CH_2\text{-})_n + x\,H_2O$$

- Kinetics expression: Yates and Satterfield[1]

$$R_i = |\nu_i| \frac{\rho_{cat} F a p_{CO} p_{H_2}}{(1 + b p_{CO})^2}$$

Modern catalyst: $F \approx 3$

- Chain growth mechanism:

Chance for adsorbed chain growth: α

Chance for adsorbed chain termination: 1 – α

Typically desired for low-*T* FT: α > 0.9

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[1] Yates and Satterfield, *Energy & Fuels* (1991)

Transport and consumption H_2 - CO

Diffusivity

$$D_{i,eff} = \frac{\varepsilon_{cat}}{\tau_{cat}} D_{i,bulk} = \frac{\varepsilon_{cat}}{\tau_{cat}} D_{i,0} \exp\left(\frac{-E_{D,i}}{RT}\right)$$

@ 500 K: $\frac{D_{H2,eff}}{D_{CO,eff}} \approx 2.7$

Consumption ratio of reactants:
(α independent of chain length)

$$\frac{R_{H2}}{R_{CO}} = 3 - \alpha \approx 2.1$$

Diffusional transport ratio:

$$\frac{Diffusion(H_2)}{Diffusion(CO)} = \left(\frac{D_{H_2}}{D_{CO}}\right) \times \left(\frac{\nabla Concentration_{H_2}}{\nabla Concentration_{CO}}\right) \approx \underbrace{2.7}_{\text{physical}} \times \underbrace{2.1}_{\text{stoichiometric}} = 5.7$$

Diffusion and consumption are intrinsically unbalanced

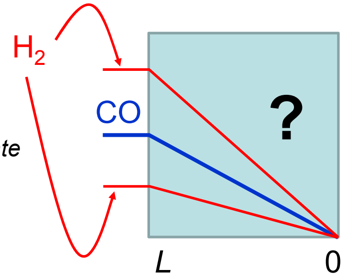
Balancing diffusion with consumption: Back-of-the-envelope

- Degrees of freedom (1):
  - Diffusivities (physical) are fixed
  - Consumption ratio (desired product) is fixed
  - H_2 / CO (bulk) can be varied
- Balance ratios (H_2 / CO):

$$diffusivity \times \nabla concentration = consumption\ rate$$

$$2.7 \times \nabla concentration = 2.1$$

$$\nabla concentration = 0.8$$



Preserving the syngas ratio inside the particle may be possible at low bulk feed ratios H_2/CO

Model Equations

Reaction-diffusion equations

- Internal:

$$\underbrace{0 = \frac{1}{z^s}\frac{d}{dz}\left(z^s \frac{dy_i}{dz}\right) - \phi_i^2 \psi_i}_{\text{Steady state reaction-diffusion}} \qquad \underbrace{\phi_i = \sqrt{\frac{\ell_{cat}^2}{D_{i,eff} c_{i,0}} R_{i,0}}}_{\text{Thiele modulus}} \qquad \underbrace{\psi_i = \frac{R_i}{R_{i,0}}}_{\text{Dimensionless reaction rate}}$$

s = 0 (slab), 1 (cylinder), or $\underbrace{\text{2 (sphere)}}_{\text{This presentation}}$ *$\ell_{cat} = V_{cat} / S_{cat}$*

- Boundary conditions:

center: $\left.\frac{dy_i}{dz}\right|_{z=0} = 0$

surface: $\left. y_i \right|_{z=s+1} = 1$

- External limitations: *(not considered in this presentation)*

surface: $\left.\frac{dy_i}{dz}\right|_{z=s+1} = Bi_m \left(1 - y_{i,0}\right)$

Reaction-diffusion equations

- Internal:

$$\underbrace{0=\nabla^2 y_i-\phi_i^2\psi_i}_{\textbf{Steady state reaction-diffusion}} \qquad \underbrace{\phi_i=\sqrt{\frac{\ell_{cat}^2}{D_{i,eff}c_{i,0}}R_{i,0}}}_{\textbf{Thiele modulus}} \qquad \underbrace{\psi_i=\frac{R_i}{R_{i,0}}}_{\textbf{Dimensionless reaction rate}}$$

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- Boundary conditions: center: $\nabla y_i\big|_{z=0}=0$

surface: $y_i\big|_{z=s+1}=1$

- External limitations:
(not considered in this presentation) surface: $\left.\frac{dy_i}{dz}\right|_{z=s+1}=Bi_m\left(1-y_{i,0}\right)$

Catalyst Isothermicity

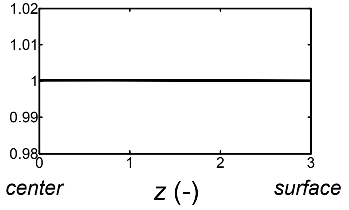
Internal: $$\gamma\overline{\beta_{\text{int}}}\left(\eta\ \phi^2\right)=\underbrace{\left(\frac{E_A}{RT}\right)}_{\textbf{Dimensionless activation energy}}\underbrace{\left(\frac{(-\Delta H_r)D_{CO,eff}c_{CO,0}}{\lambda_{cat,eff}T}\right)}_{\textbf{Internal Prater number}}\underbrace{\left(\frac{R_{CO}\rho_{cat}\ell_{cat}^2}{D_{CO,eff}c_{CO,0}}\right)}_{\textbf{Wheeler-Weisz modulus}}=0.017<\underbrace{0.05}_{\textbf{criterion}}$$

External (Mears' criterion): $$\frac{E_A\left(-\Delta H_r\right)R_{CO}\rho_{cat}\ell_{cat}}{hRT^2}=0.026<\underbrace{0.05}_{\textbf{criterion}}$$

Numerical verification:

Conditions:
T = 500 K
P = 30 bar
H_2 / CO = 2.0 (surface)
d_{cat} = 500 µm
3 × Yates and Satterfield

$$\theta=\frac{T}{T_{surface}}$$

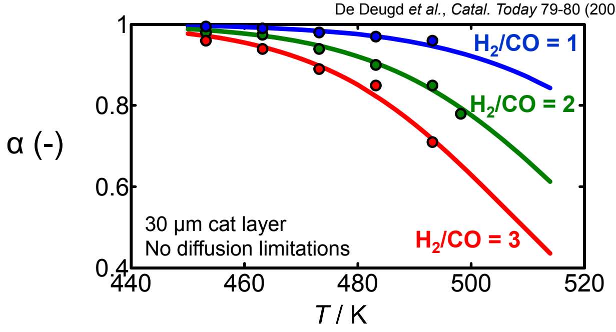


The catalyst is isothermal

Chain growth probability (α)

- Sensitive to *T* and H_2/CO

De Deugd, PhD thesis (2004)
De Deugd *et al.*, *Catal. Today* 79-80 (2003) 495-501



- Model (math)
  - Propagation / termination basis
  - α independent of chain length
  - α = *f*(*T*, H_2/CO)
  - Syngas ratio scales with power β

$$\alpha=\frac{1}{1+k_\alpha\left(\frac{c_{H_2}}{c_{CO}}\right)^{\beta}\exp\left(\frac{\Delta E_\alpha}{R}\left(\frac{1}{493.15}-\frac{1}{T}\right)\right)}$$

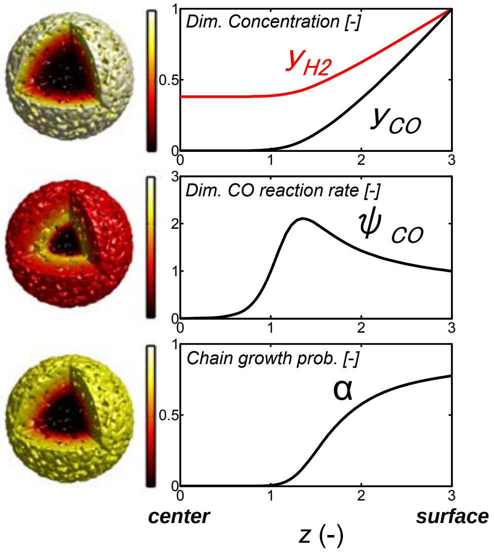
Fit: k_α = 0.0567 ± 0.0150
β = 1.76 ± 0.34
ΔE_α = 120.4 ± 16.4 (kJ mol^{-1})

Results

Results: Profiles

Conditions:
T = 500 K
P = 30 bar
H_2 / CO = 2.0 (surface)
d_{cat} = 500 μm
3 × Yates and Satterfield

Results:
φ_{CO} = 0.54
η_{cat} = 1.27
α_{ave} = 0.56



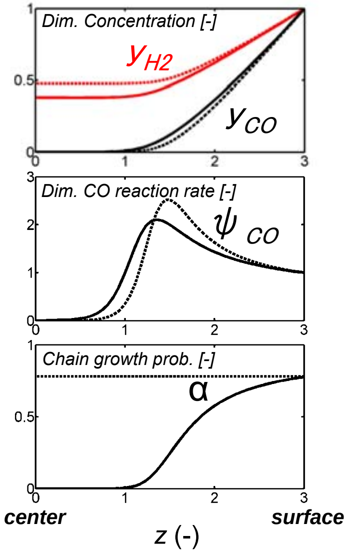
Internal diffusion limitations affect α

Results: Variable *vs.* Fixed α

Conditions:
T = 500 K
P = 30 bar
H_2 / CO = 2.0 (surface)
d_{cat} = 500 μm
3 × Yates and Satterfield

Results:

	φ_{CO}	η_{cat}	α_{ave}
α= variable (solid lines)	0.54	1.27	0.56
α= fixed (dotted lines)	0.54	1.34	0.78



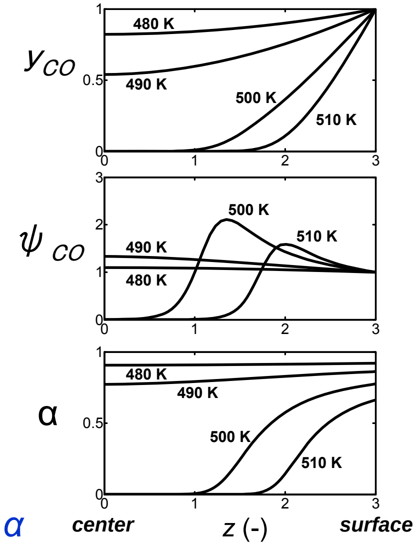
Similar rates, strong deviation in α

Results: Various Temperatures

Conditions:
P = 30 bar
H_2 / CO = 2.0 (surface)
d_{cat} = 500 μm
3 × Yates and Satterfield

Results:

T / K	φ_{CO}	η_{cat}	α_{ave}
480 K	0.12	1.04	0.92
490 K	0.26	1.10	0.84
500 K	0.54	1.27	0.56
510 K	1.08	1.05	0.41



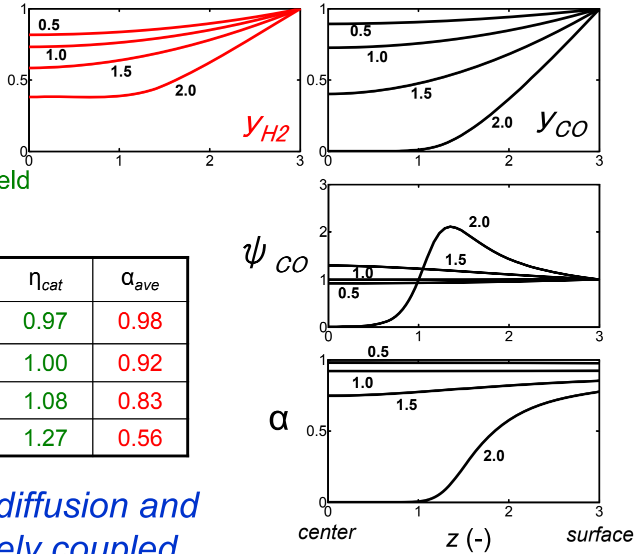
temperature, diffusion and α are intimately coupled

Results: Various H_2/CO Surface Ratios

Conditions:
P = 30 bar
T = 500 K
d_{cat} = 500 μm
3 × Yates and Satterfield

Results:

H_2/CO	φ_{CO}	η_{cat}	α_{ave}
0.5	0.07	0.97	0.98
1.0	0.19	1.00	0.92
1.5	0.34	1.08	0.83
2.0	0.54	1.27	0.56



Syngas ratio, diffusion and α are intimately coupled

Results: Back-of-the-envelope check (1)

Conditions:

T = 500 K

P = 30 bar

H_2 / CO = 0.8 (surface)

d_{cat} = 500 μm

3 × Yates and Satterfield

Results:

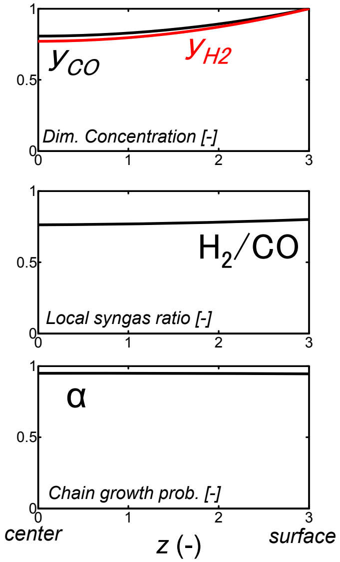
φ_{CO} = 0.14

η_{cat} = 0.98

α_{ave} = 0.94

Average H_2/CO = 0.78

(spatial)



Preserving the syngas ratio inside the particle is possible

Results: Back-of-the-envelope check (2)

Conditions:

T = 500 K

P = 30 bar

H_2 / CO = 0.8 (surface)

d_{cat} = 500 μm

10 × Yates and Satterfield

Results:

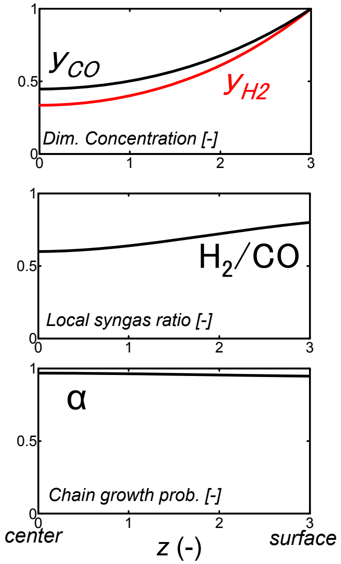
φ_{CO} = 0.45

η_{cat} = 0.91

α_{ave} = 0.95

Average H_2/CO = 0.69

(spatial)



Preserving the syngas ratio inside the particle is possible

Results: Back-of-the-envelope check (3)

Conditions:

T = 500 K

P = 30 bar

H_2 / CO = 0.8 (surface)

d_{cat} = 1 000 μm

3 × Yates and Satterfield

Results:

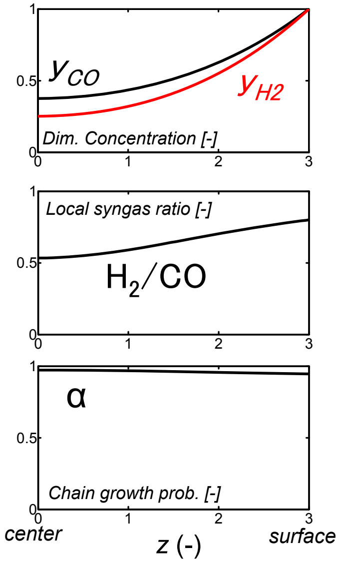
φ_{CO} = 0.54

η_{cat} = 0.88

α_{ave} = 0.95

Average H_2/CO = 0.65

(spatial)



Preserving the syngas ratio inside the particle is possible

Results: Back-of-the-envelope check (4)

Conditions:

T = 500 K

P = 30 bar

H_2 / CO = 0.8 (surface)

d_{cat} = 2 000 μm

3 × Yates and Satterfield

Results:

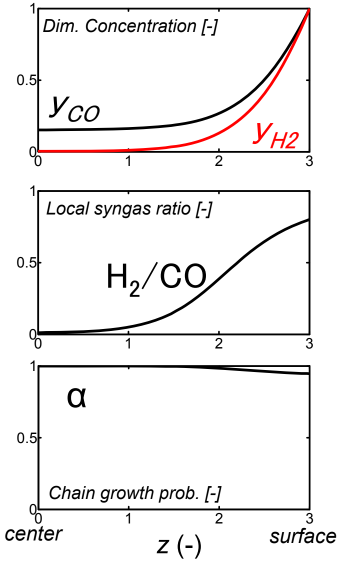
φ_{CO} = 2.16

η_{cat} = 0.60

α_{ave} = 0.96

Average H_2/CO = 0.28

(spatial)

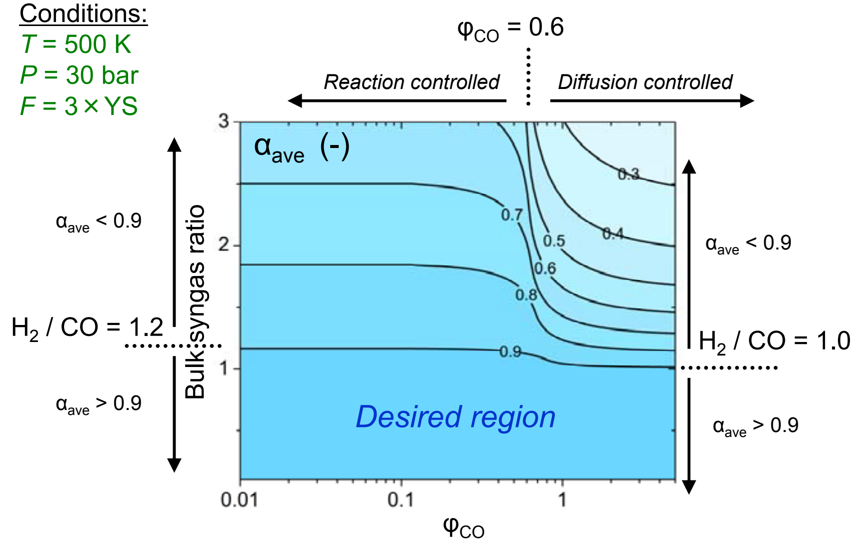


Preserving the syngas ratio becomes difficult at high φ

Results: Average α

Conditions:

T = 500 K
P = 30 bar
F = 3 × YS

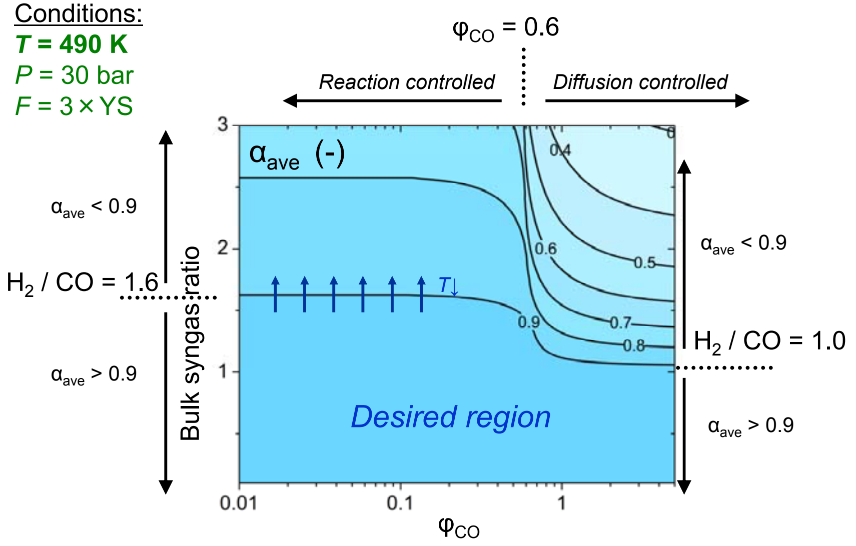


@500 K: α < 0.9 at stoichiometric syngas ratios (ϕ_{CO} < 0.6)

Results: Average α

Conditions:

***T* = 490 K**
P = 30 bar
F = 3 × YS

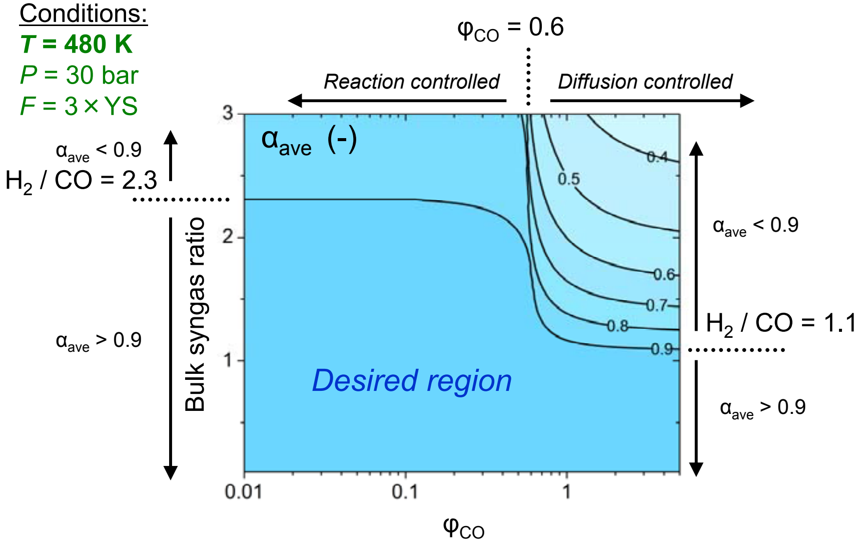


@490 K: α < 0.9 at stoichiometric syngas ratios (ϕ_{CO} < 0.6)

Results: Average α

Conditions:

***T* = 480 K**
P = 30 bar
F = 3 × YS

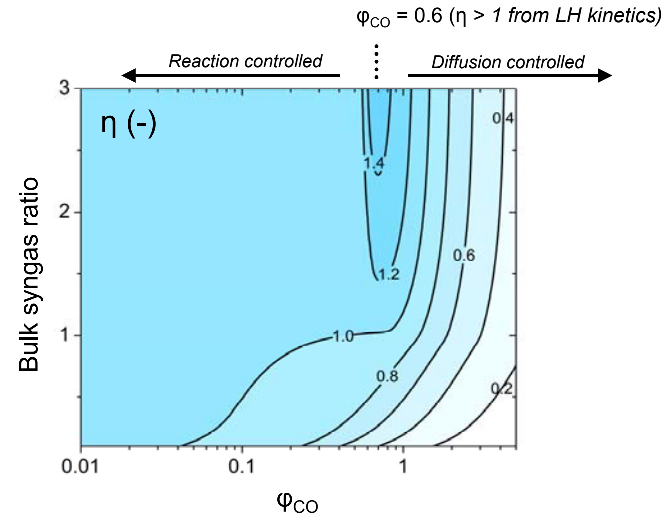


@480 K: α > 0.9 at stoichiometric syngas ratios (ϕ_{CO} < 0.6)

Results: Catalyst effectiveness

Conditions:

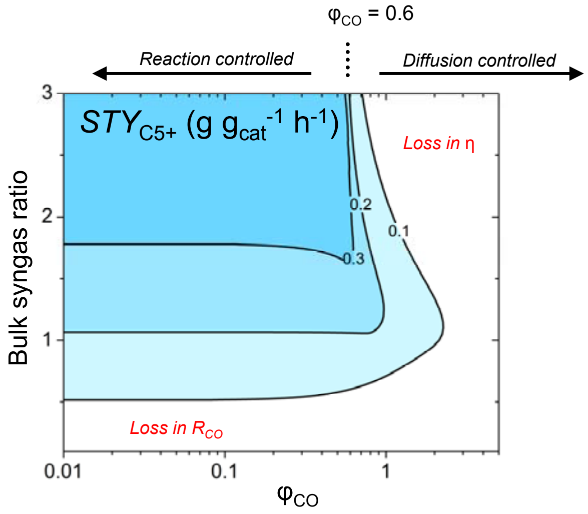
***T* = 490 K**
P = 30 bar
F = 3 × YS



Generally *η* is acceptable at ϕ_{CO} < 1.0

Results: C_{5+} Space Time Yield

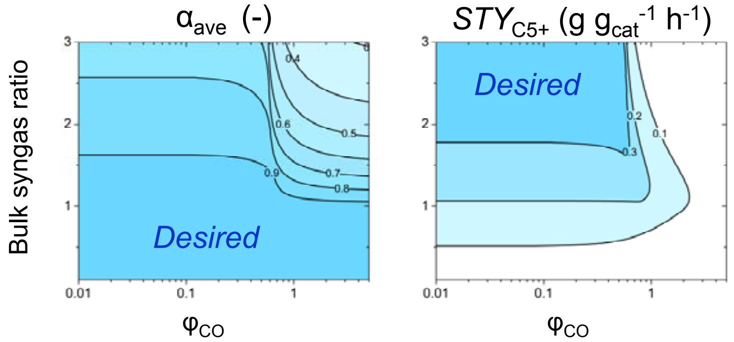
Conditions:
T = 490 K
P = 30 bar
F = 3 × YS



Productivity is largest at high syngas ratios and $\phi_{CO} < 0.6$

Results: Selectivity vs. Productivity

Conditions:
T = 490 K
P = 30 bar
F = 3 × YS



Selectivity and productivity are conflicting

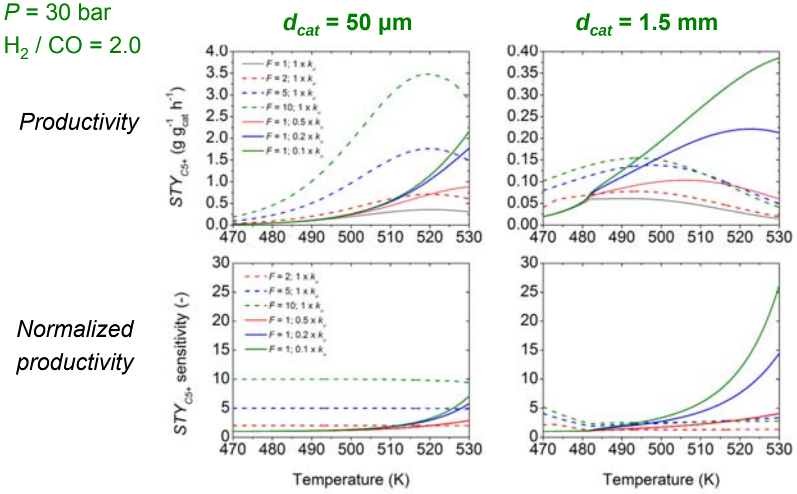
(Selectivity chosen for economical reasons)

Utilization

- *Catalyst development*
- *Operational conditions*
- *Reactor operation*

Catalyst Design: Improve Activity or Selectivity?

P = 30 bar
H_2 / CO = 2.0



Improve activity

Depends on conditions

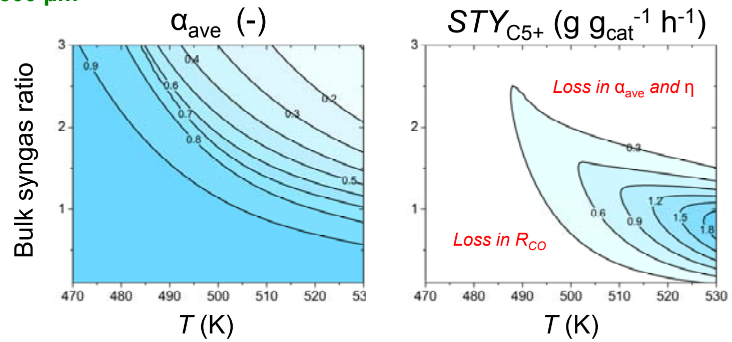
Operating conditions: *T* and syngas ratio

Conditions:

P = 30 bar

3 × Y&S

d d_{cat} **= 500 µm**



Interesting conditions: high *T* (530 K) and low syngas ratio (0.8)

(NB1: olefin/paraffin ratio, coke formation, H_2 limitations in reactor)

(NB2: kinetic relation not valid >530 K)

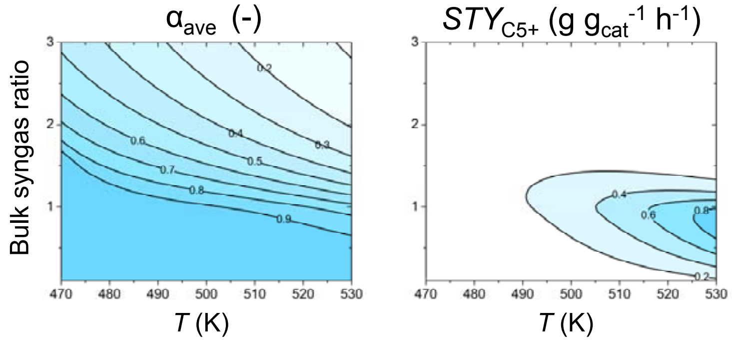
Operating conditions: *T* and syngas ratio

Conditions:

P = 30 bar

3 × Y&S

d_{cat} **= 1.5 mm**

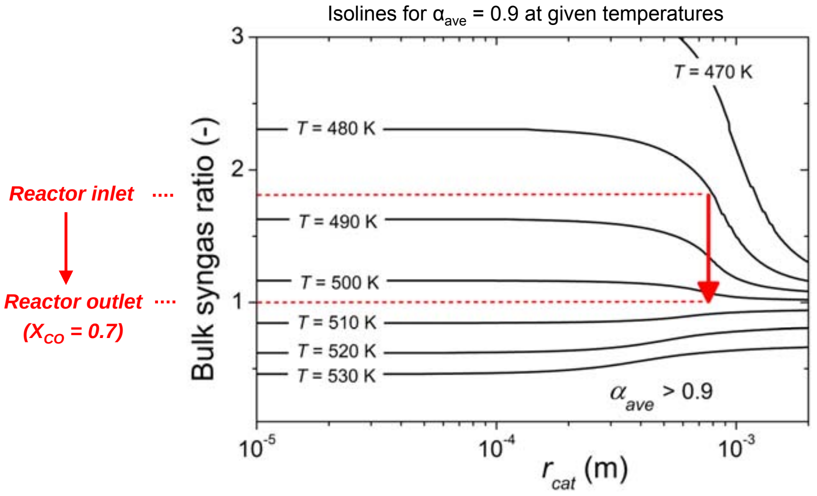


Also for larger particles: high *T* (530 K) and low syngas ratio (0.8)

(NB1: olefin/paraffin ratio, coke formation, H_2 limitations in reactor)

(NB2: kinetic equation not valid >530 K)

Reactor Design: Conserving α in a PFR



Determine allowed temperature rise to keep α_{ave} > 0.9

(In this example: 480 K → 505 K. NB: match with U_{ov} and d_{tube})

Conclusions

Fischer-Tropsch Synthesis in a Co-catalyst particle

- Diffusion and consumption of H_2 and CO
  - intrinsically unbalanced
  - play an important role in conversion and selectivity
- Optimal conditions selectivity and activity conflicting
- Operating conditions: high *T* and low syngas ratio
  - in agreement with back-of-the-envelope analysis
  - WGS functionality needed
- Guides
  - Optimal reactor operation: temperature profile
  - Catalyst improvement: Focus on activity

Acknowledgment

This research is supported by the Dutch Technology Foundation STW, which is the applied science division of NWO, and the Technology Program of the Ministry of Economic Affairs, Agriculture and Innovation.

Research carried out in the framework of the Green & Sustainable Process Technology programme

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Assumptions

- Single particle consideration
  - external (film) transport not included
    - may strengthen diffusional unbalance
- Chain growth probability model applies
  - Variable probability dependency on T and H_2/CO ratio
  - based on methane production
- Yates and Satterfield kinetics
  - temperature dependency components identical
    - e.g. methane formation higher *Ea*
- Deactivation not considered
  - larger CO amounts