

Seminarios 2021

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Catalizadores estructurados de espumas como soporte de catalizadores para la síntesis de Fischer-Tropsch

Alejo Aguirre

I N T E C





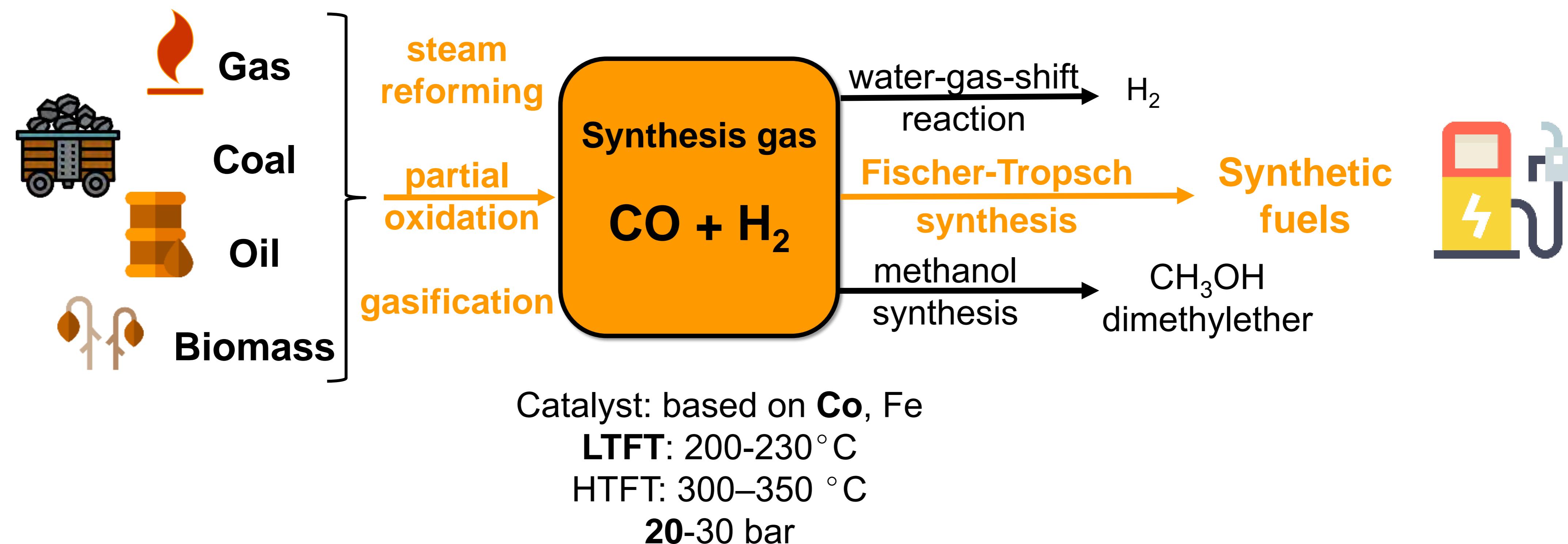
Open-cell foams as catalysts support for the Fischer-Tropsch Synthesis

Alejo Aguirre

M. Fernanda Neira d'Angelo
John van der Schaaf

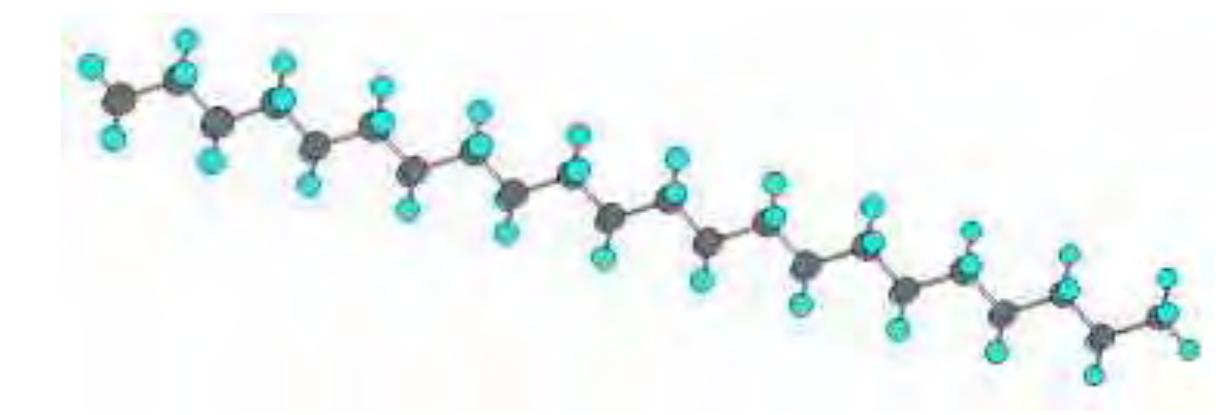
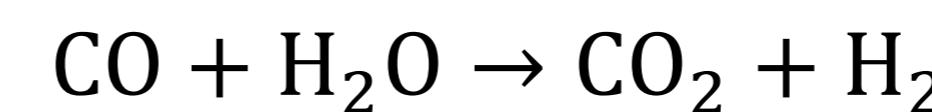
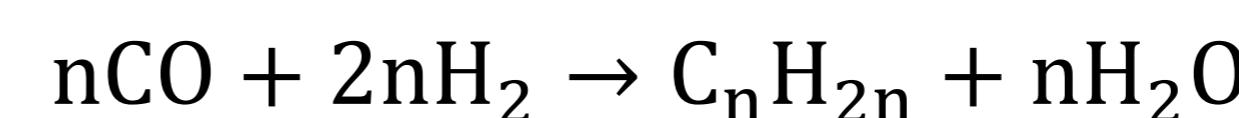
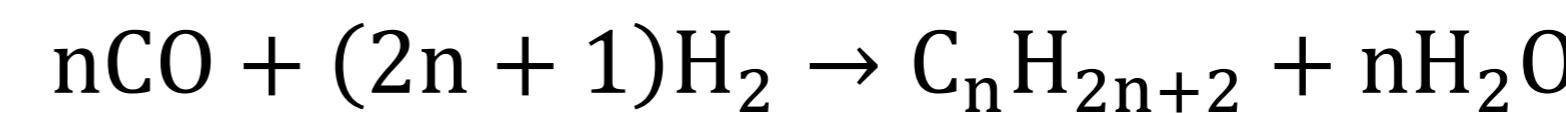
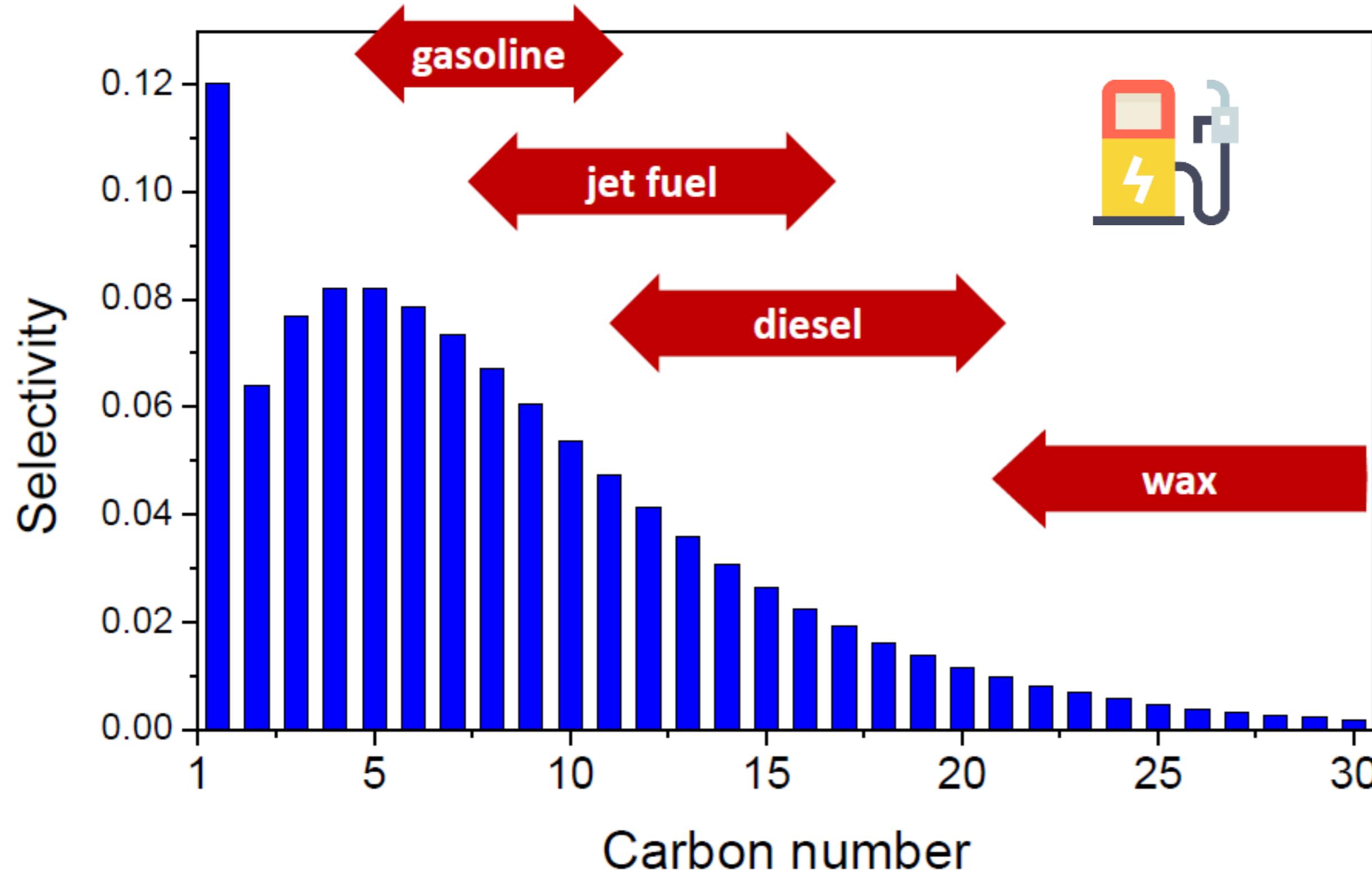
1. INTRODUCTION

Fischer-Tropsch



1. INTRODUCTION

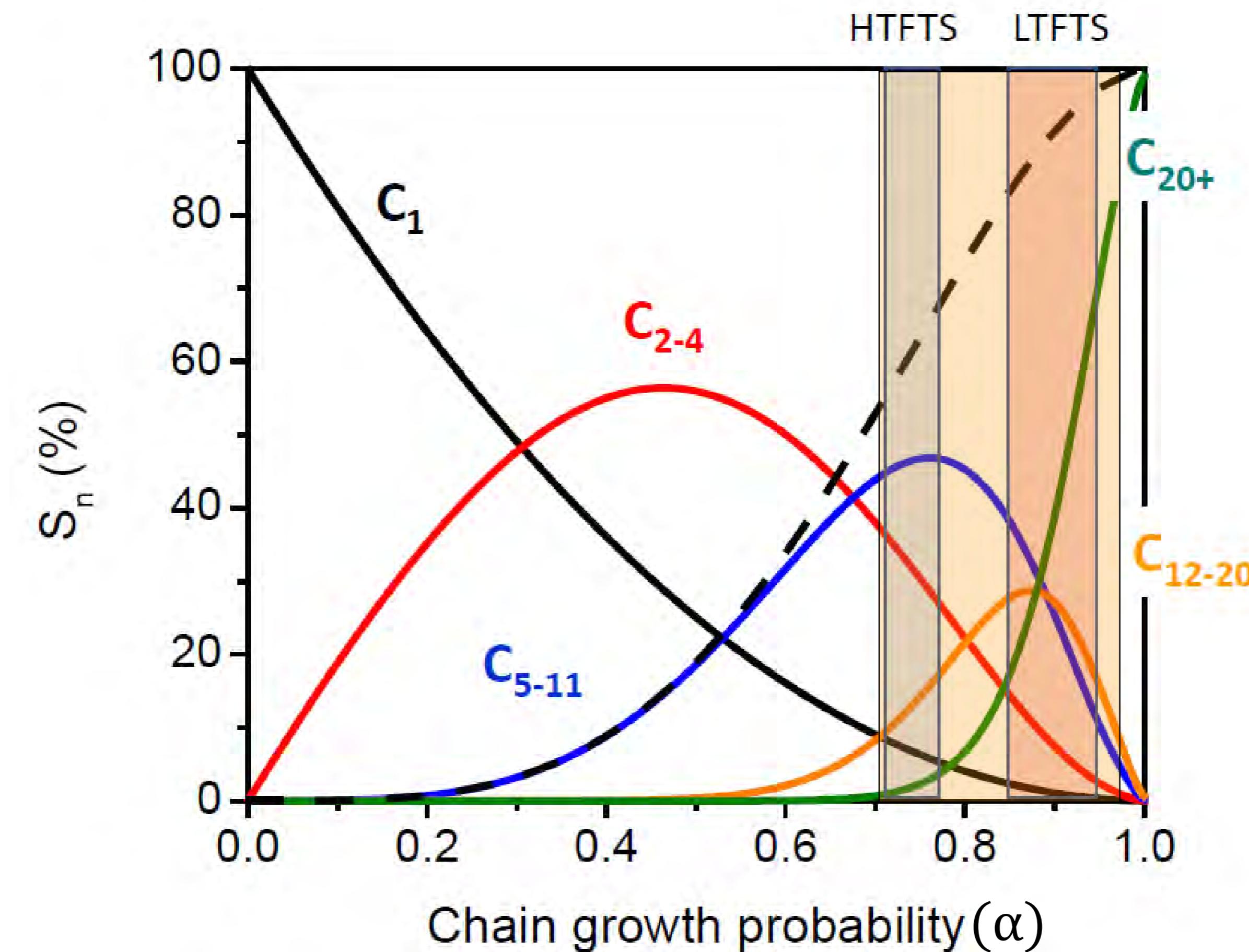
Fischer-Tropsch



1. INTRODUCTION

Product distribution

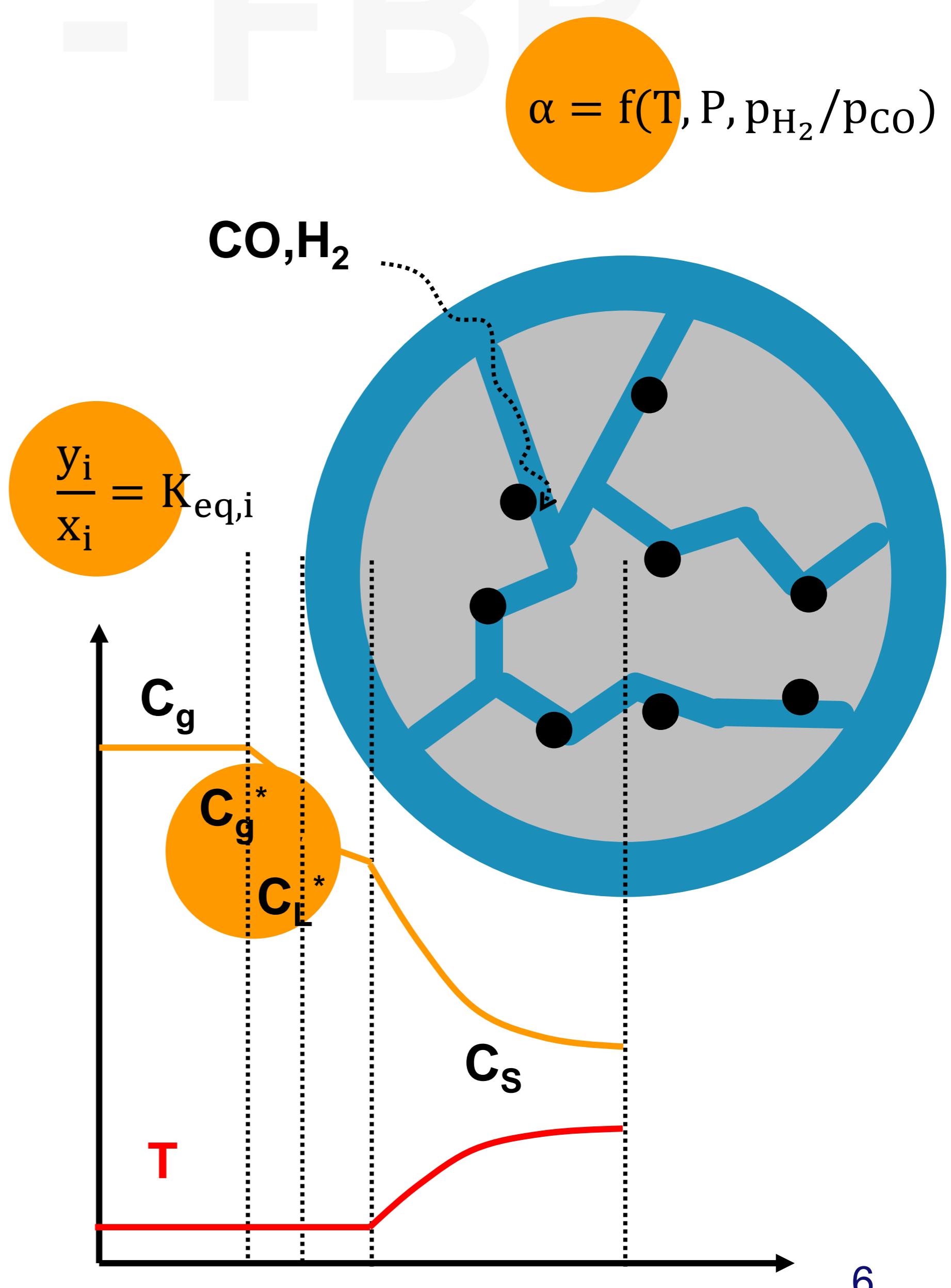
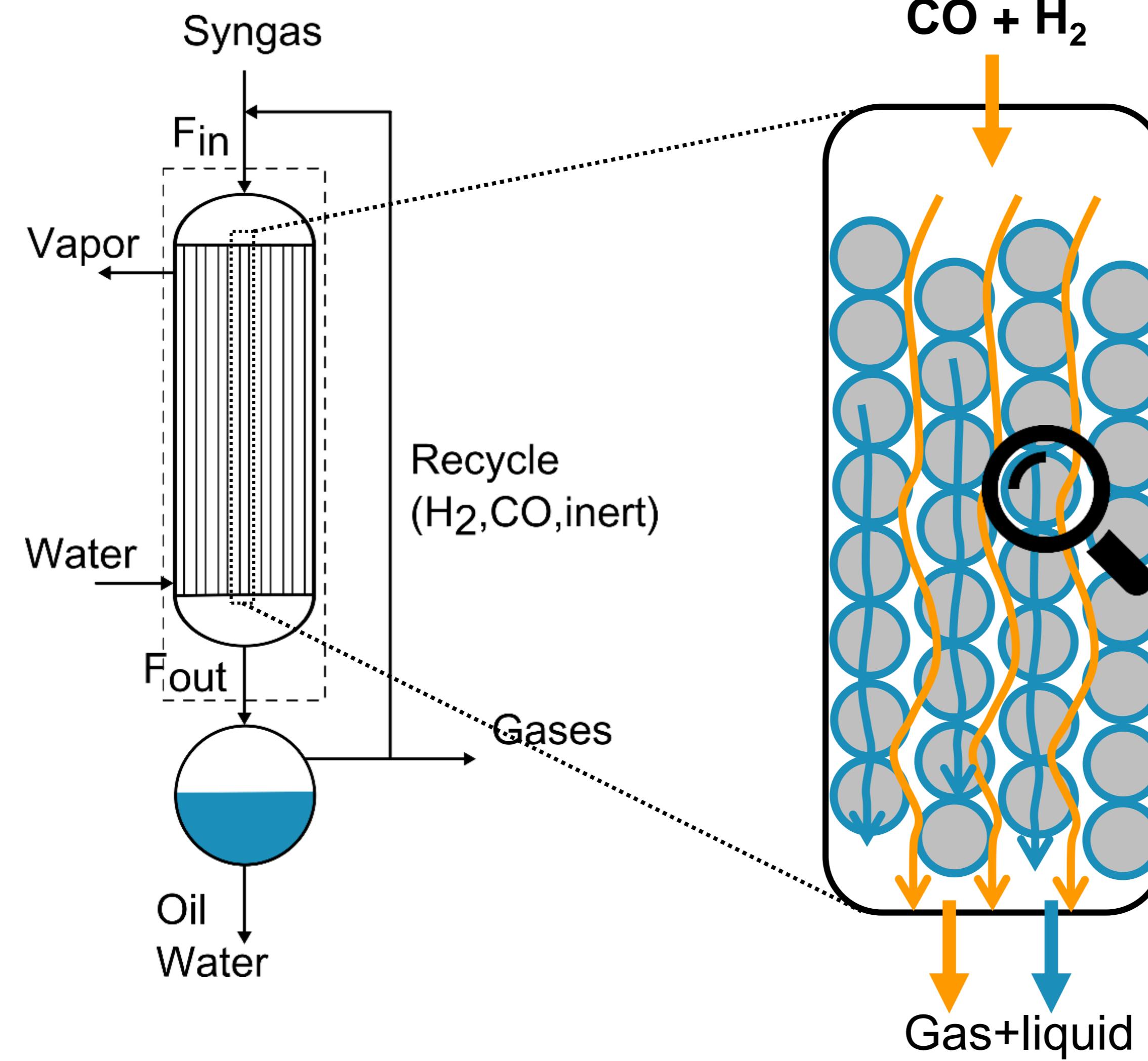
$$S_n = n(1 - \alpha)^2 \alpha^{n-1}$$



$$\alpha = f(T, P, p_{H_2}/p_{CO})$$

1. INTRODUCTION

LTFT Reactor - FBR



1. INTRODUCTION

Intensification of FT

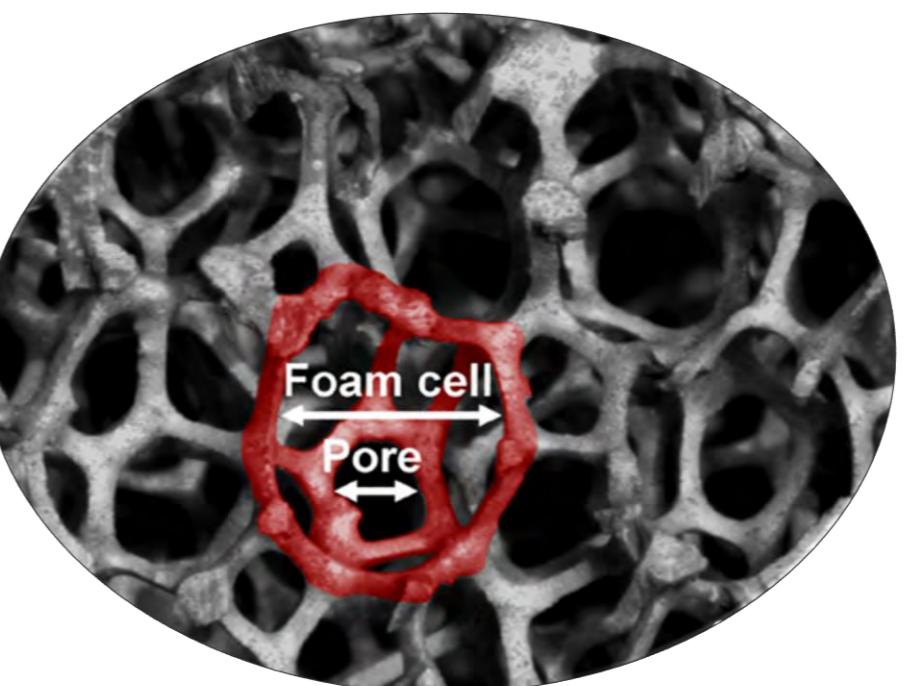
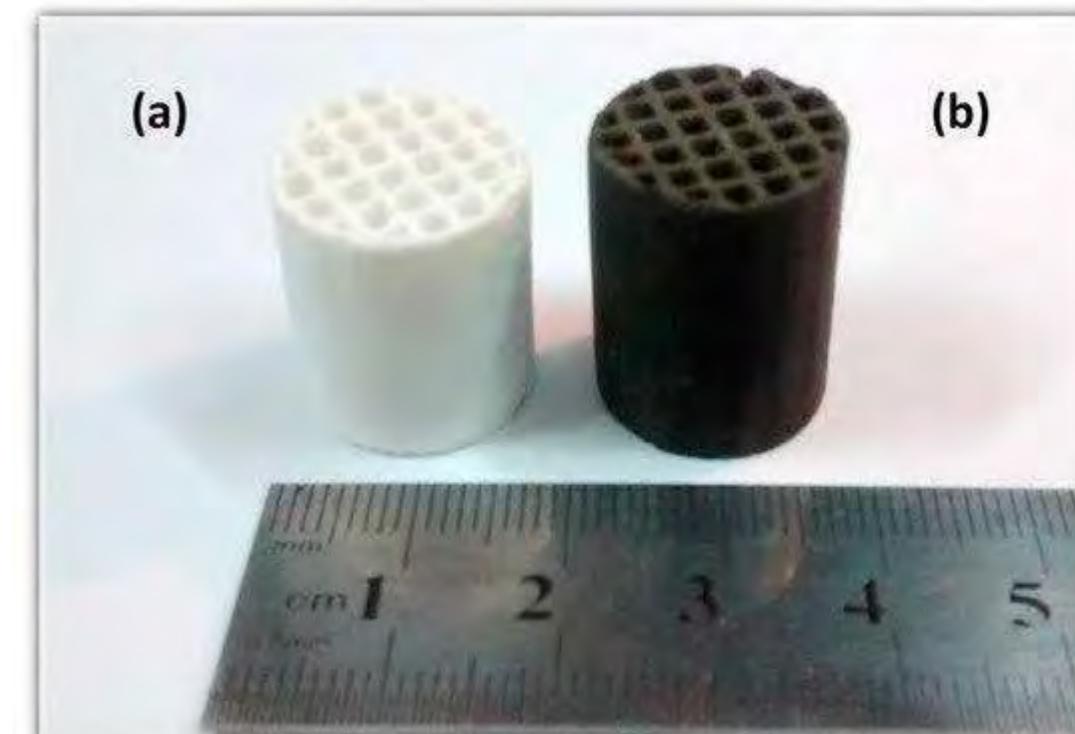
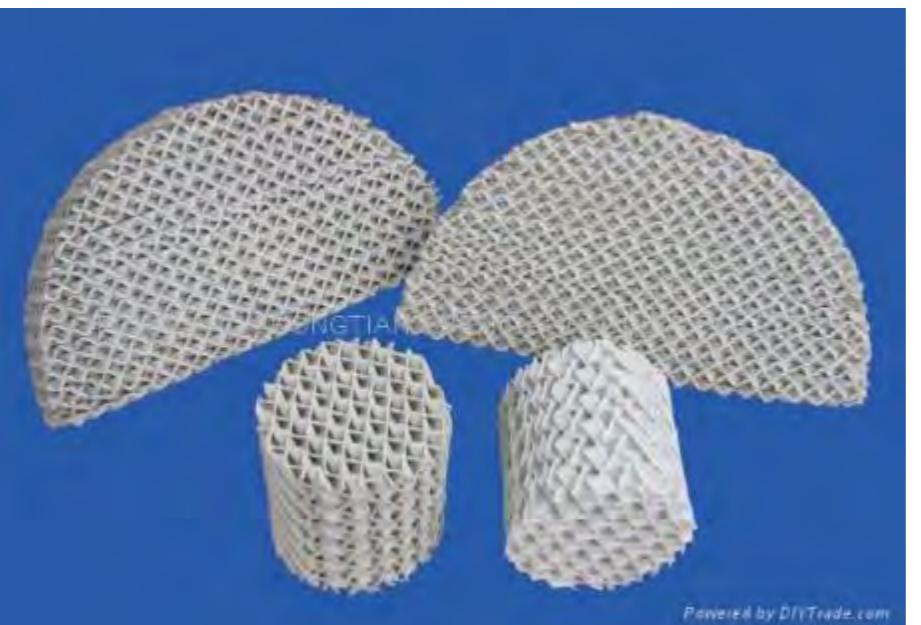
Possibilities of process intensification

fixed bed catalyst

high catalyst efficiency due to short diffusion distances

highly efficient gas-liquid mass transfer

isothermal operation at high temperatures



1. INTRODUCTION

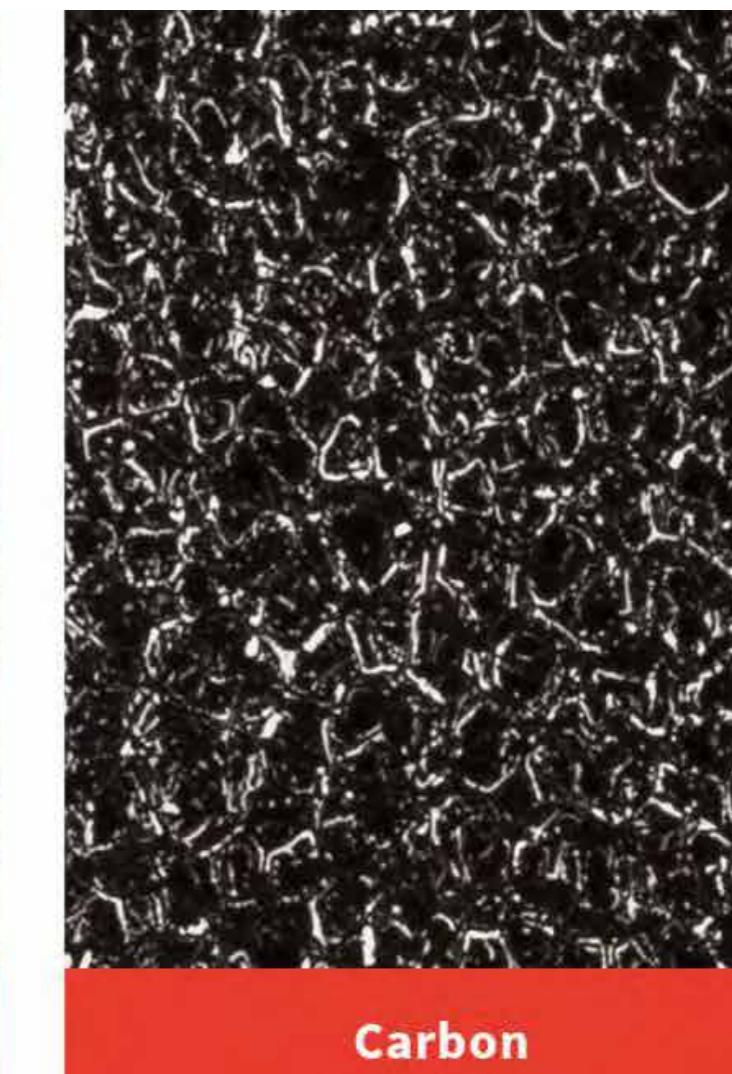
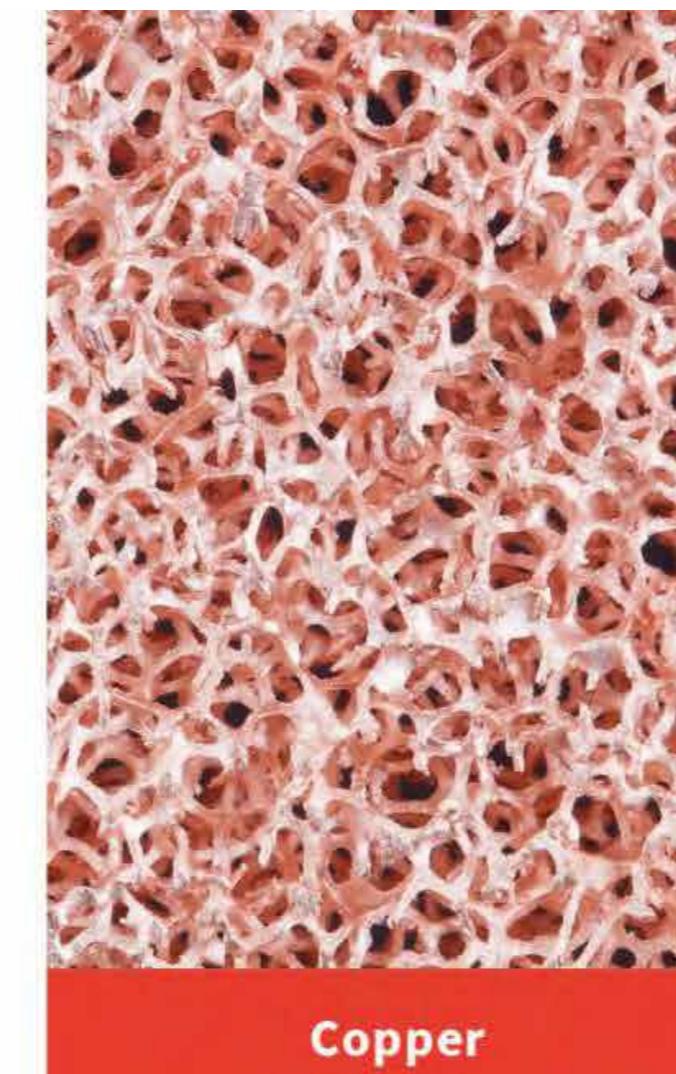
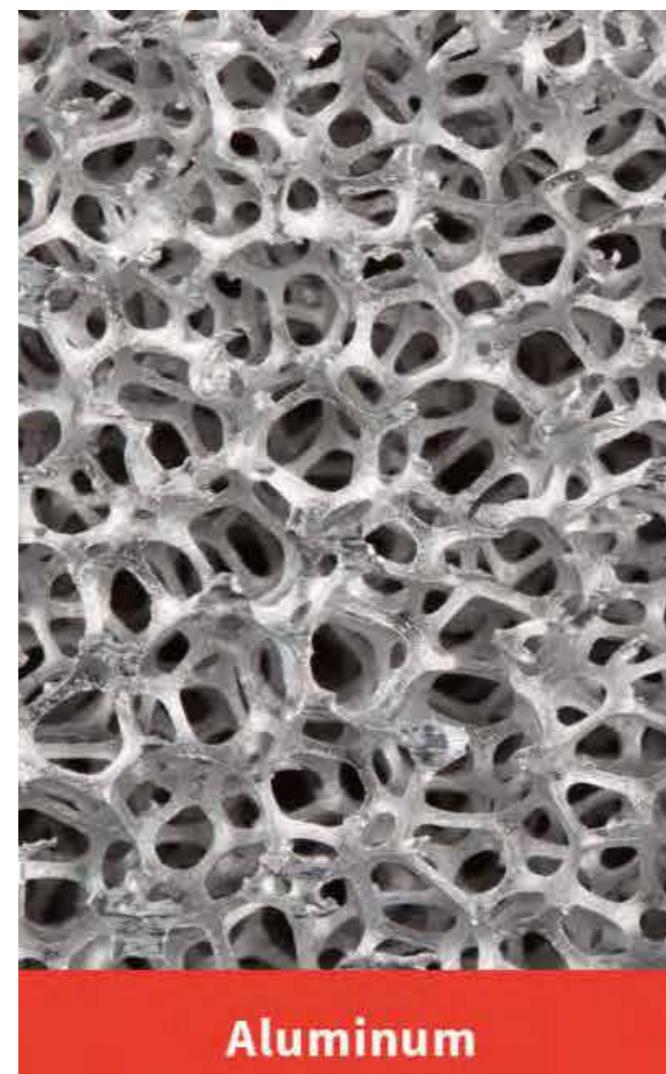
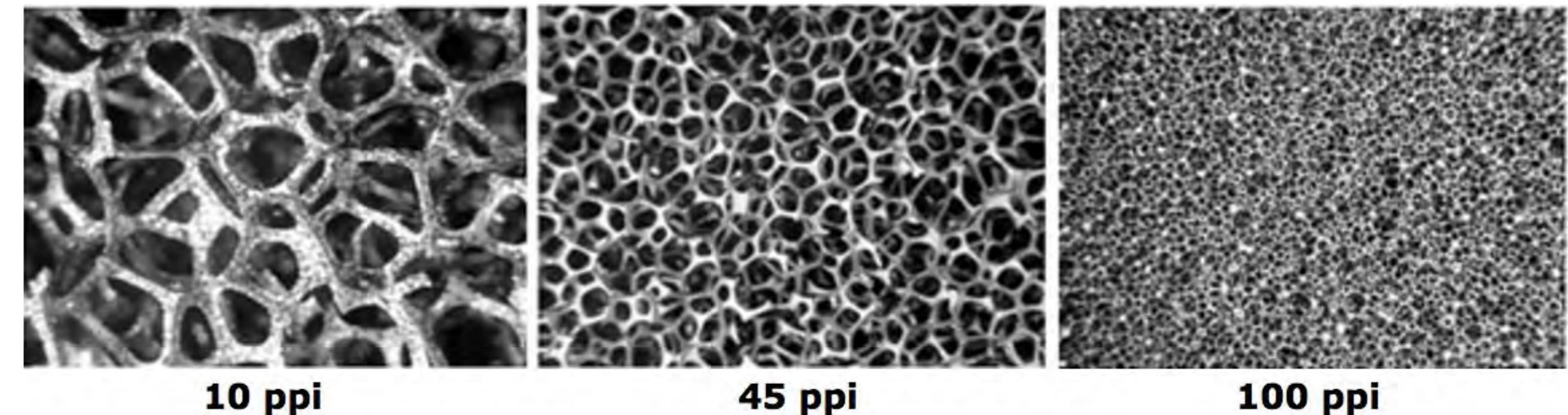
Foams

Network structure

Pore density (PPI)

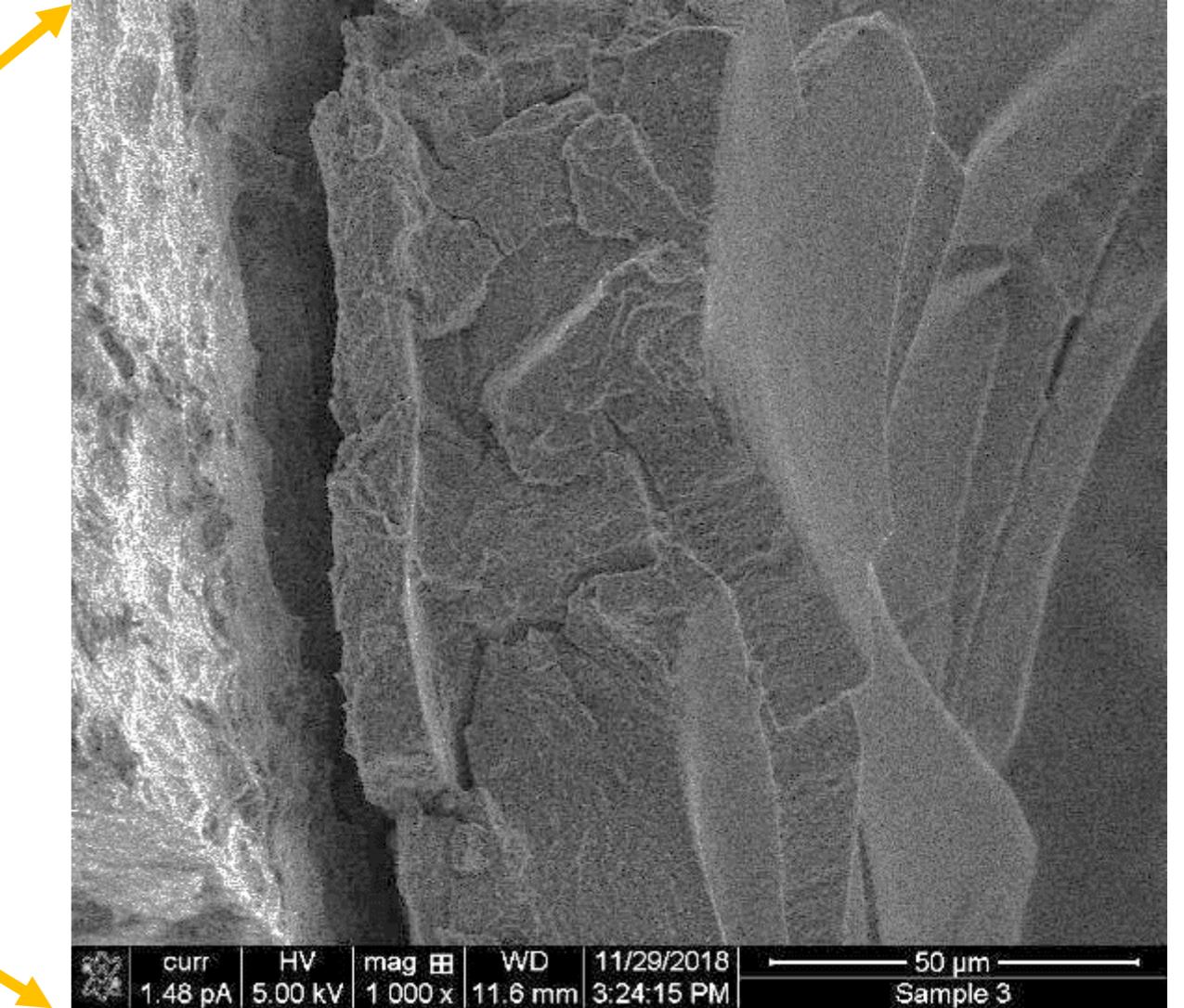
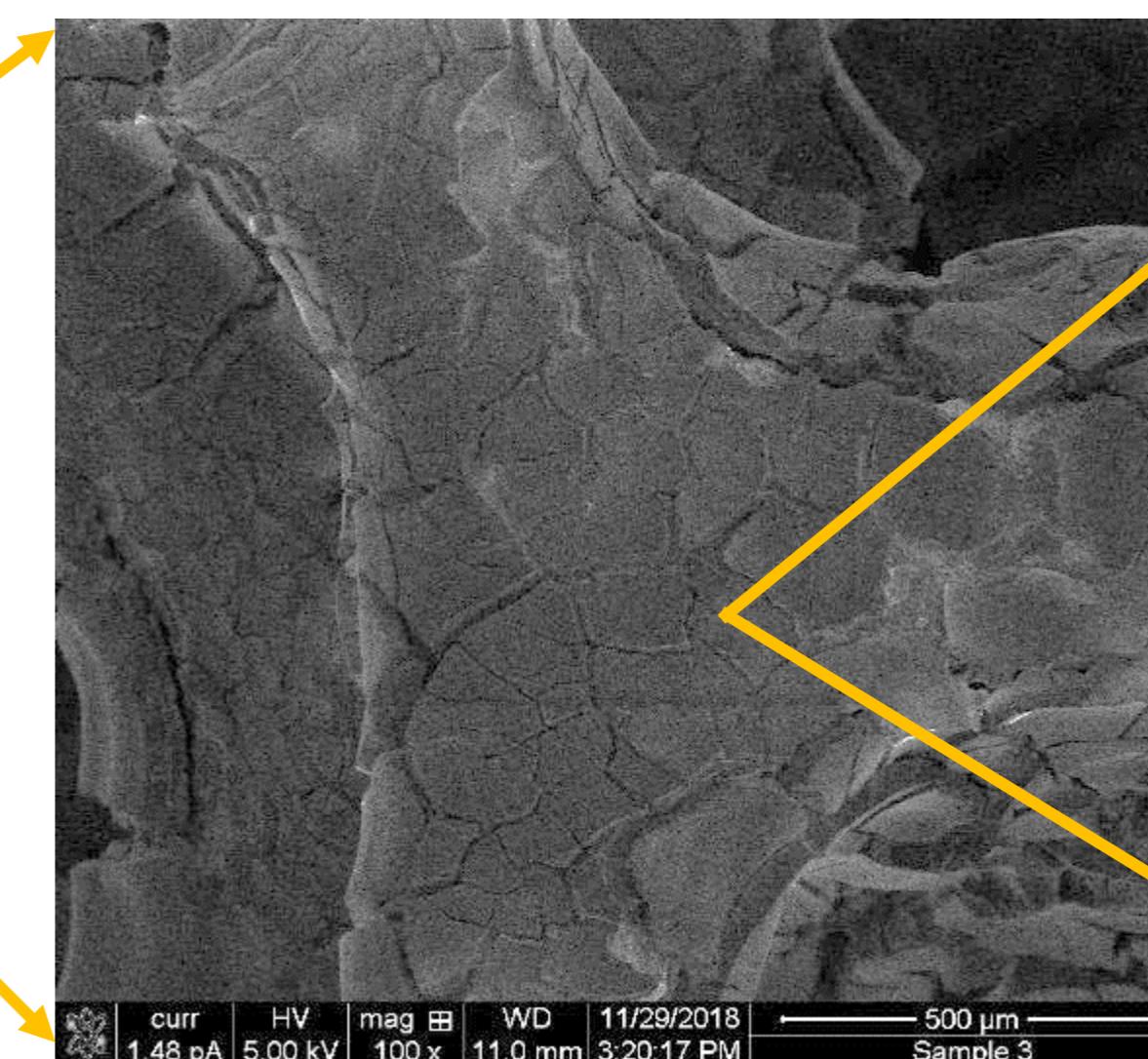
Porosity

Materials



1. INTRODUCTION

Foams



High geometric surface area

High dispersion of catalyst on a thin wash-coated layer

Improve heat and mass transfer

Objectives

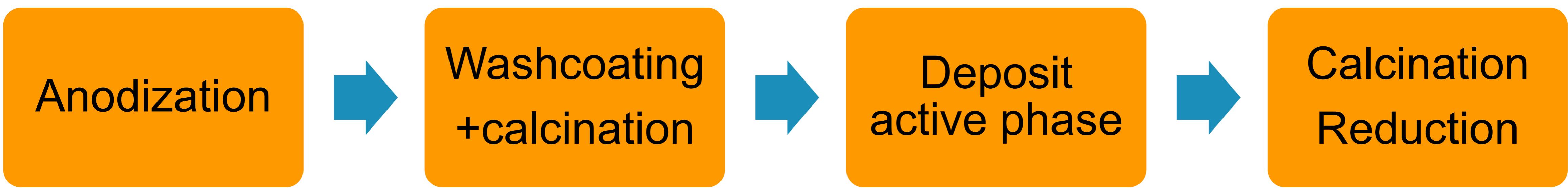
- Develop an active, stable and with tunable washcoat thickness foam catalyst for the FTS
- Test and demonstrate the enhanced performance of open-foam catalysts
- Characterize the transport properties: internal and external mass transfer
- Develop a reactor model



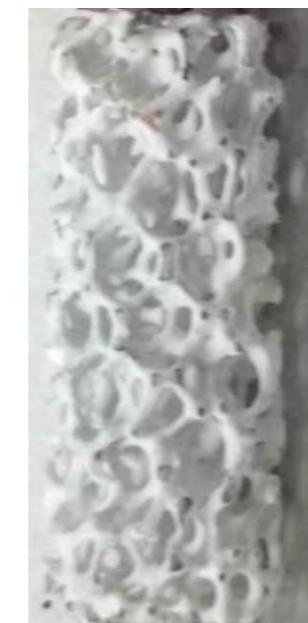
3. EXPERIMENTAL

Catalyst preparation

Develop an **active, stable and with tunable washcoat thickness** foam catalyst for the FTS



Foam 20 ppi
 $S_{geo}=1560 \text{ m}^2/\text{m}^3$



Loading: 10-50%
Layer 20-100 μm
 Al_2O_3
 TiO_2



$\text{Co}(15\%)/\gamma\text{-Al}_2\text{O}_3$



3. EXPERIMENTAL

FTS on Co/Al₂O₃/Foam

Catalyst:

Co(15%)/ γ -Al₂O₃

3 thickness: 28 - 43 - 68 μm

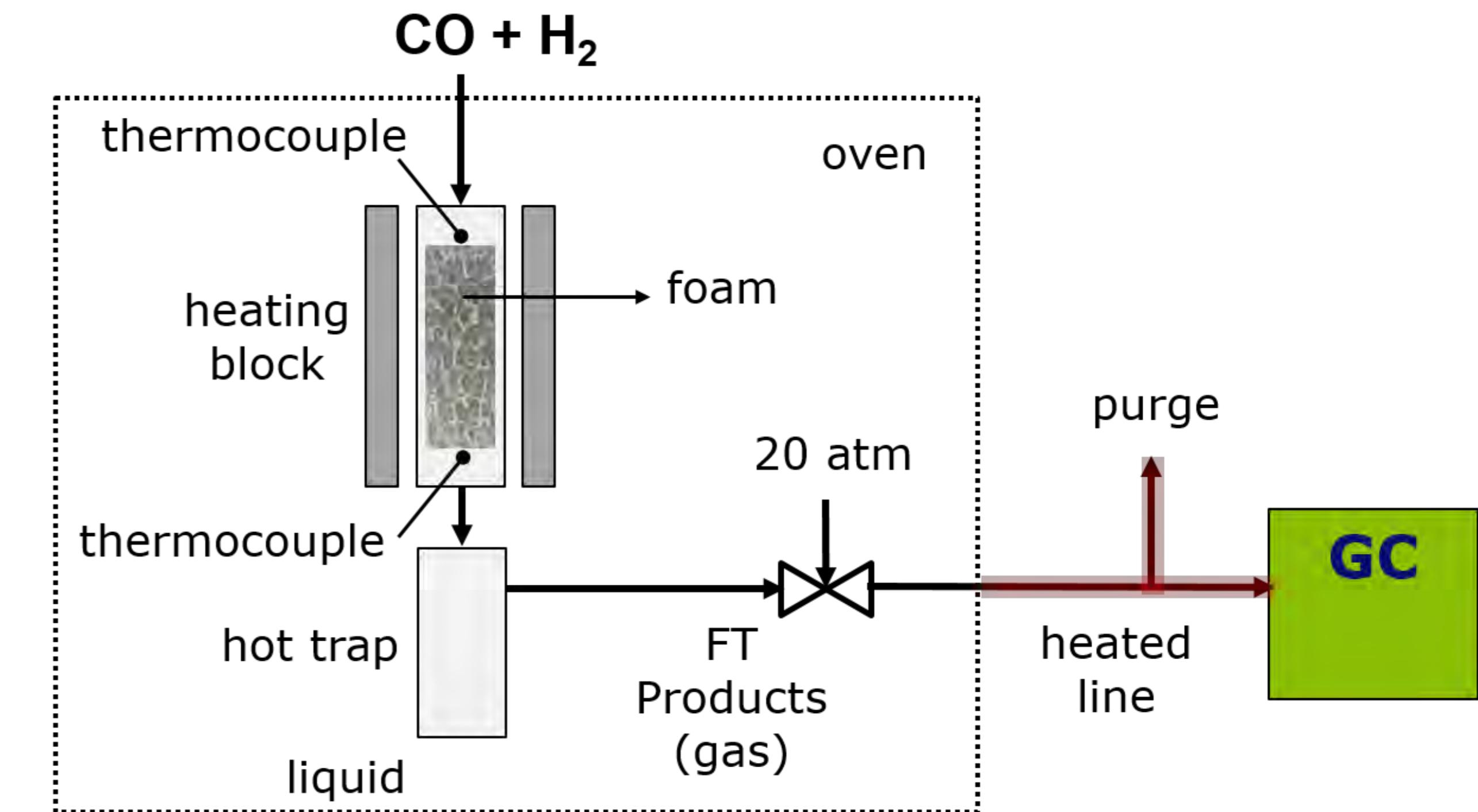
Conditions:

T = 210 , 220 , 230°C

P = 20 bar

GHSV = 3820 – 1910 h^{-1}

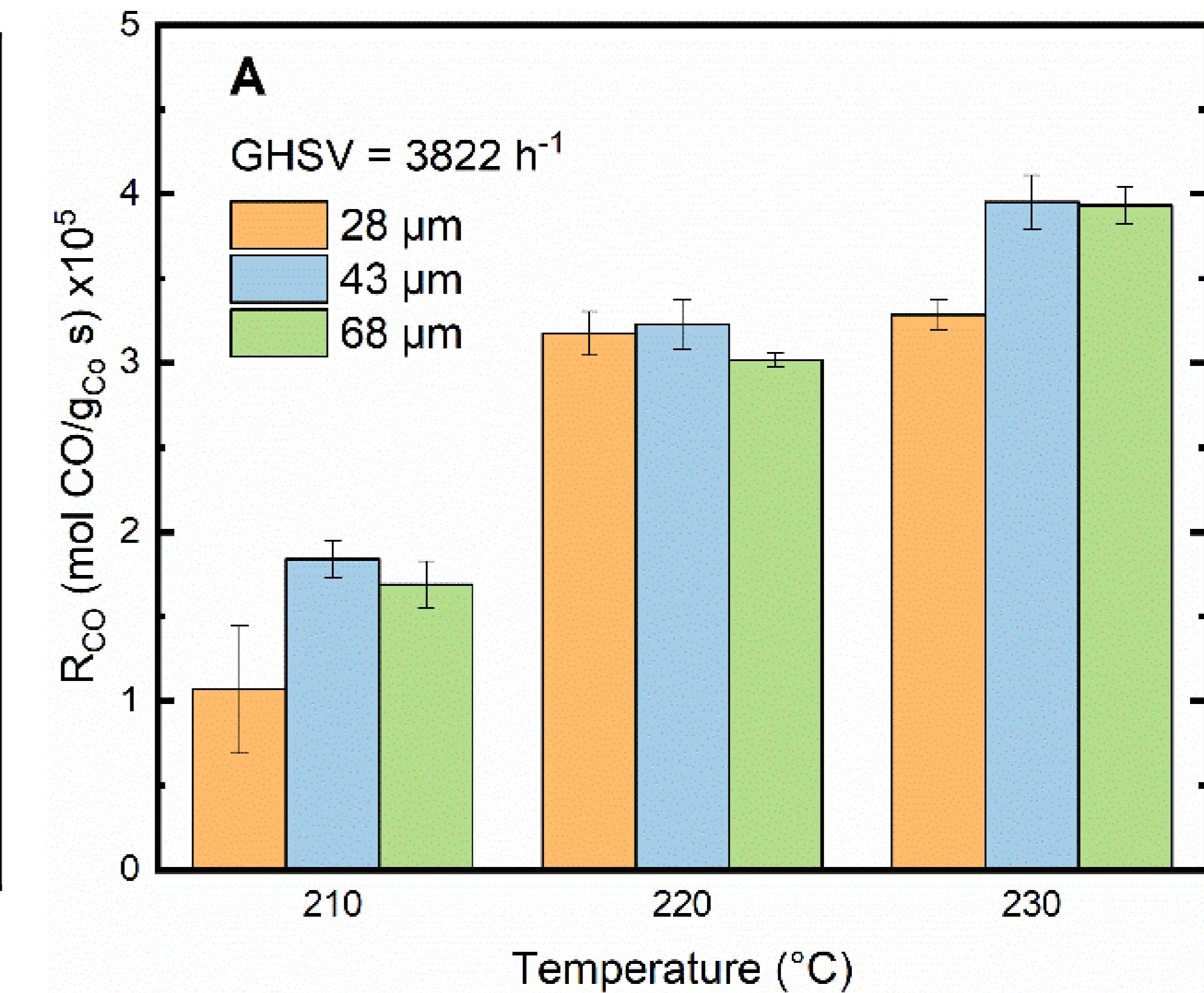
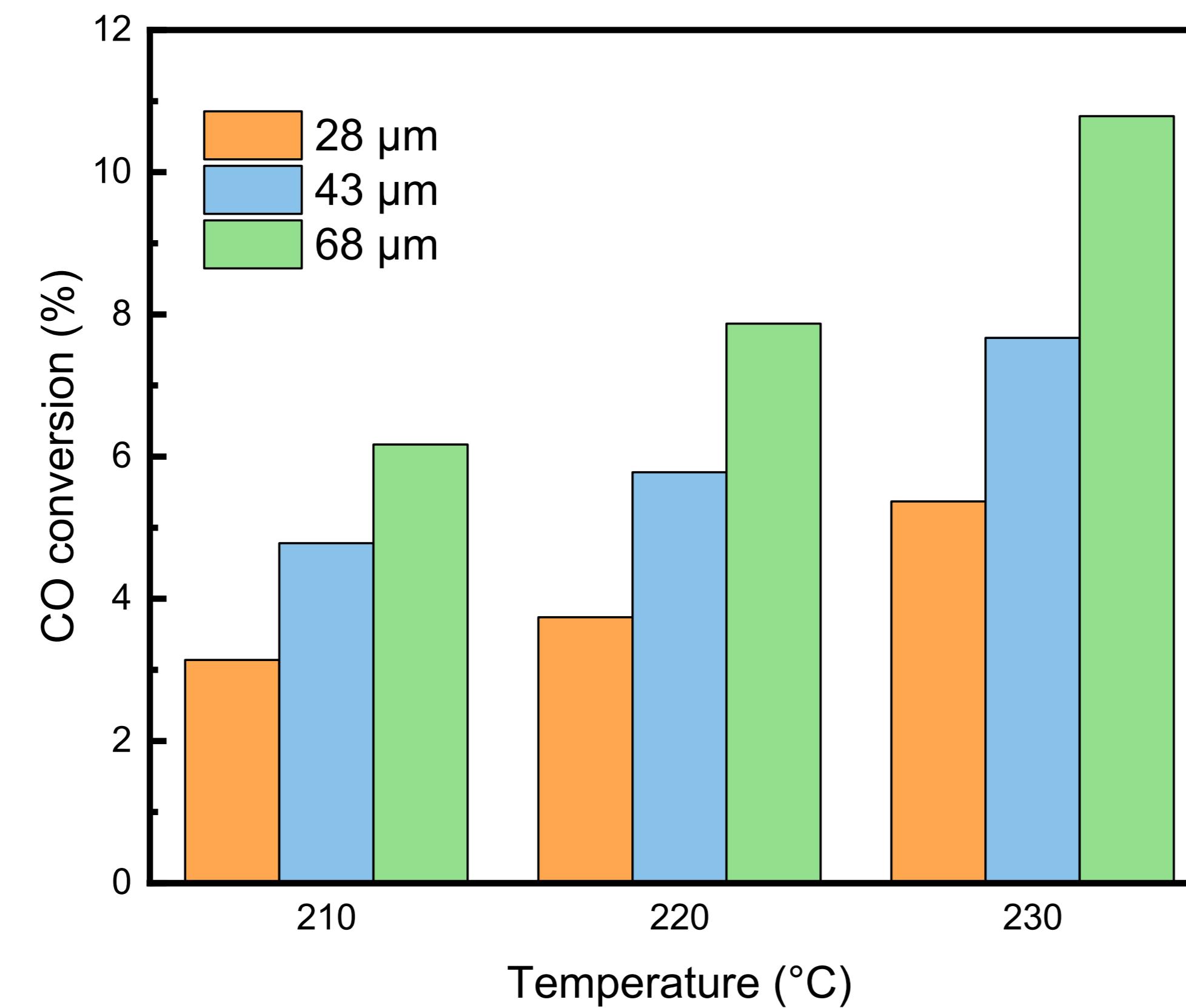
H₂/CO/N₂ = 6/3/1



4. RESULTS

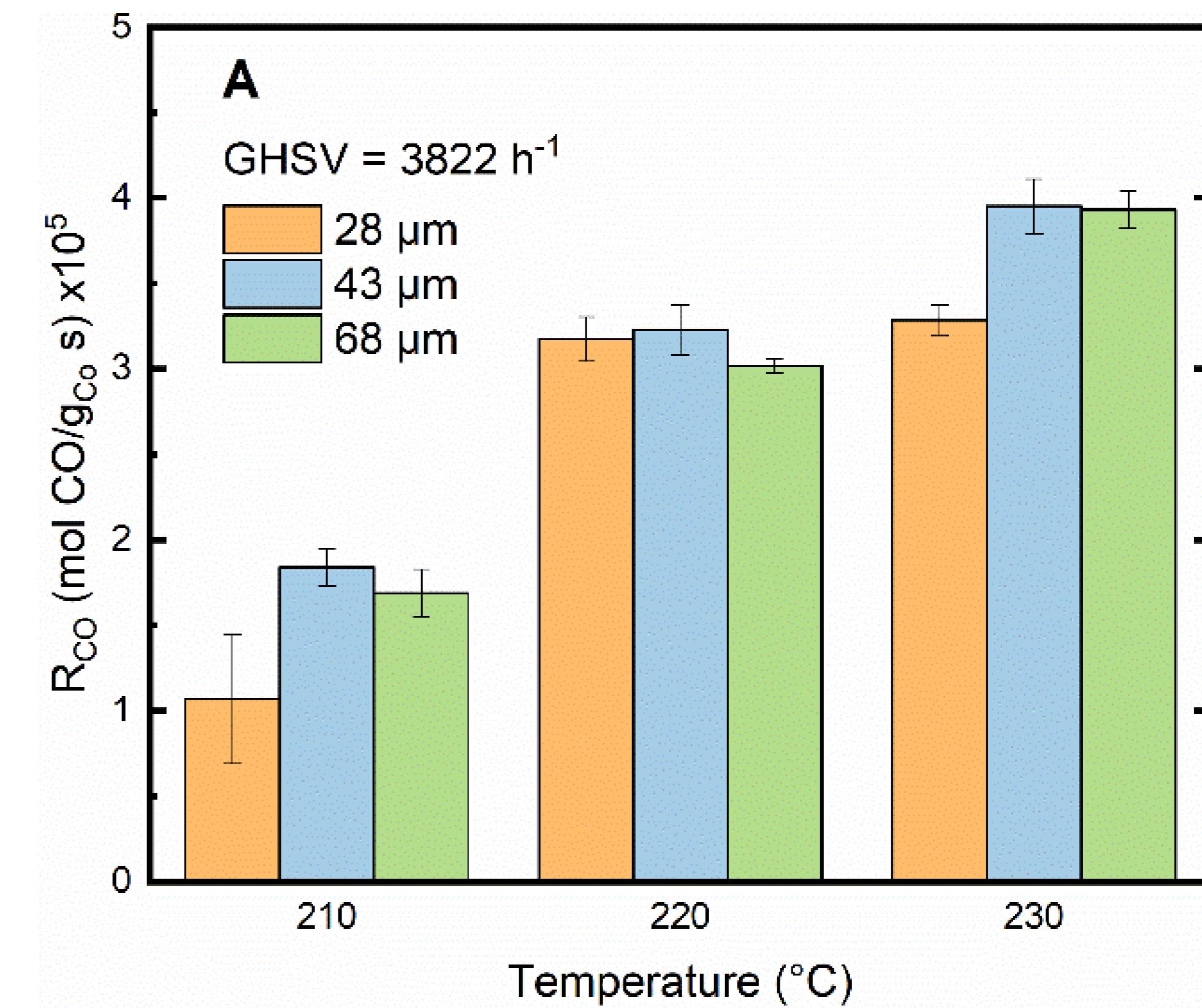
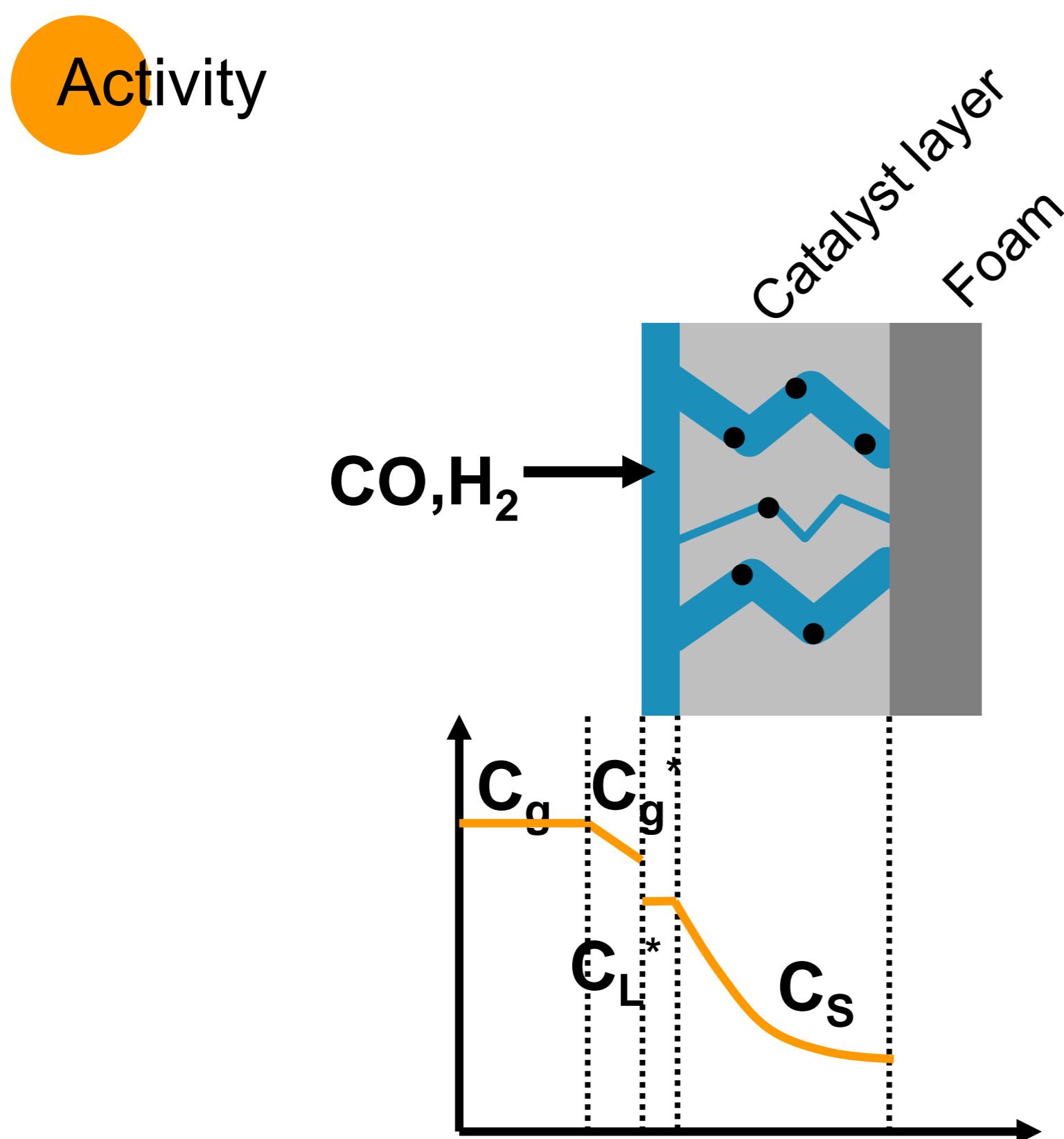
FTS on Co/Al₂O₃/Foam

Activity



4. RESULTS

FTS on Co/Al₂O₃/Foam



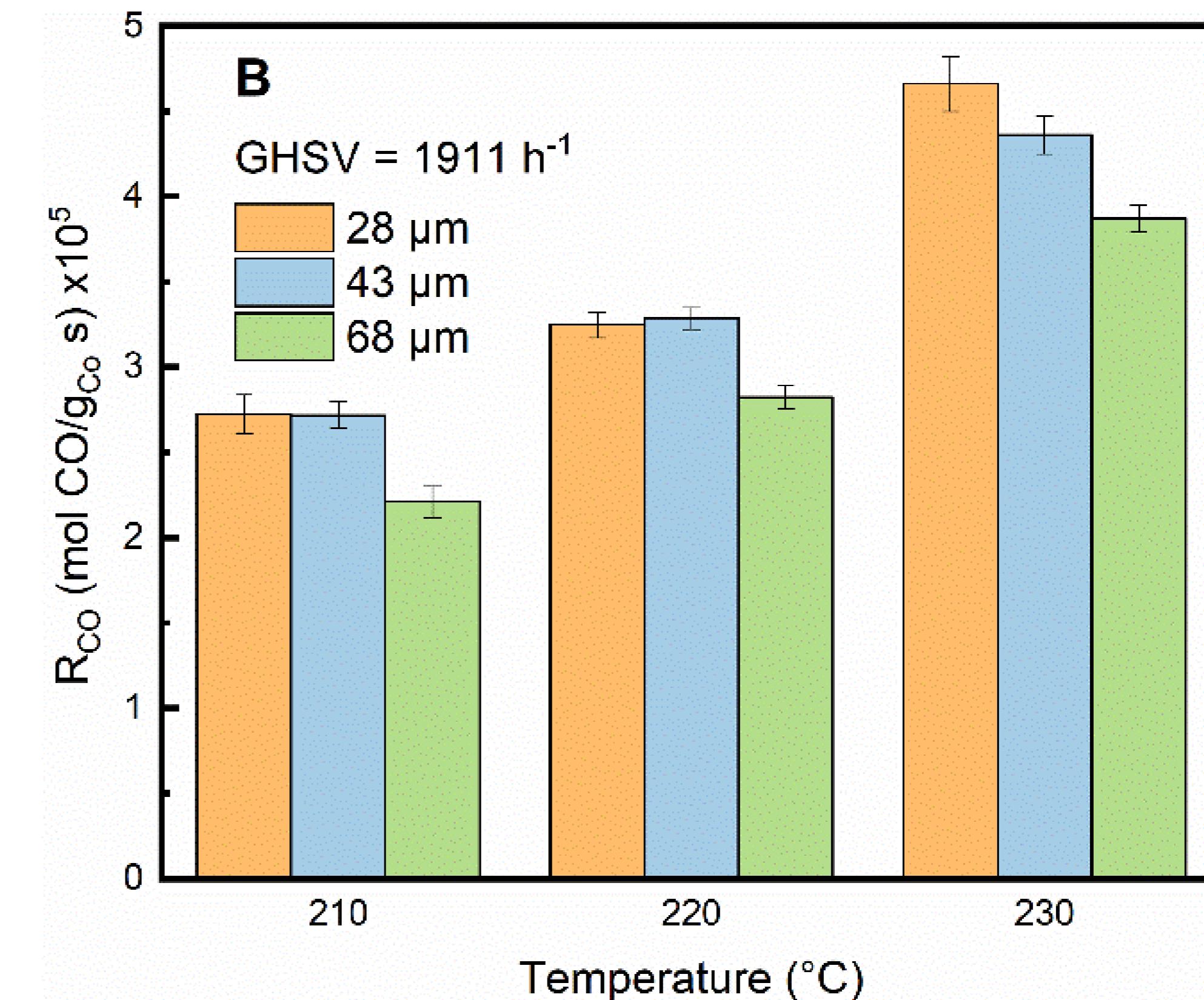
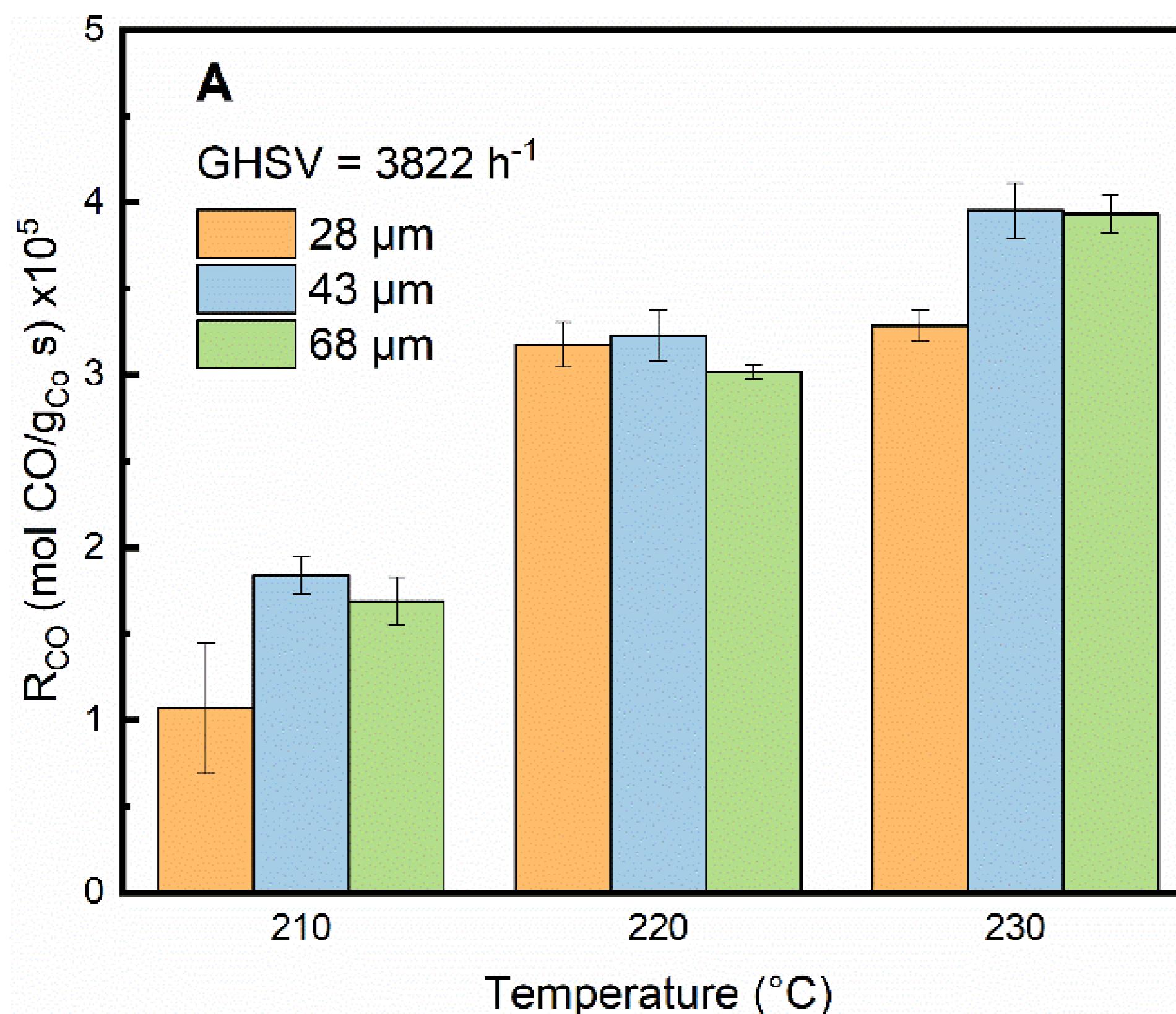
Diffusion limitations?

4. RESULTS

FTS on Co/Al₂O₃/Foam

Activity

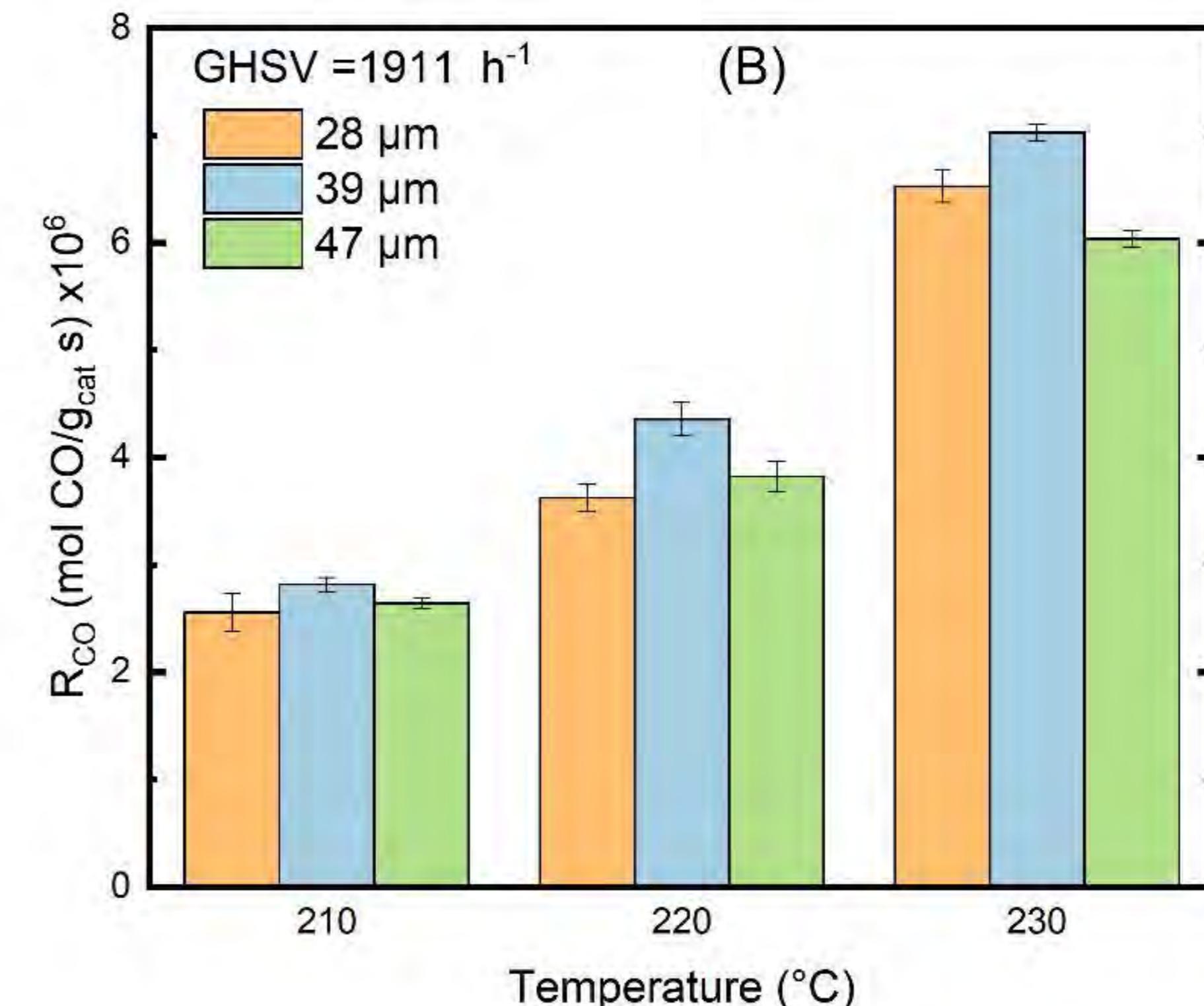
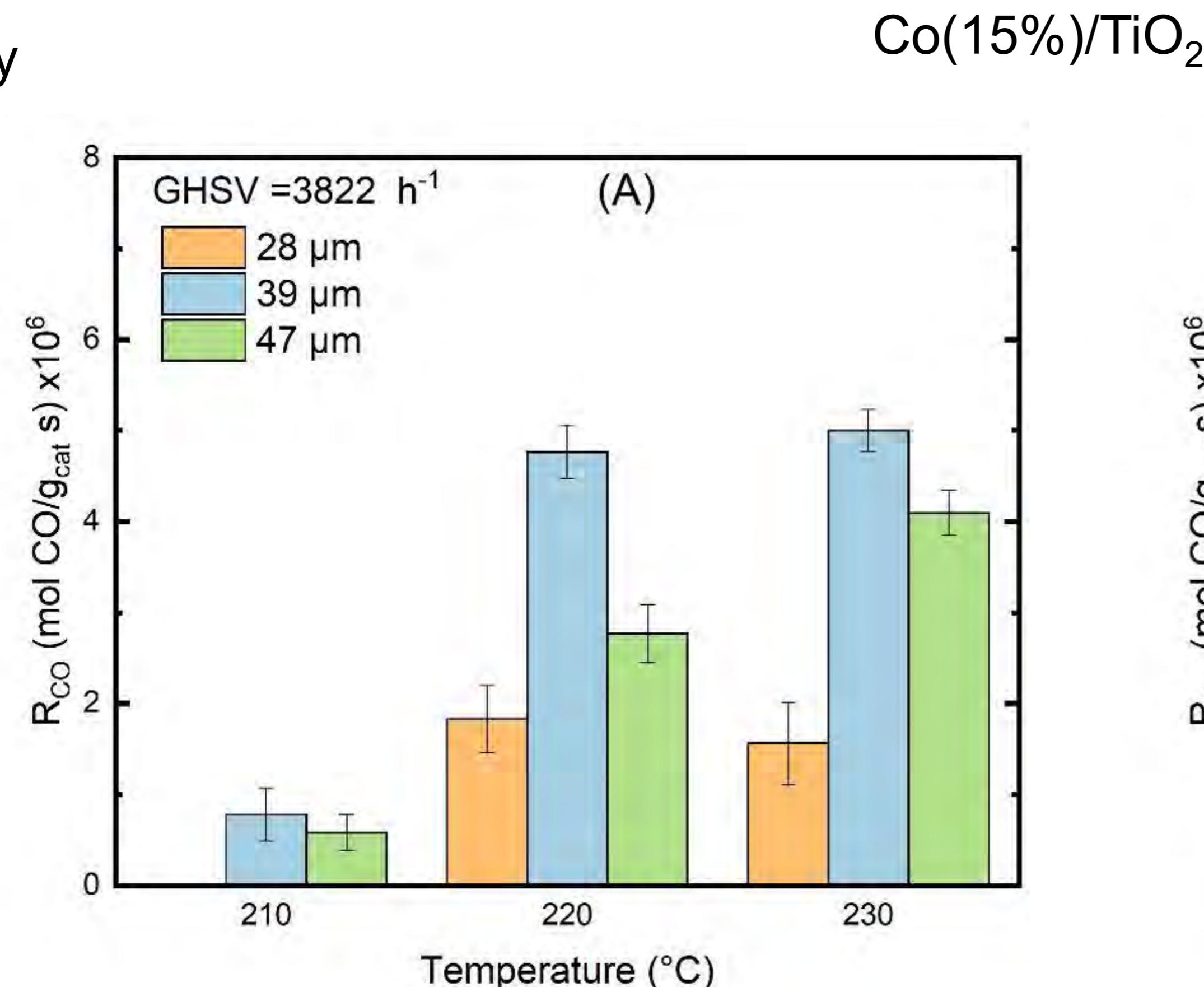
Co(15%)/γ-Al₂O₃



4. RESULTS

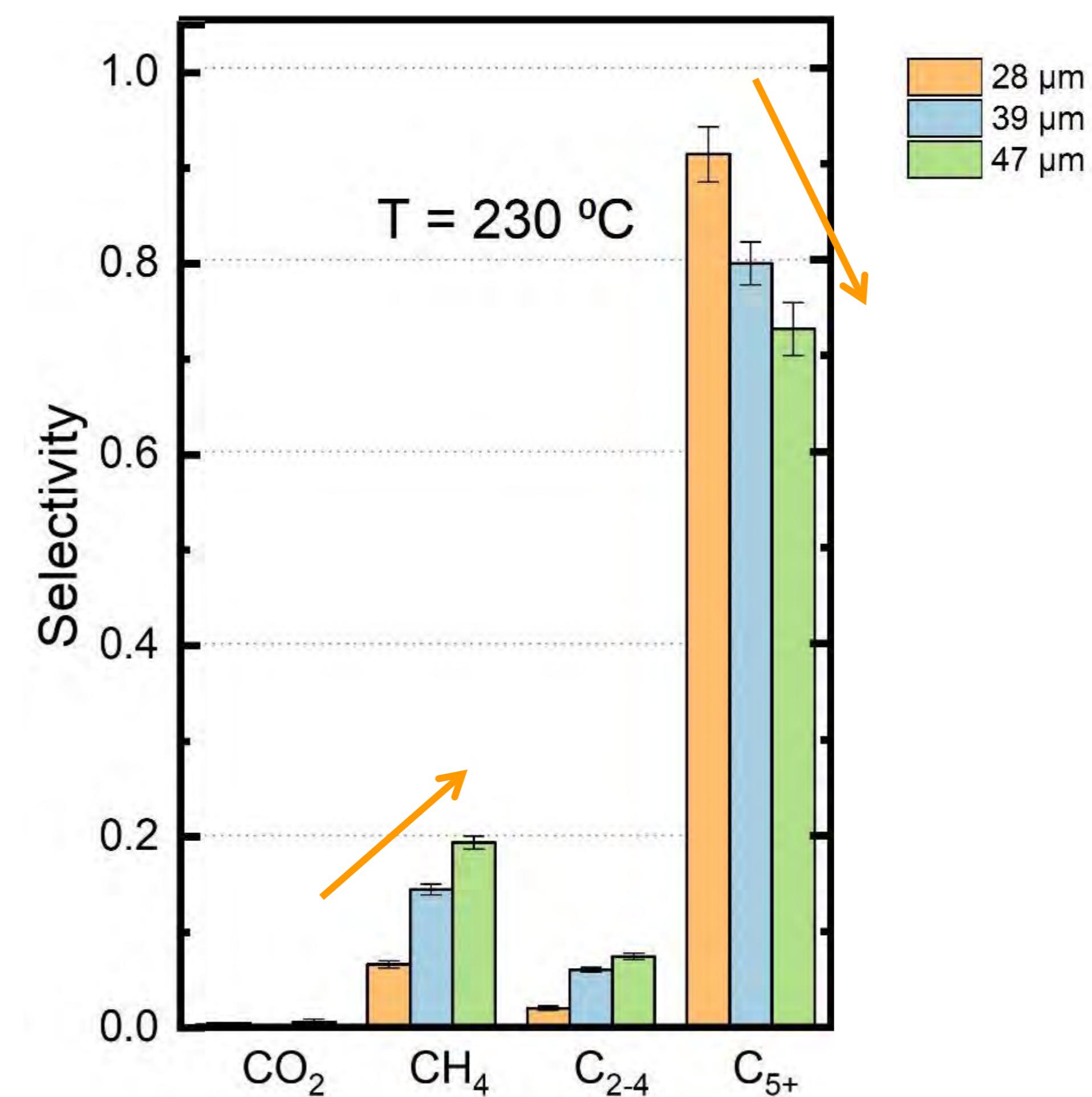
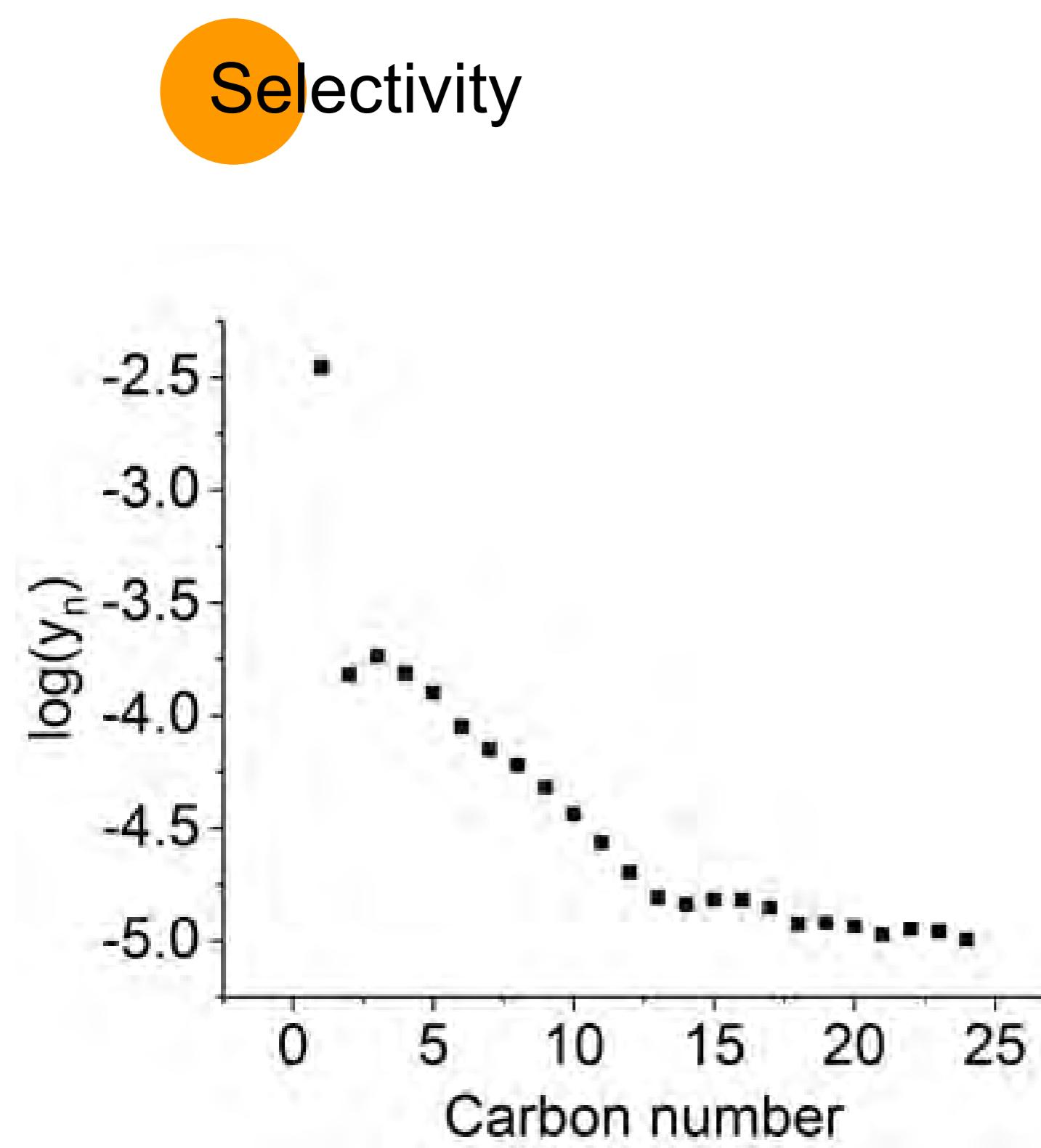
FTS on Co/TiO₂/Foam

Activity



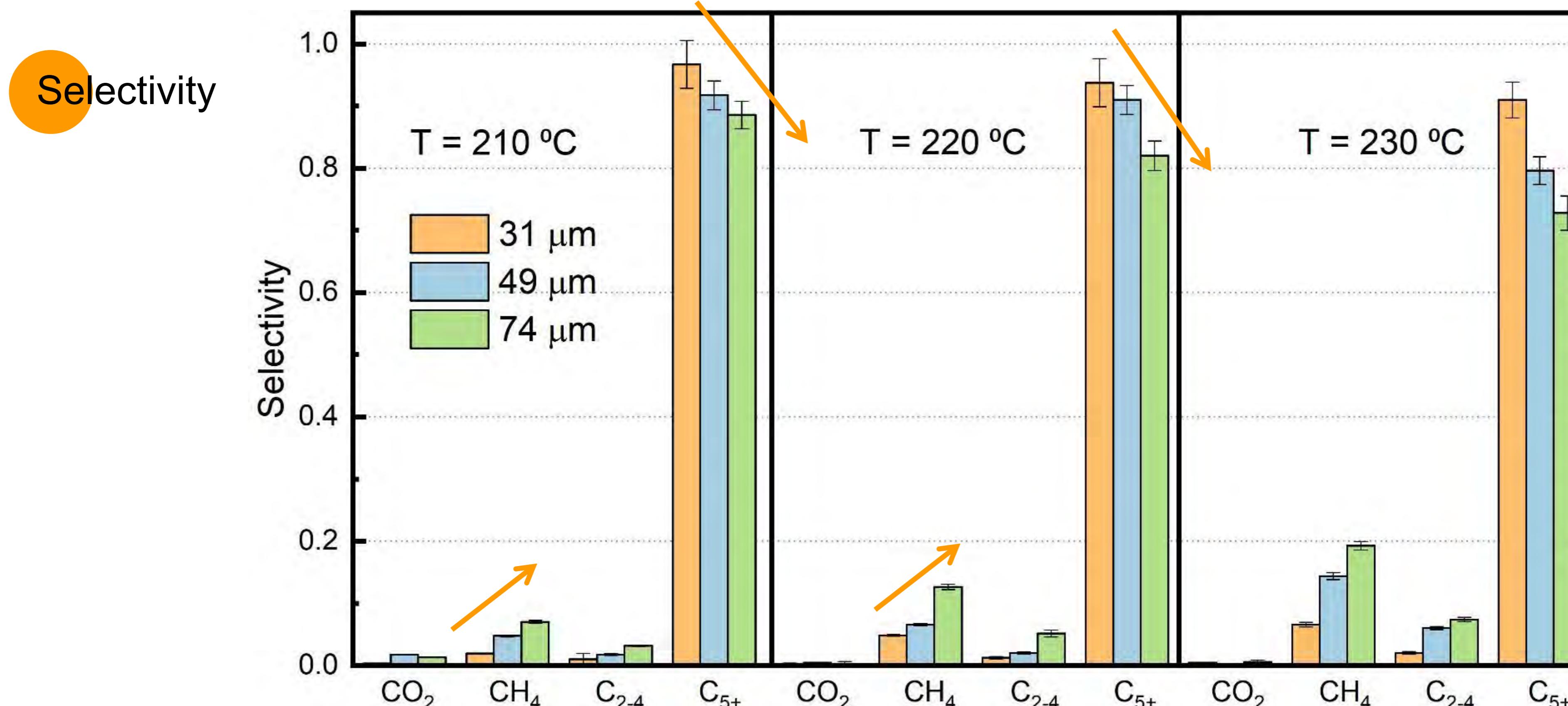
4. RESULTS

FTS on Co/Al₂O₃/Foam



4. RESULTS

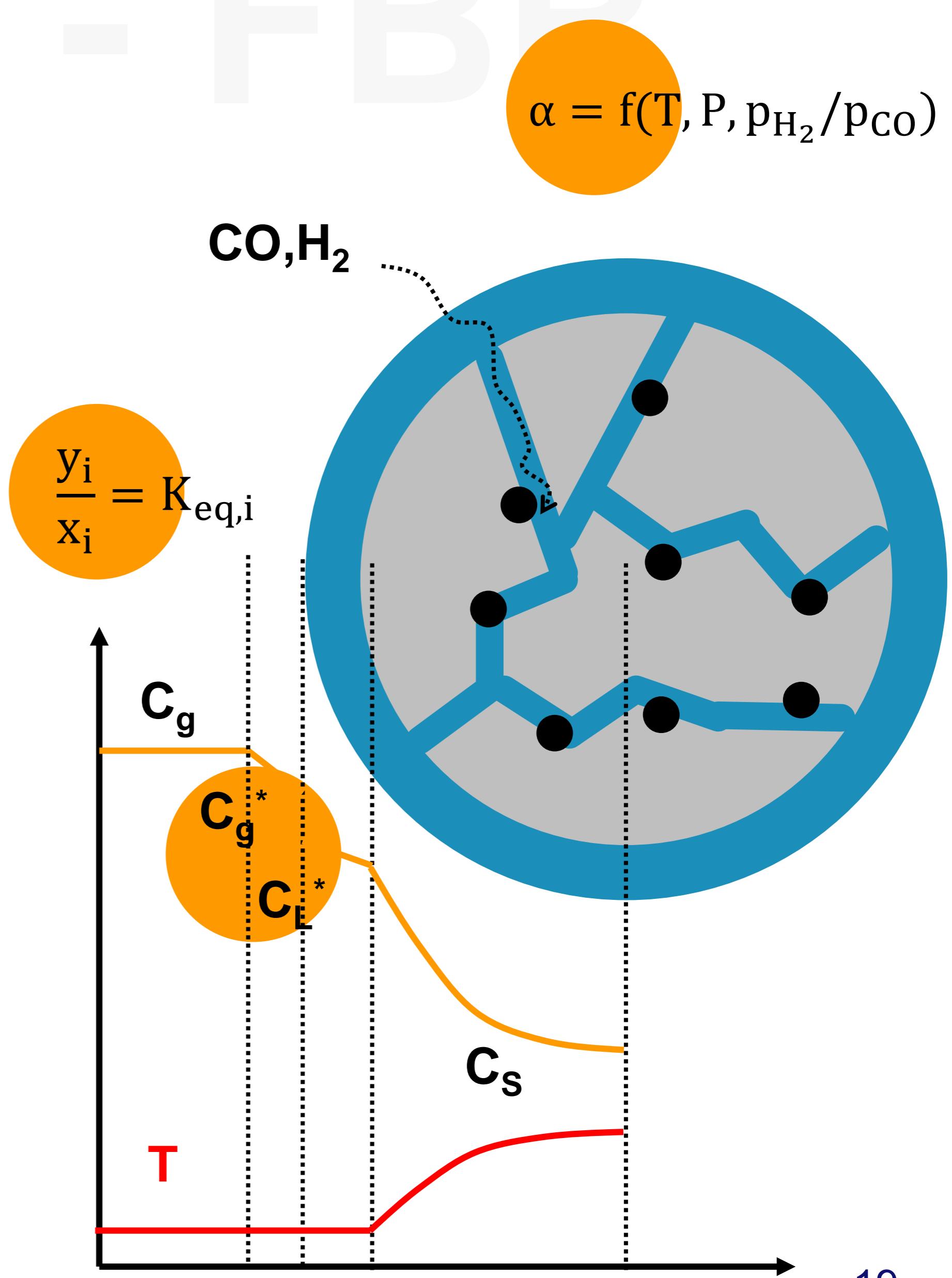
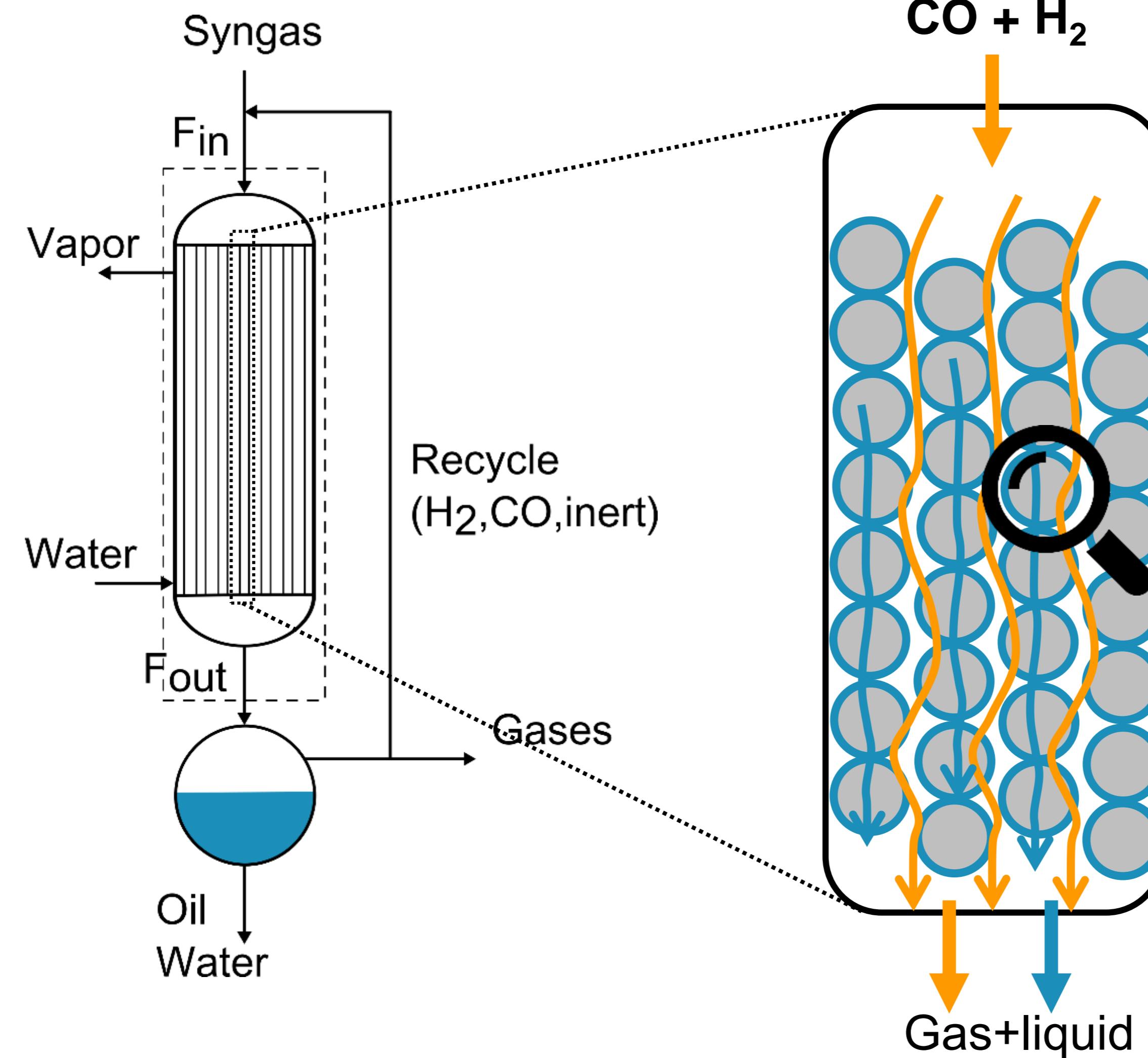
FTS on Co/Al₂O₃/Foam



The layer thickness affects the selectivity and the reactor performance

4. RESULTS

LTFT Reactor - FBR

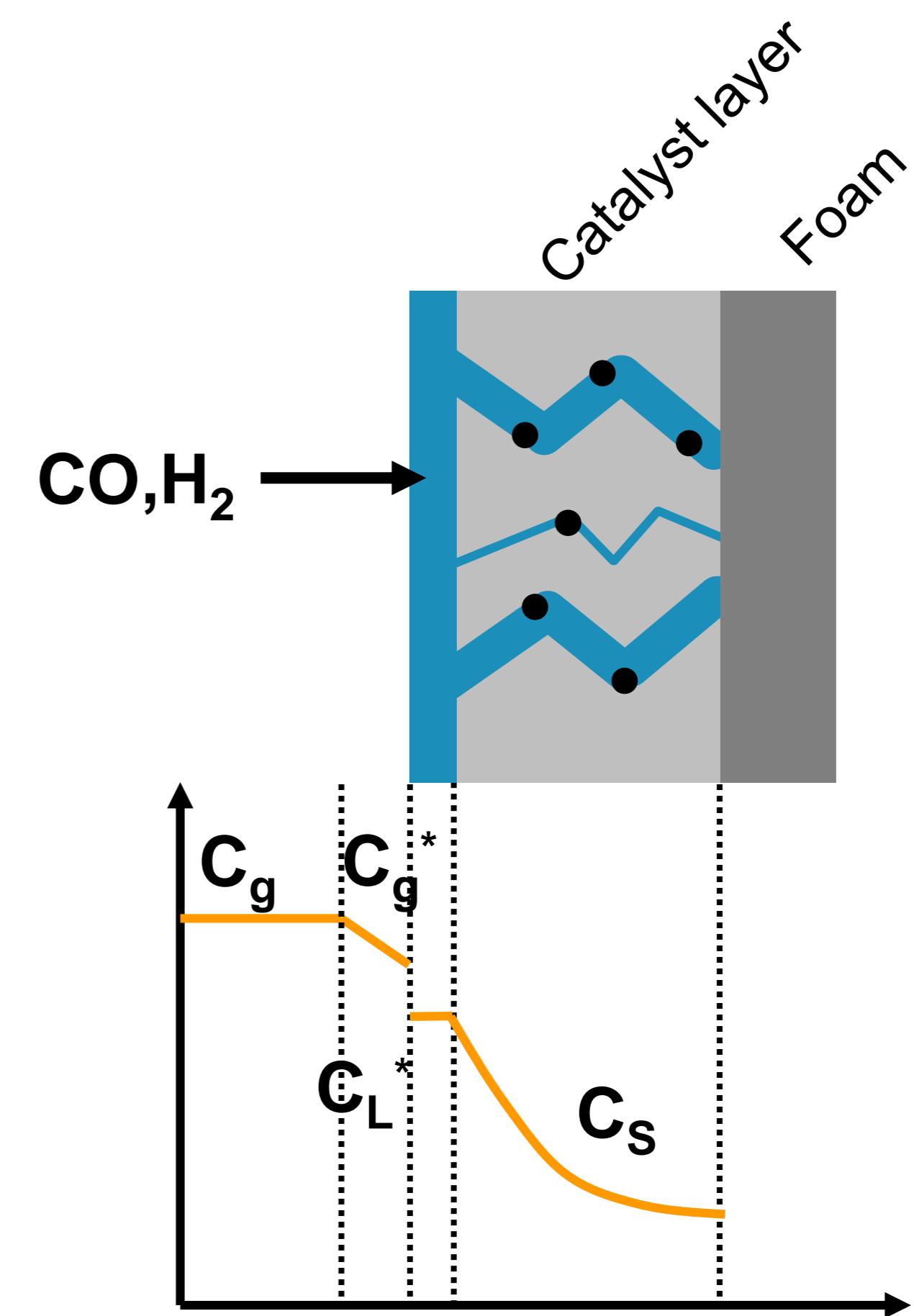


4. RESULTS

Mass transfer limitations

Systematic analysis of the mass transfer limitations in foams

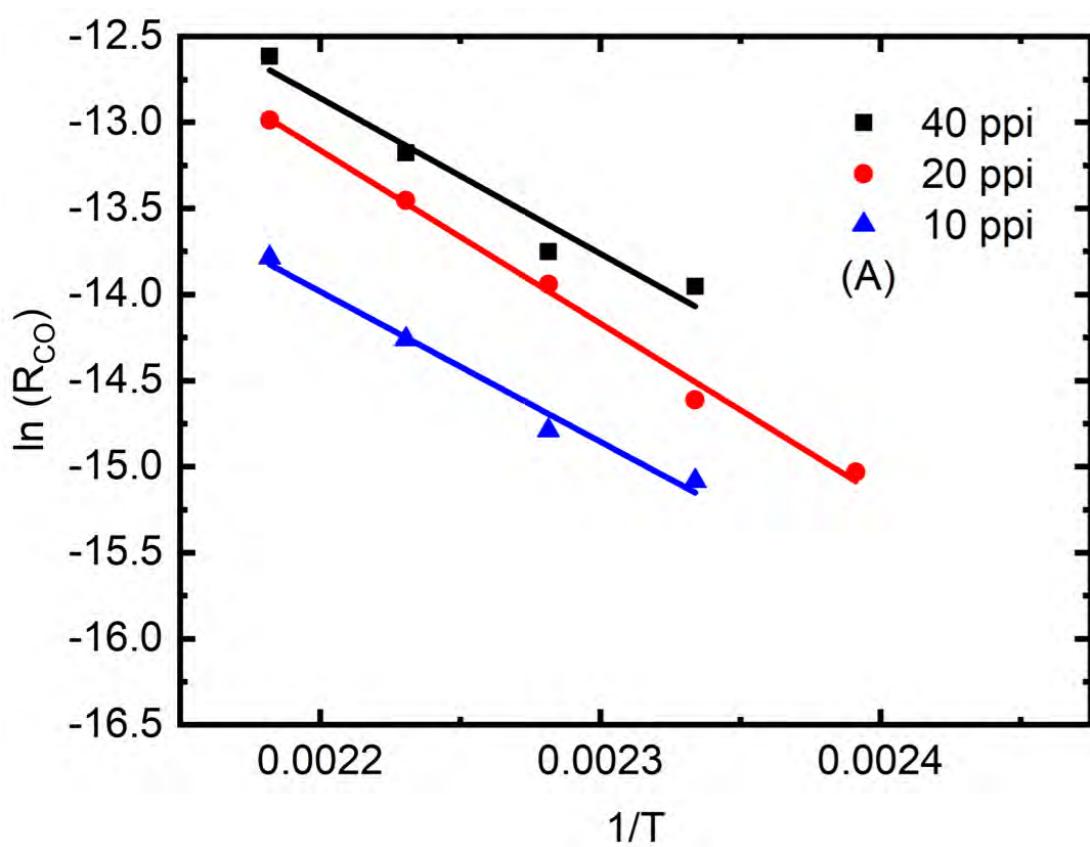
How important is the **external mass transfer** in open-foams?



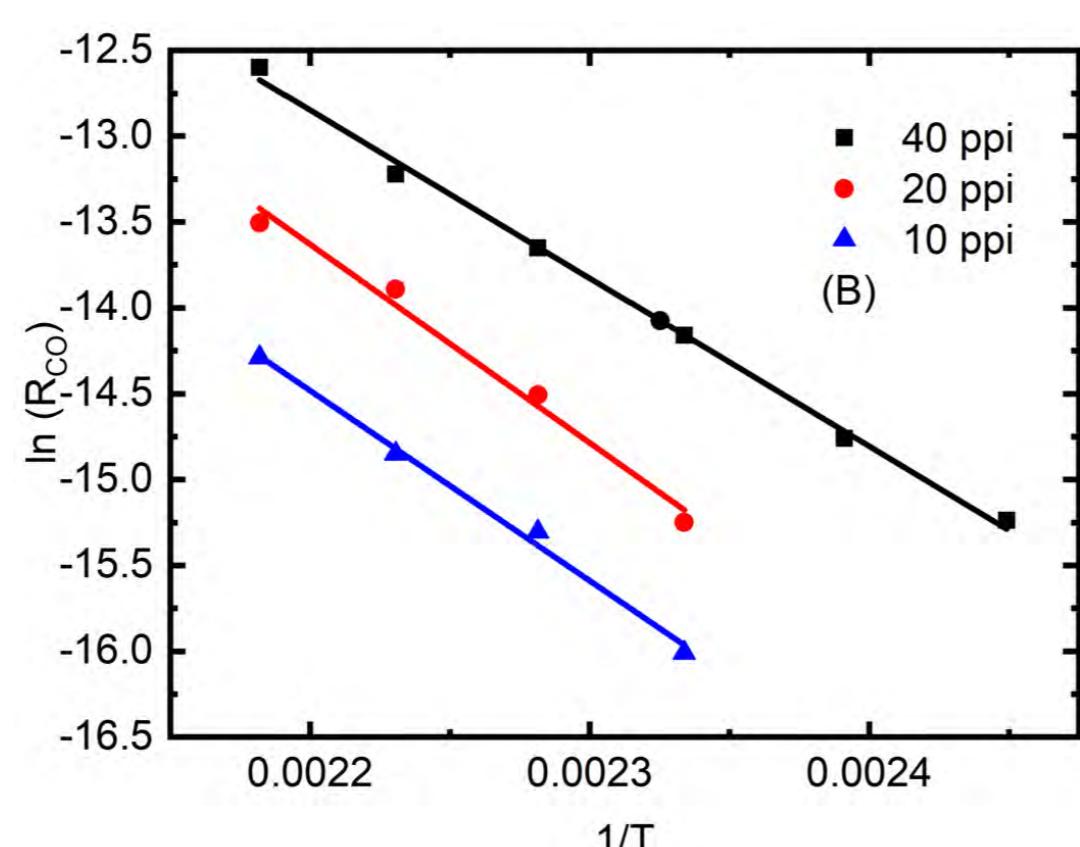
4. RESULTS

Mass transfer limitations

Reaction test: CO oxidation on Pt(1%)/ γ -Al₂O₃



36 mL/min
(5%)CO+(10%)O₂



73 mL/min
(5%)CO+(10%)O₂

Foam ppi	Geometrical surface area (m ² /m ³)
40	1663
20	1240
10	758

Conditions:

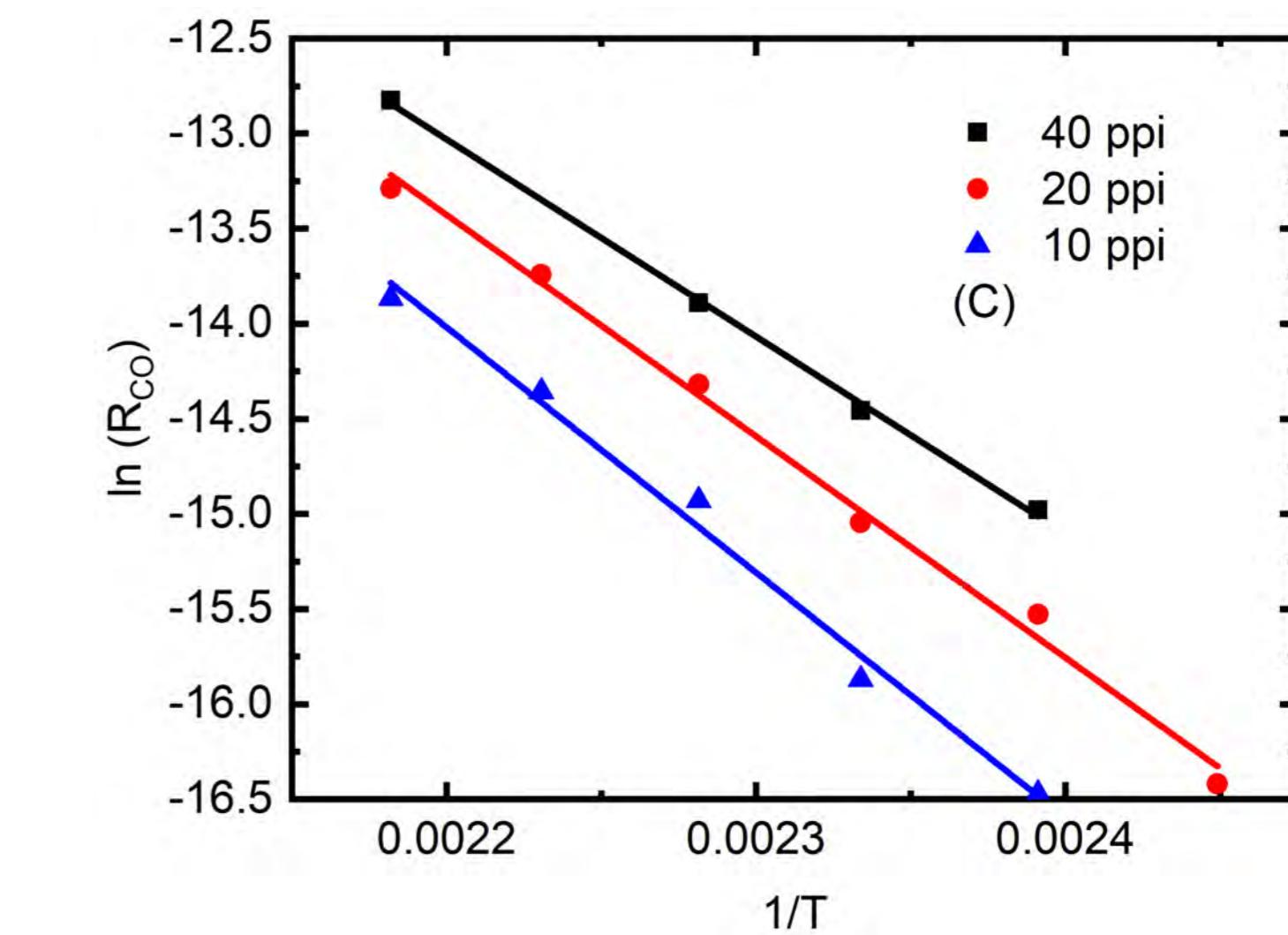
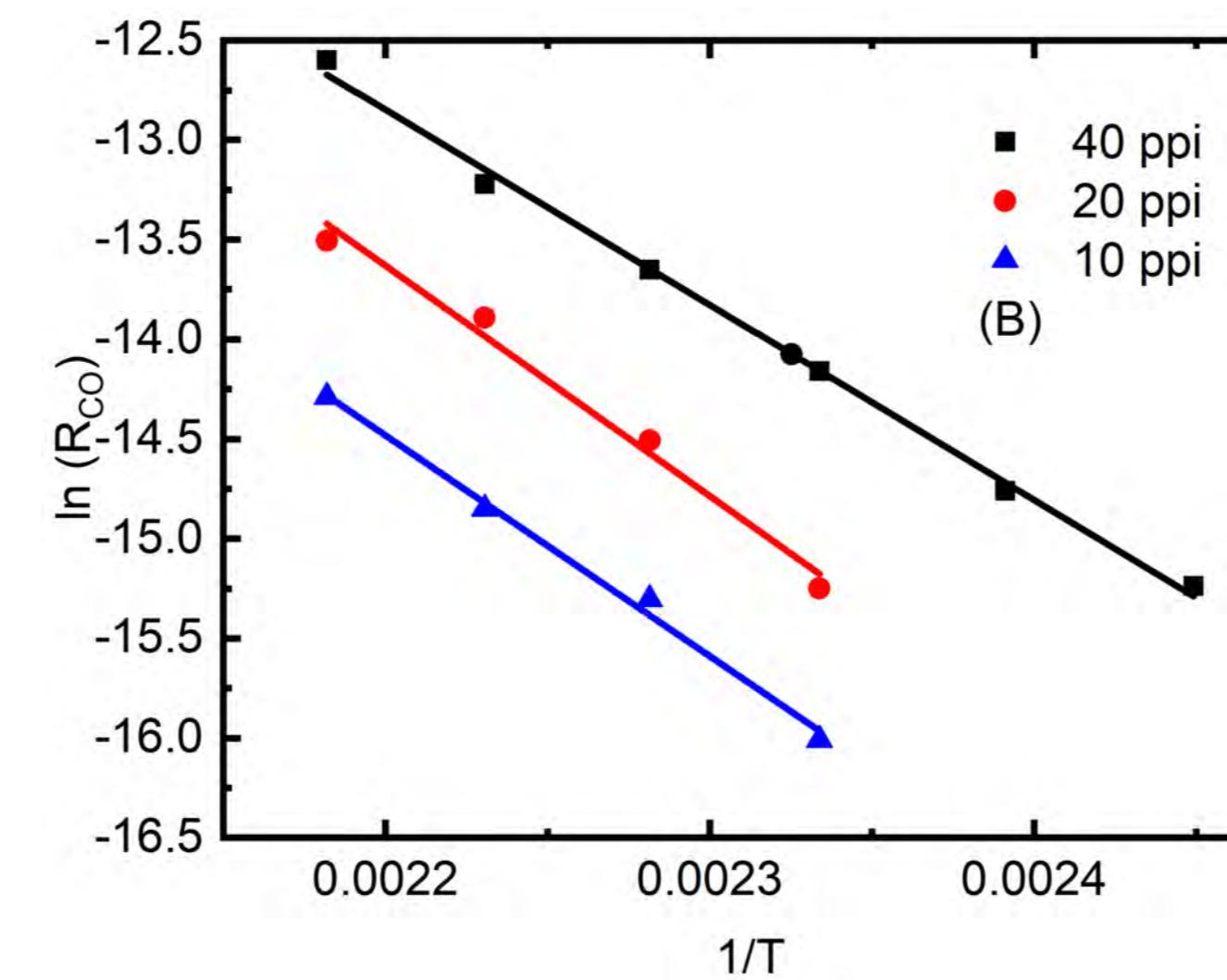
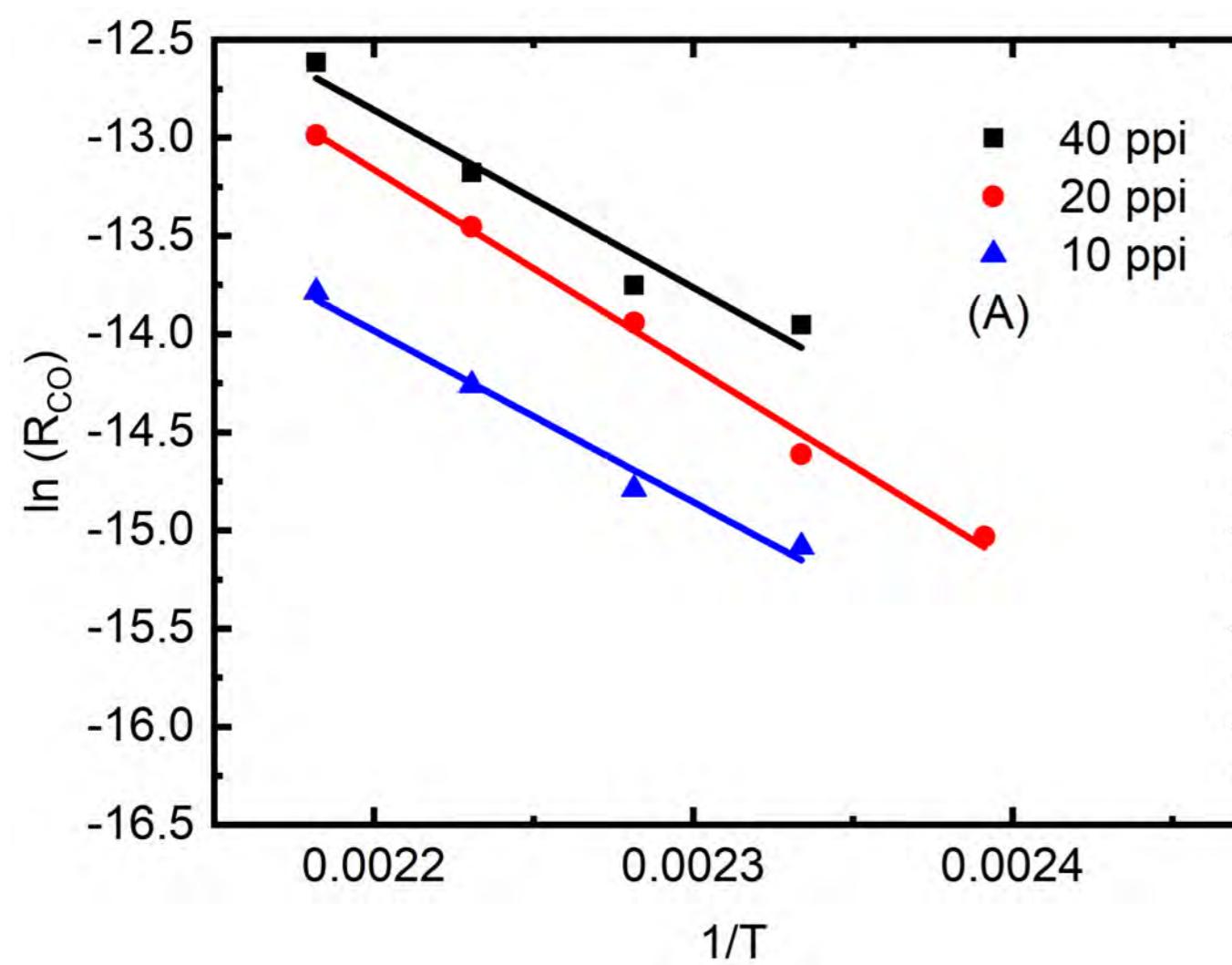
T = 135-185°C
P = 1 bar
Total flow = 30-80 mL/min
CO/O₂ = 1/2

4. RESULTS

Mass transfer limitations

Reaction test

CO oxidation on Pt(1%)/ γ -Al₂O₃

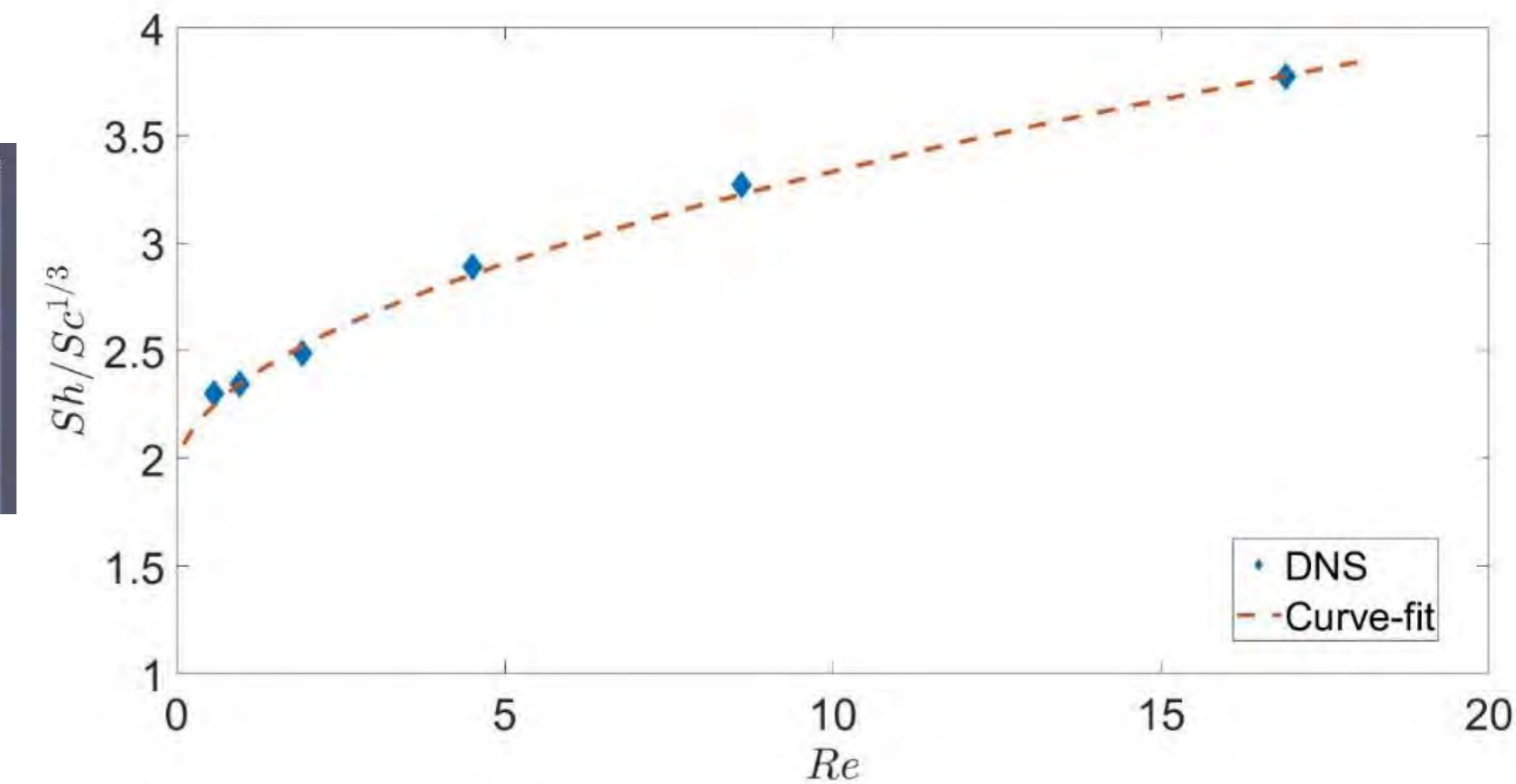
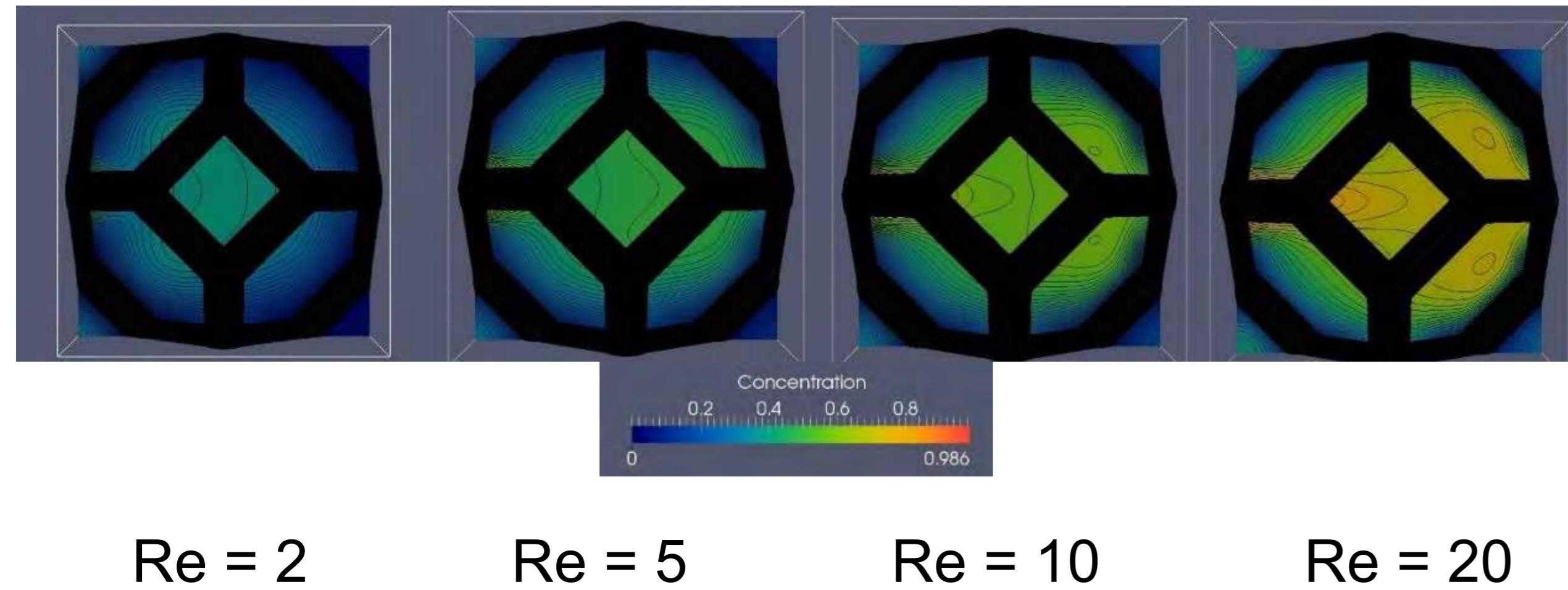


The external surface area affects the activity: external mass transfer limitations?

4. RESULTS

Mass transfer limitations

Direct numeric simulation



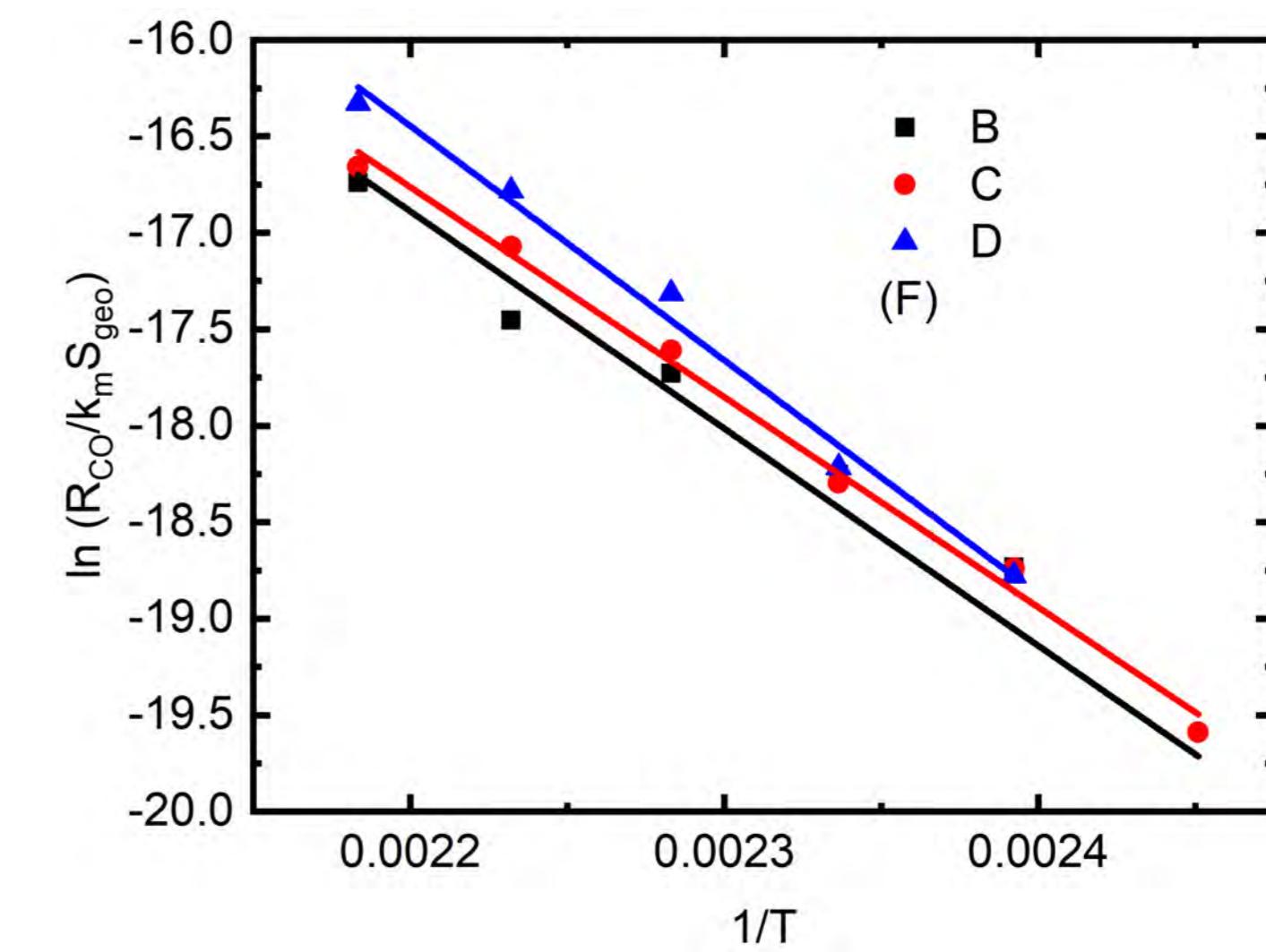
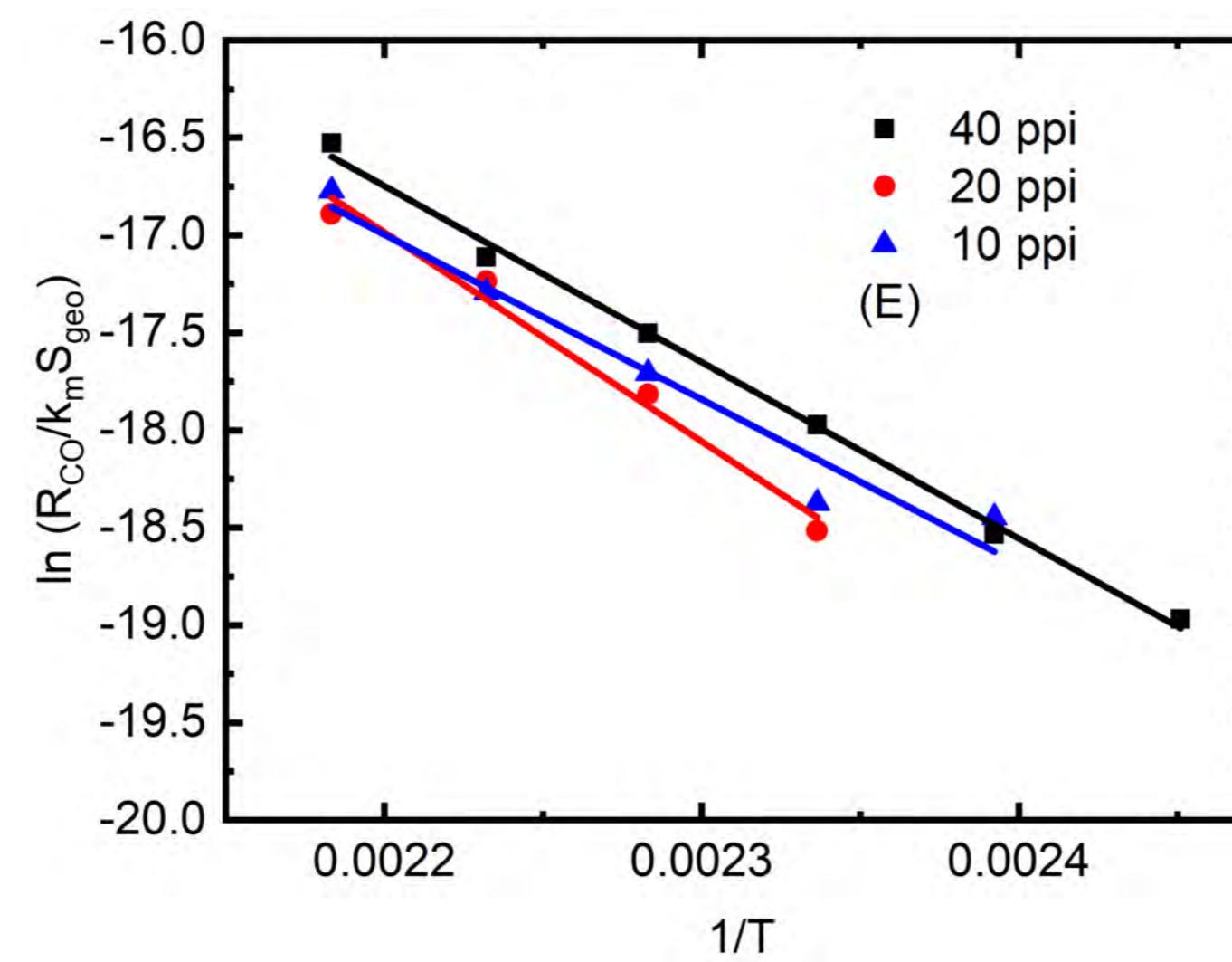
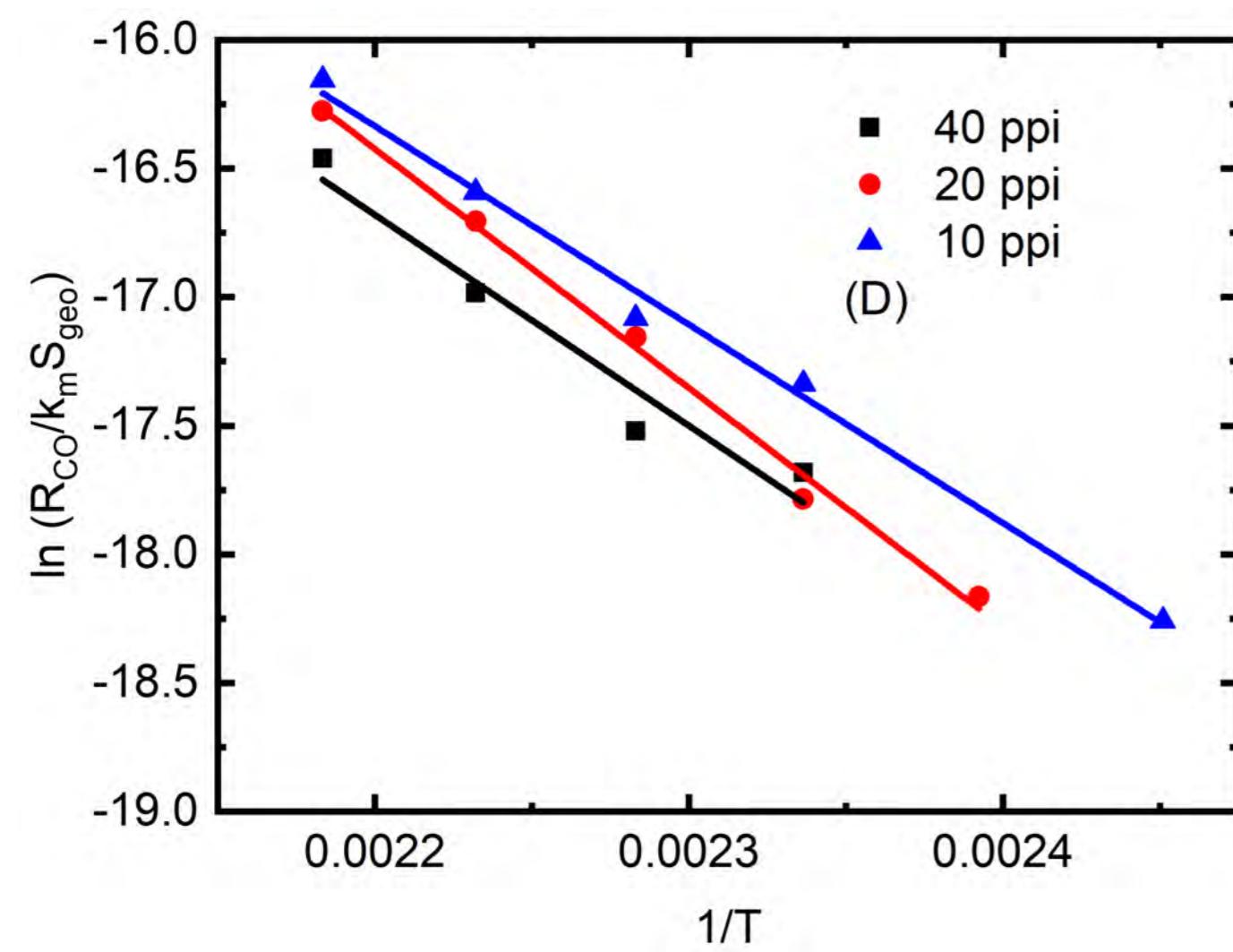
$$Sh = 1.94 + 0.41Re^{0.53}Sc^{0.33}$$

4. RESULTS

Mass transfer limitations

Reaction test

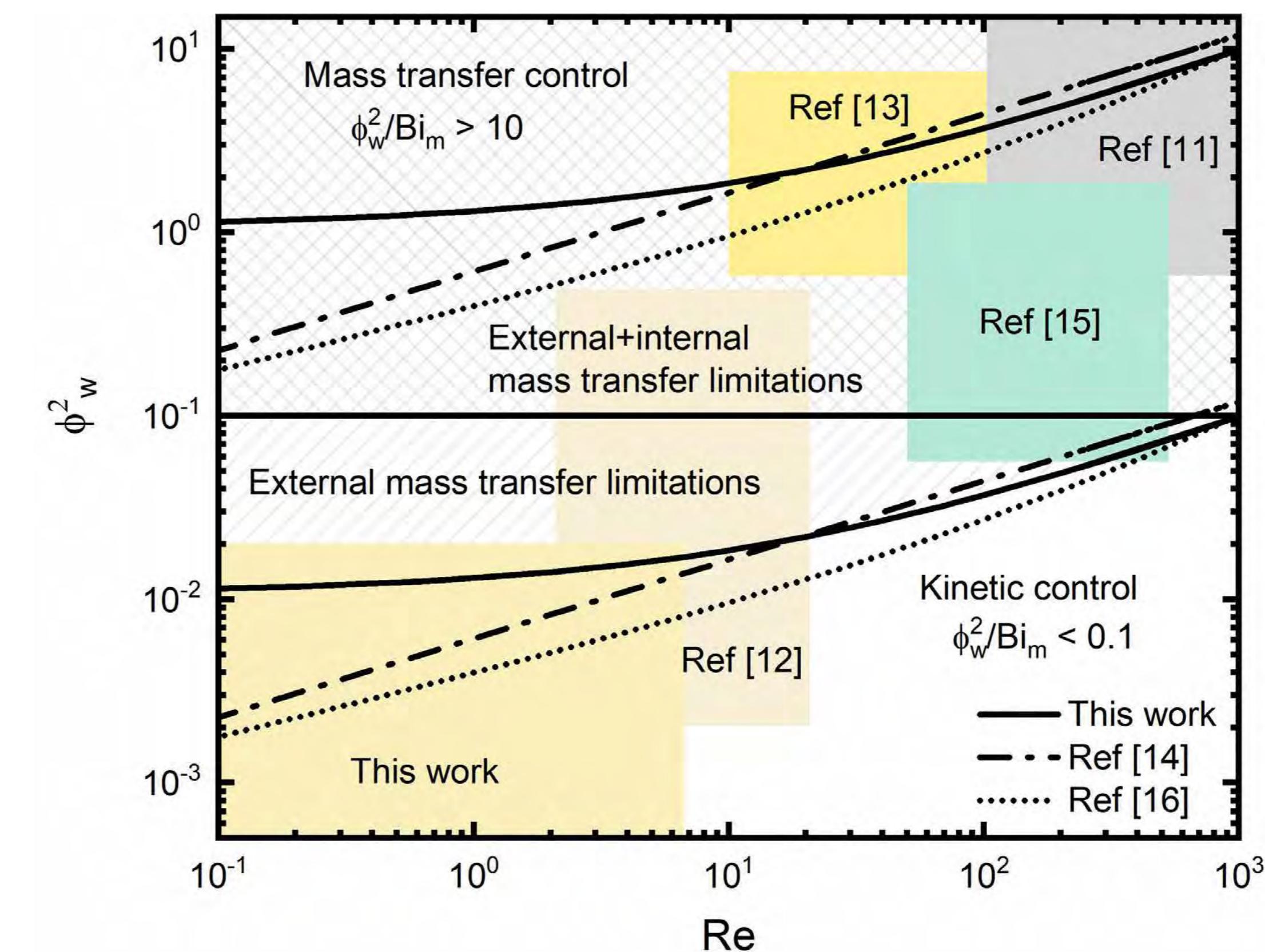
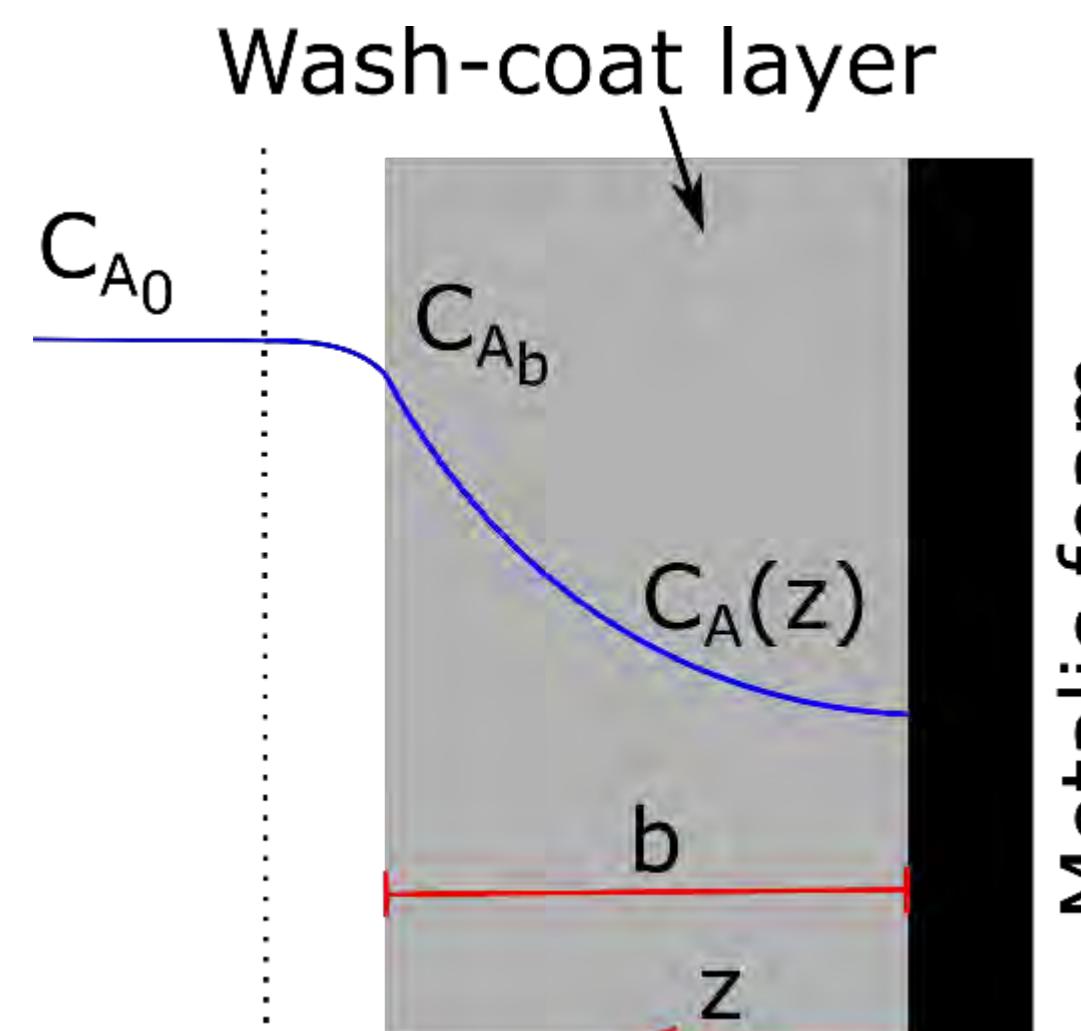
CO oxidation on Pt(1%)/ γ -Al₂O₃



4. RESULTS

Mass transfer limitations

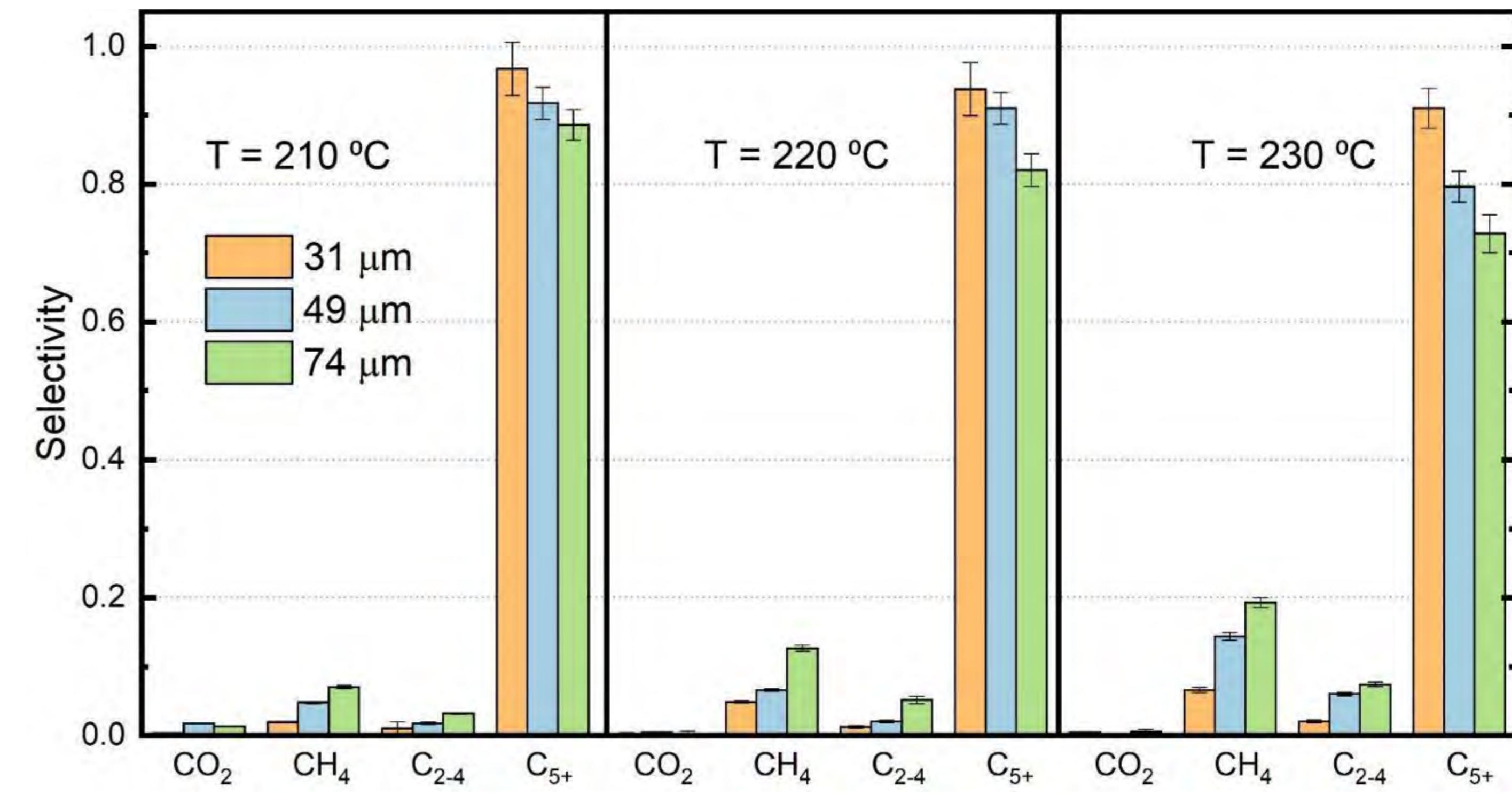
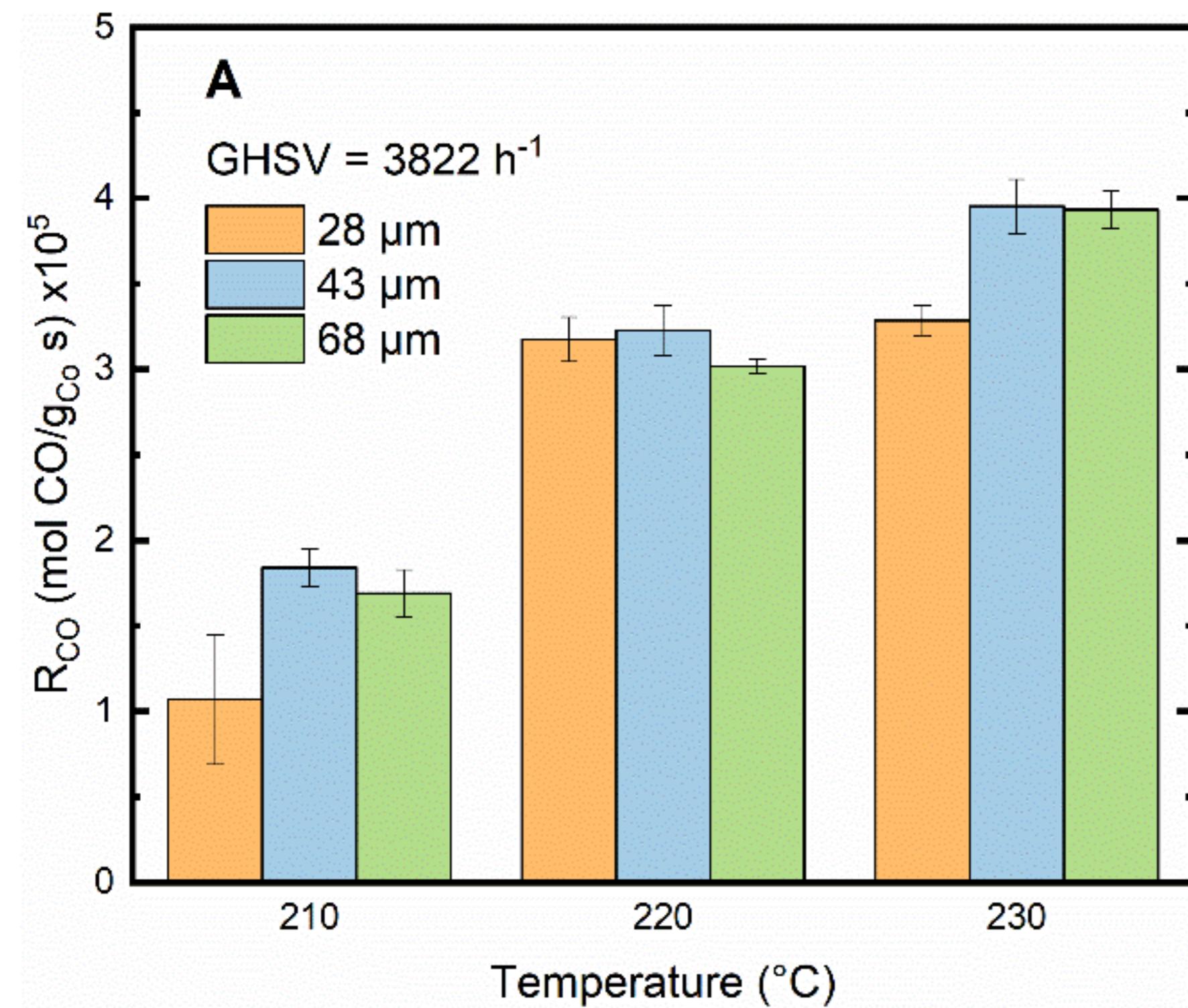
Direct numeric simulation



4. RESULTS

Reactor model

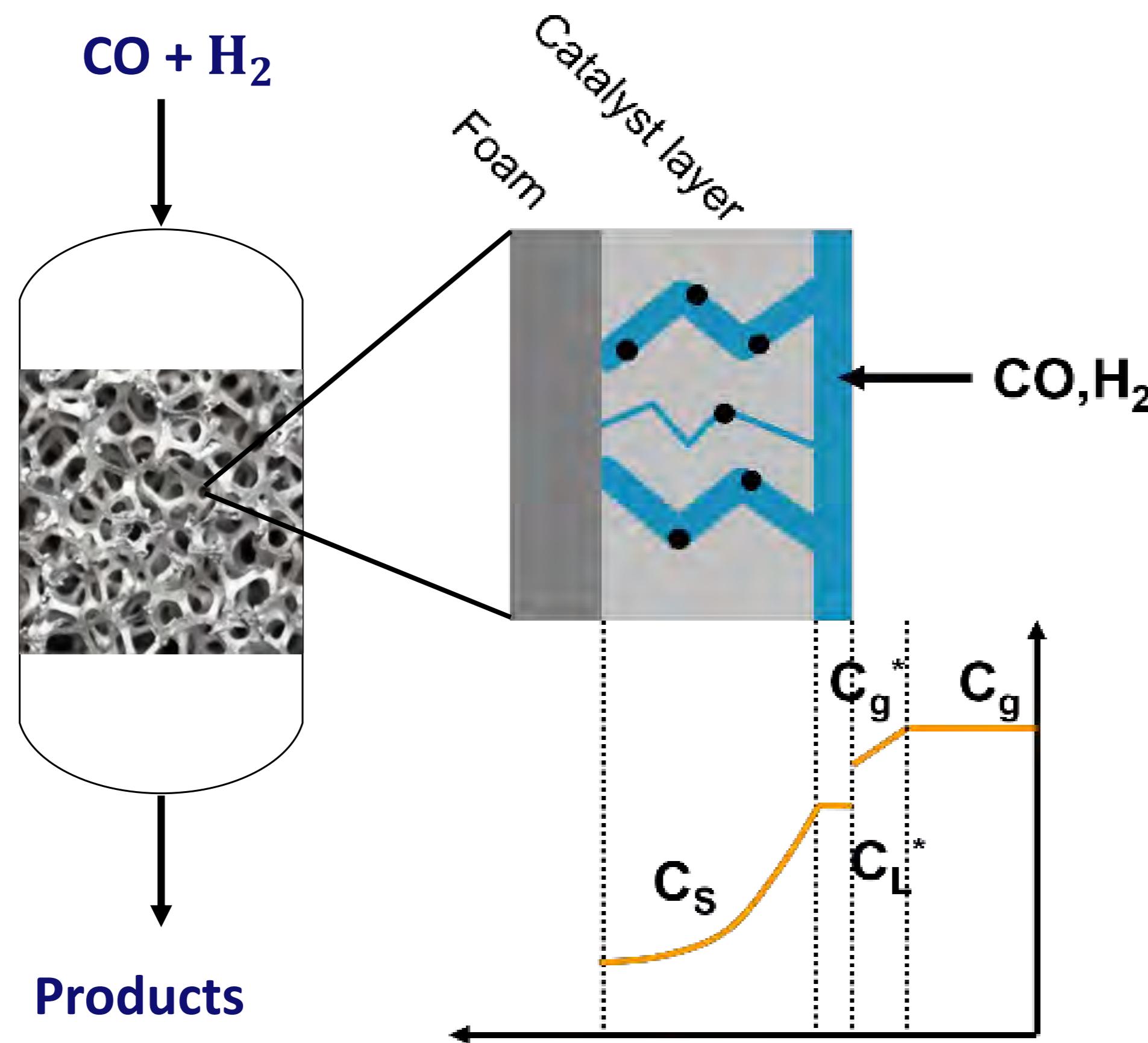
Model considerations



4. RESULTS

Reactor model

Model considerations



Reactor:

- 1-D model, multi-scale, isothermal plug flow reactor

Washcoat layer:

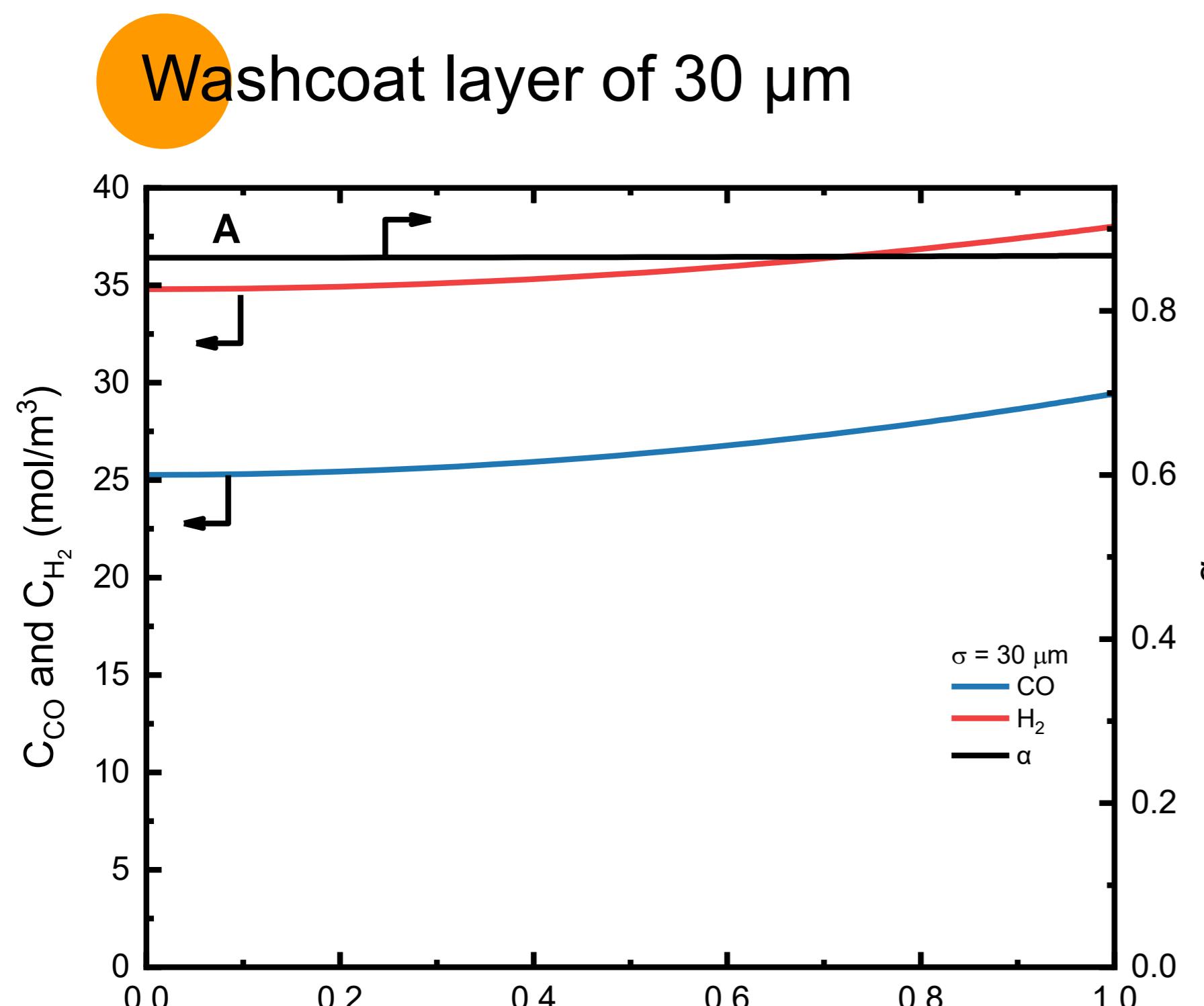
- No internal and external heat transfer limitations
- The gas and liquid phase are in equilibrium
- Pores are filled with waxes

$$R = \frac{aP_{\text{CO}}P_{\text{H}_2}}{(1 + bP_{\text{CO}})^2}$$

$$\alpha = \frac{1}{1 + k_\alpha \left(\frac{C_{\text{H}_2}}{C_{\text{CO}}} \right)^\beta \exp \left[\frac{\Delta E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]}$$

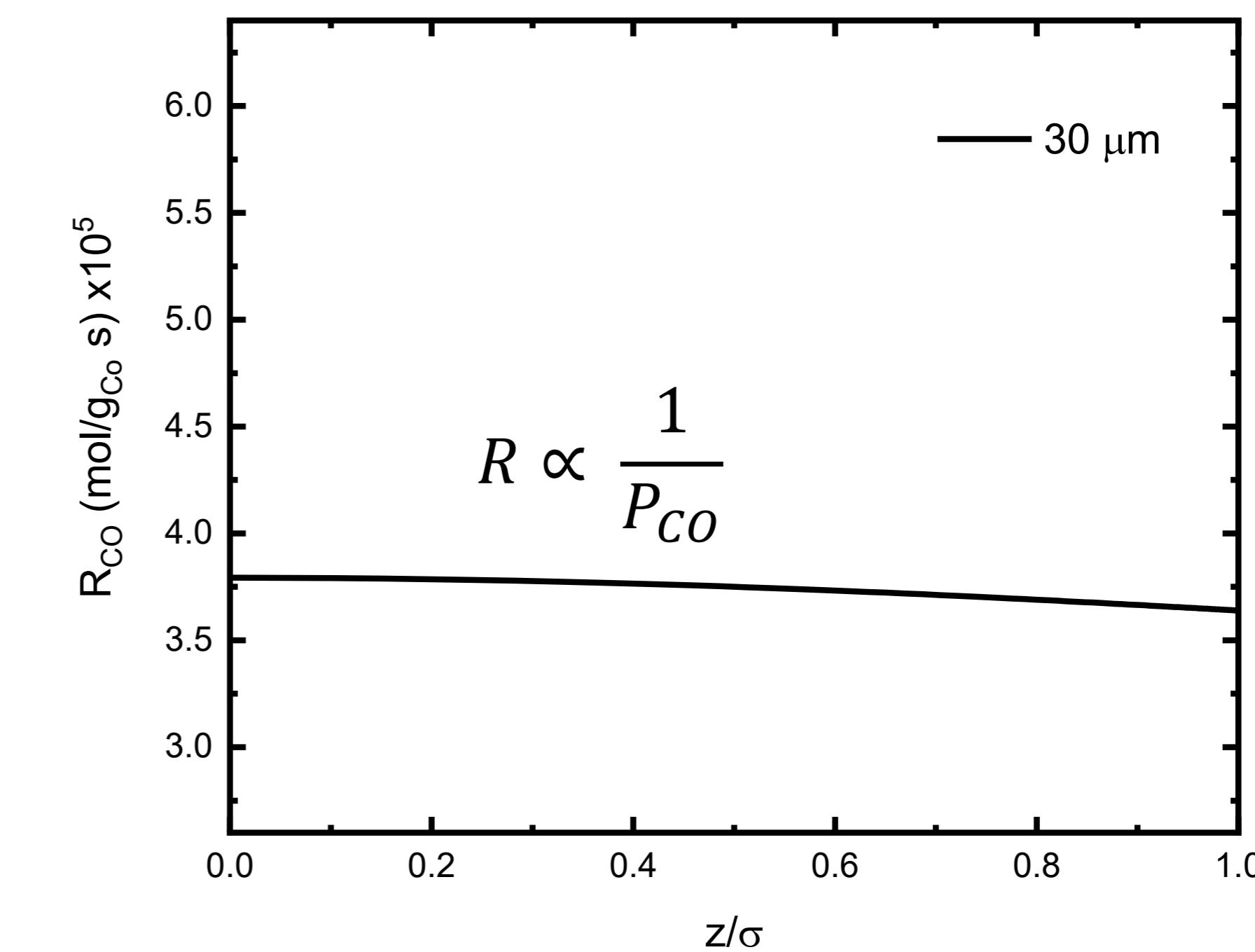
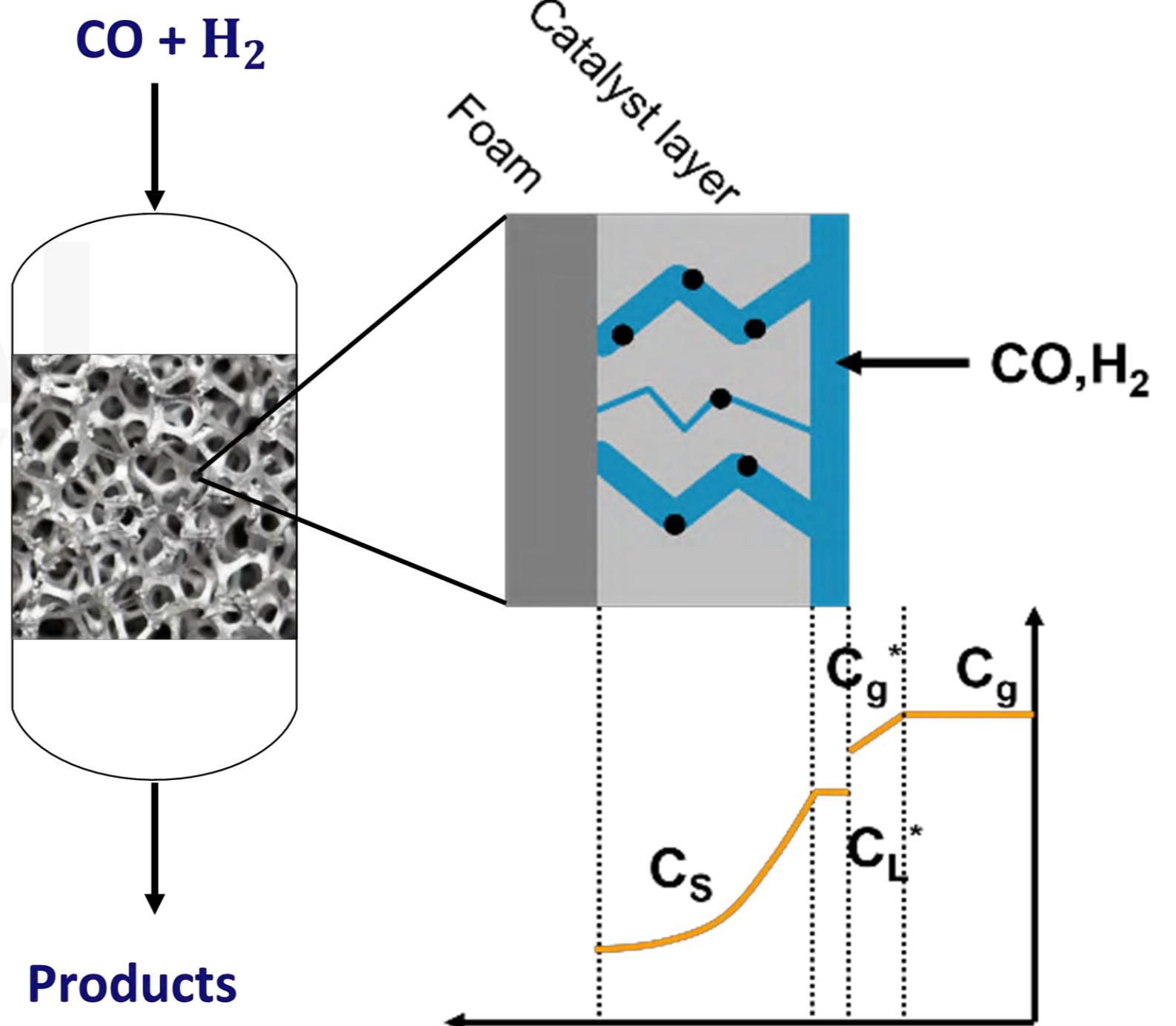
4. RESULTS

Reactor model



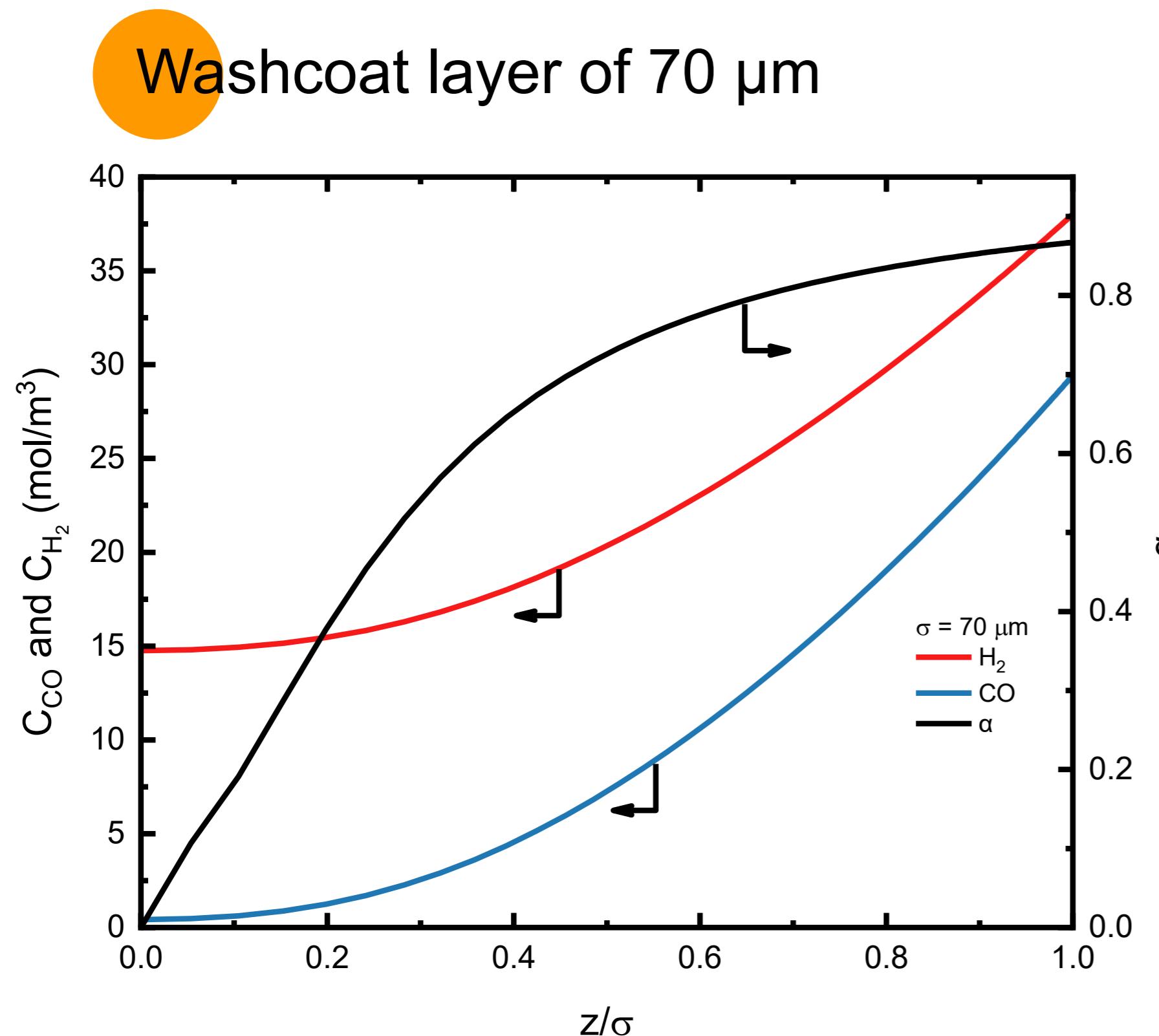
$$\alpha = \frac{1}{1 + k_\alpha \left(\frac{C_{\text{H}_2}}{C_{\text{CO}}} \right)^\beta \exp \left[\frac{\Delta E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]}$$

$$R = \frac{a P_{\text{CO}} P_{\text{H}_2}}{(1 + b P_{\text{CO}})^2}$$



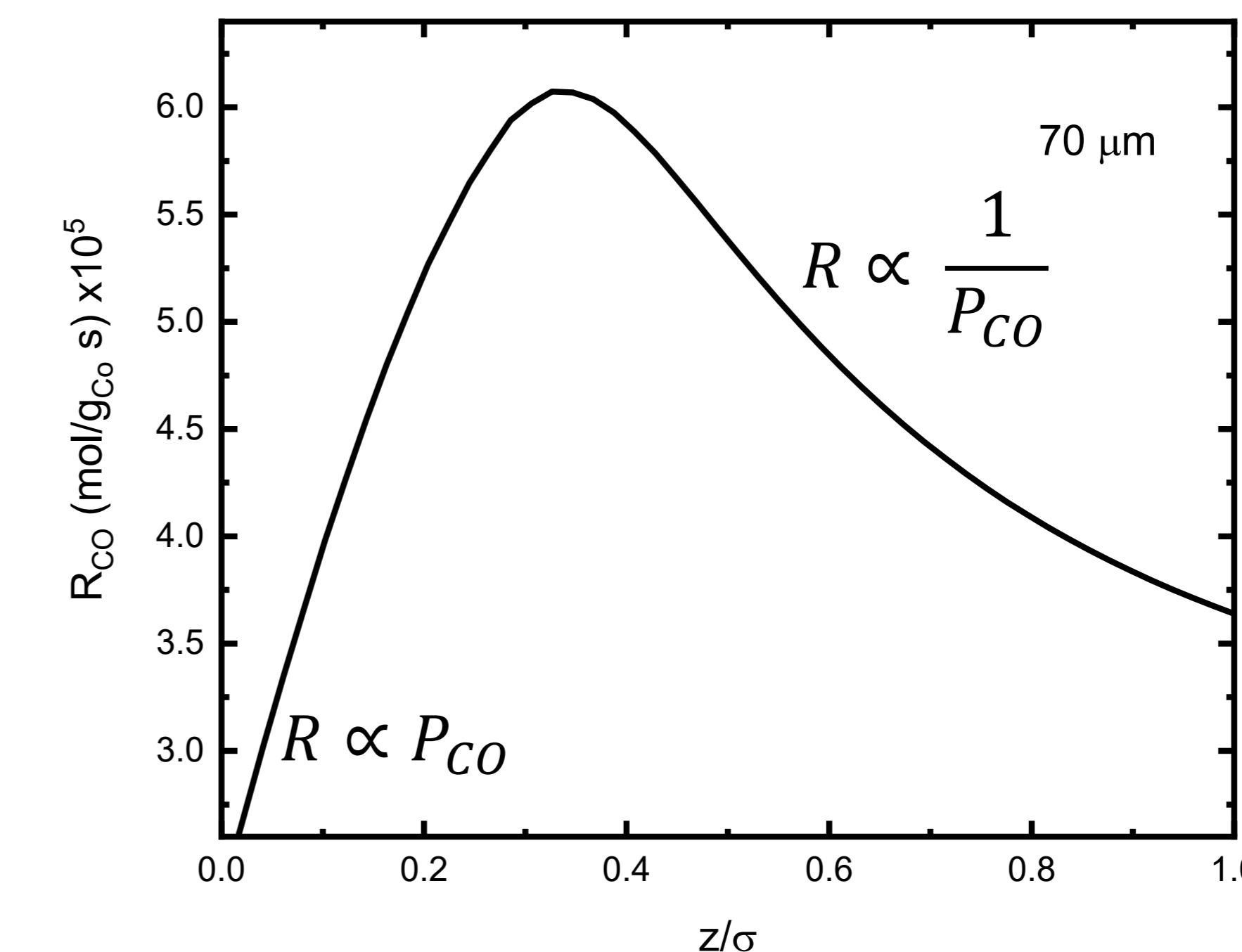
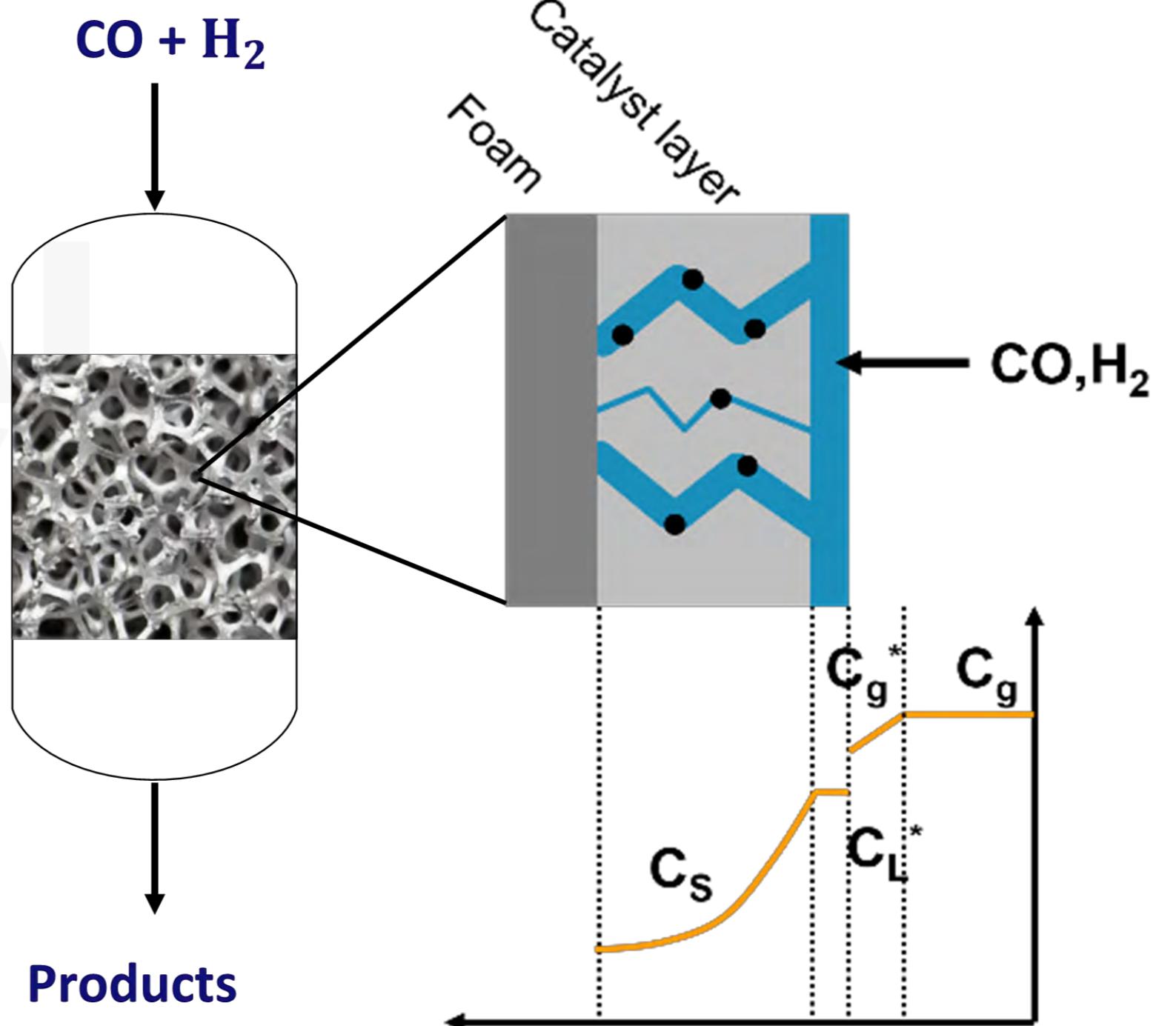
4. RESULTS

Reactor model



$$\alpha = \frac{1}{1 + k_\alpha \left(\frac{C_{\text{H}_2}}{C_{\text{CO}}} \right)^\beta \exp \left[\frac{\Delta E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]}$$

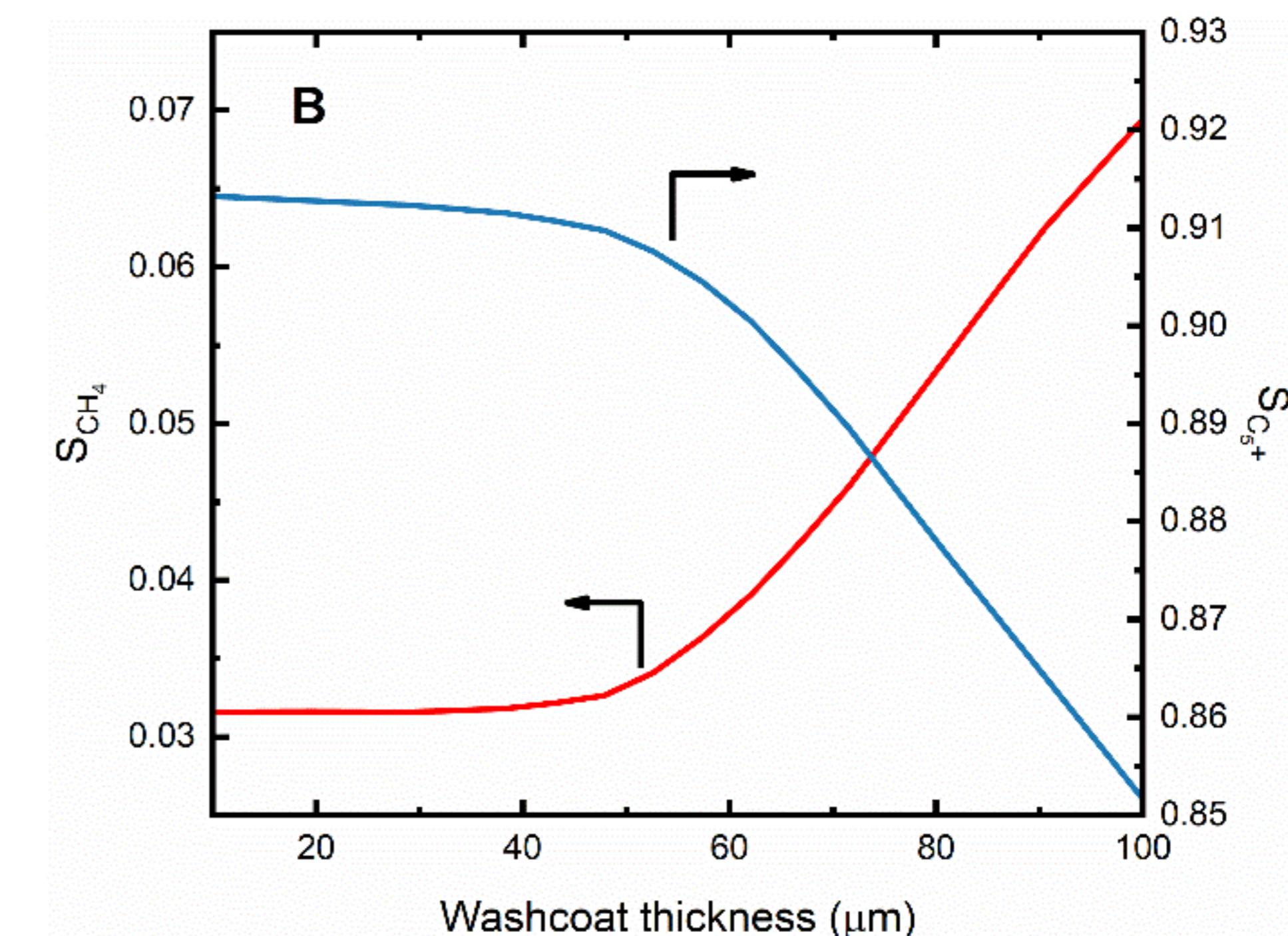
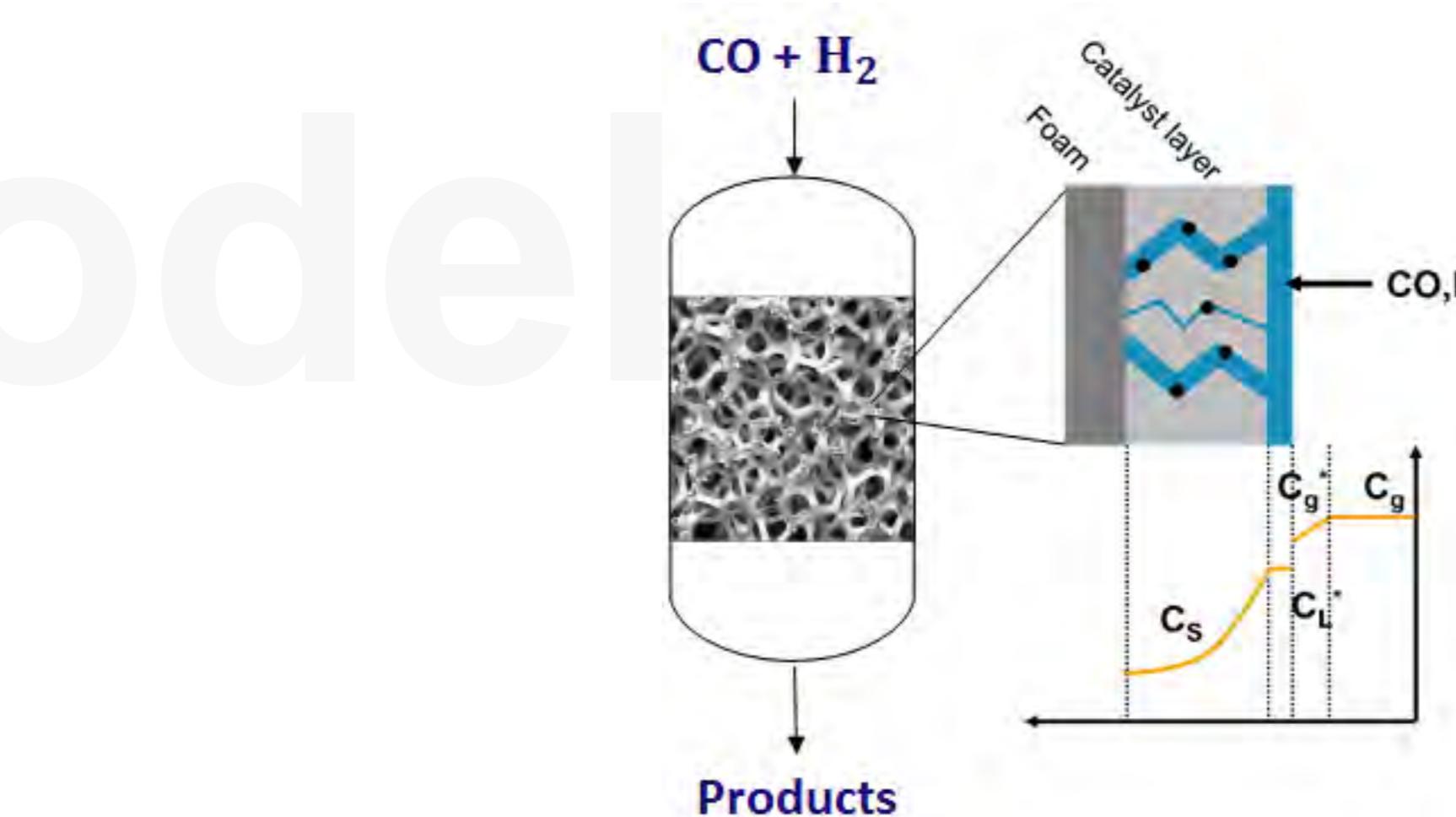
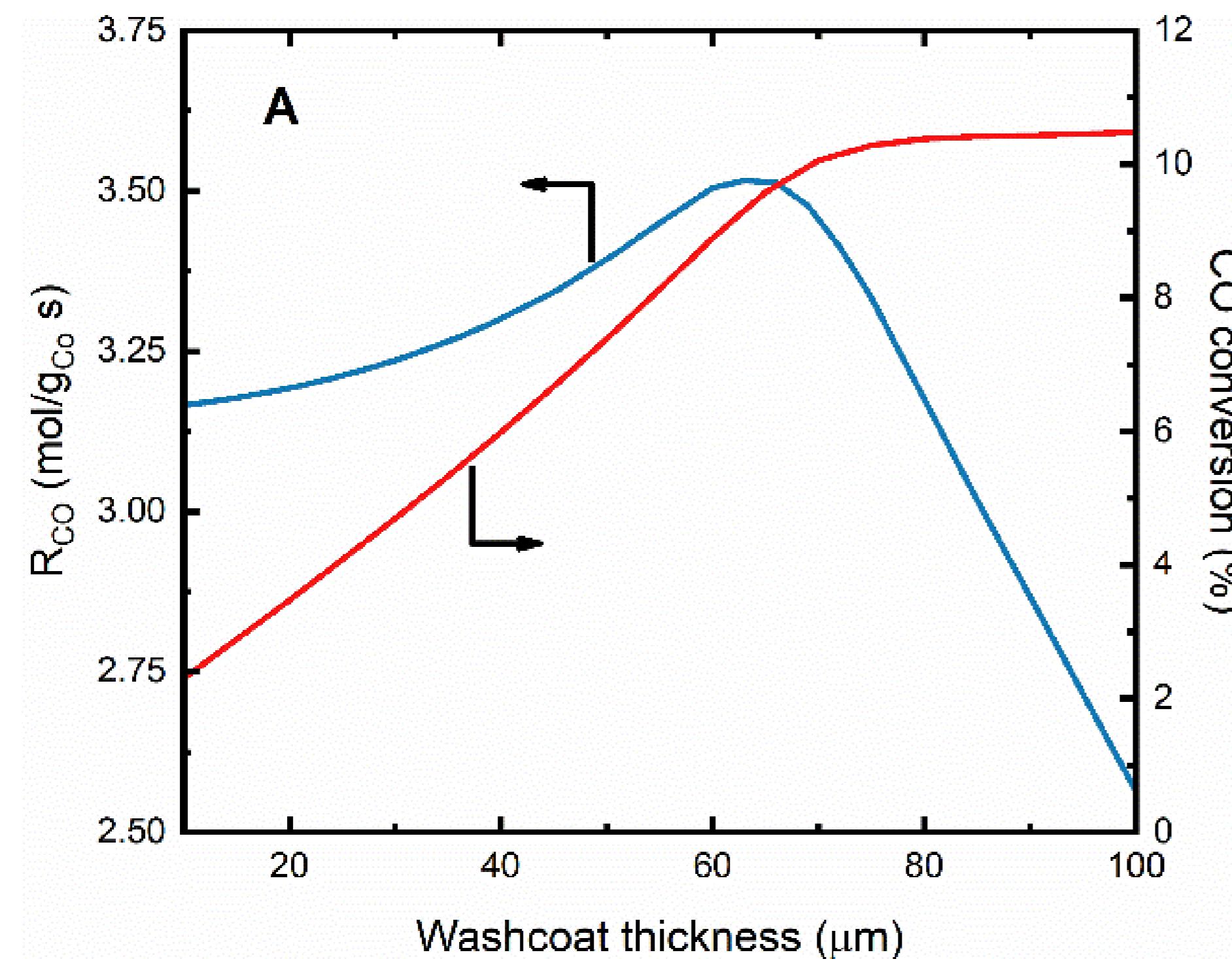
$$R = \frac{a P_{\text{CO}} P_{\text{H}_2}}{(1 + b P_{\text{CO}})^2}$$



4. RESULTS

Reactor model

Reactor



$$R = \frac{a P_{\text{CO}} P_{\text{H}_2}}{(1 + b P_{\text{CO}})^2}$$

Reactor model

Parameter estimation: $a_0, E_a, b_0, \Delta H_b, k_\alpha, \beta, \Delta E_\alpha$

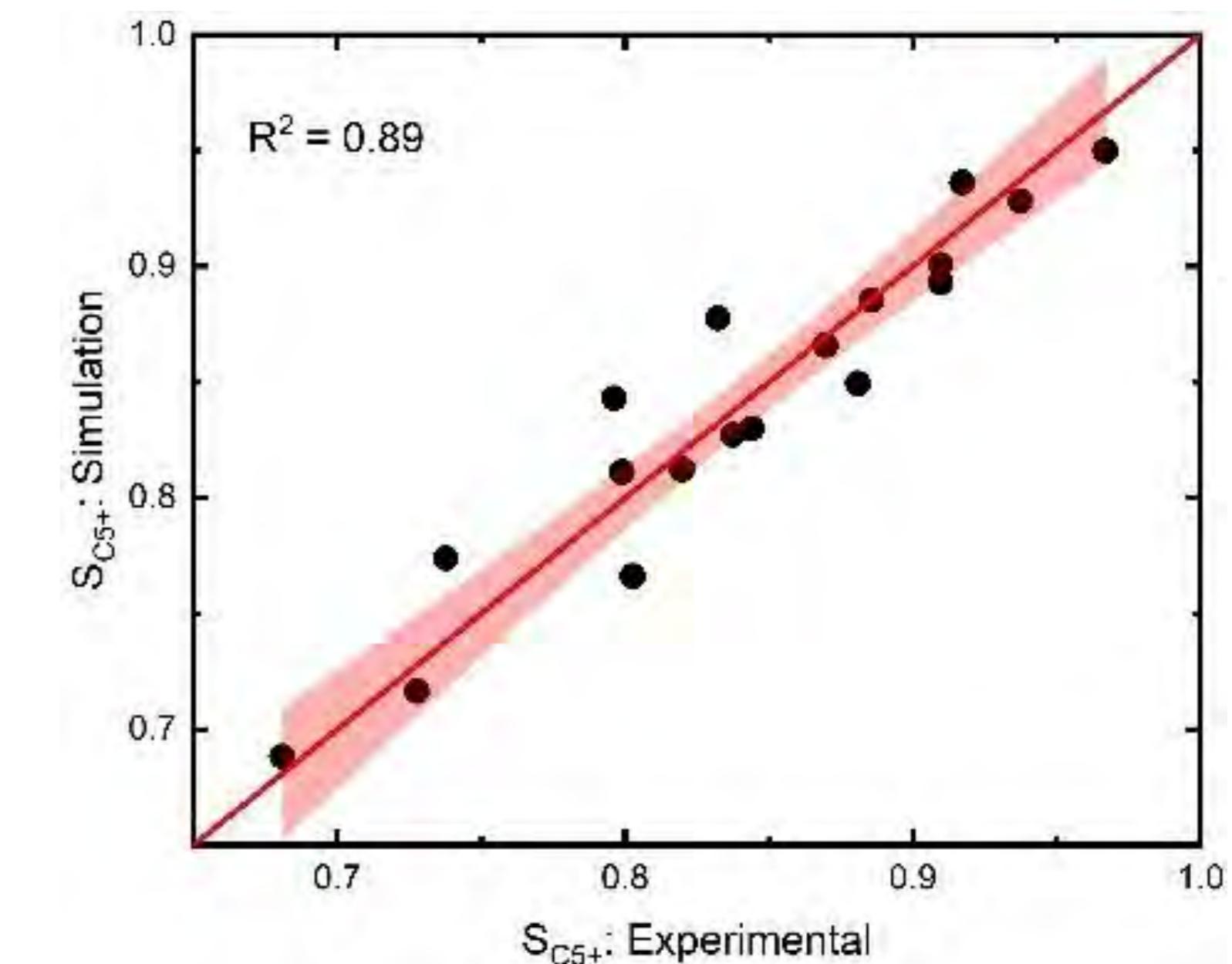
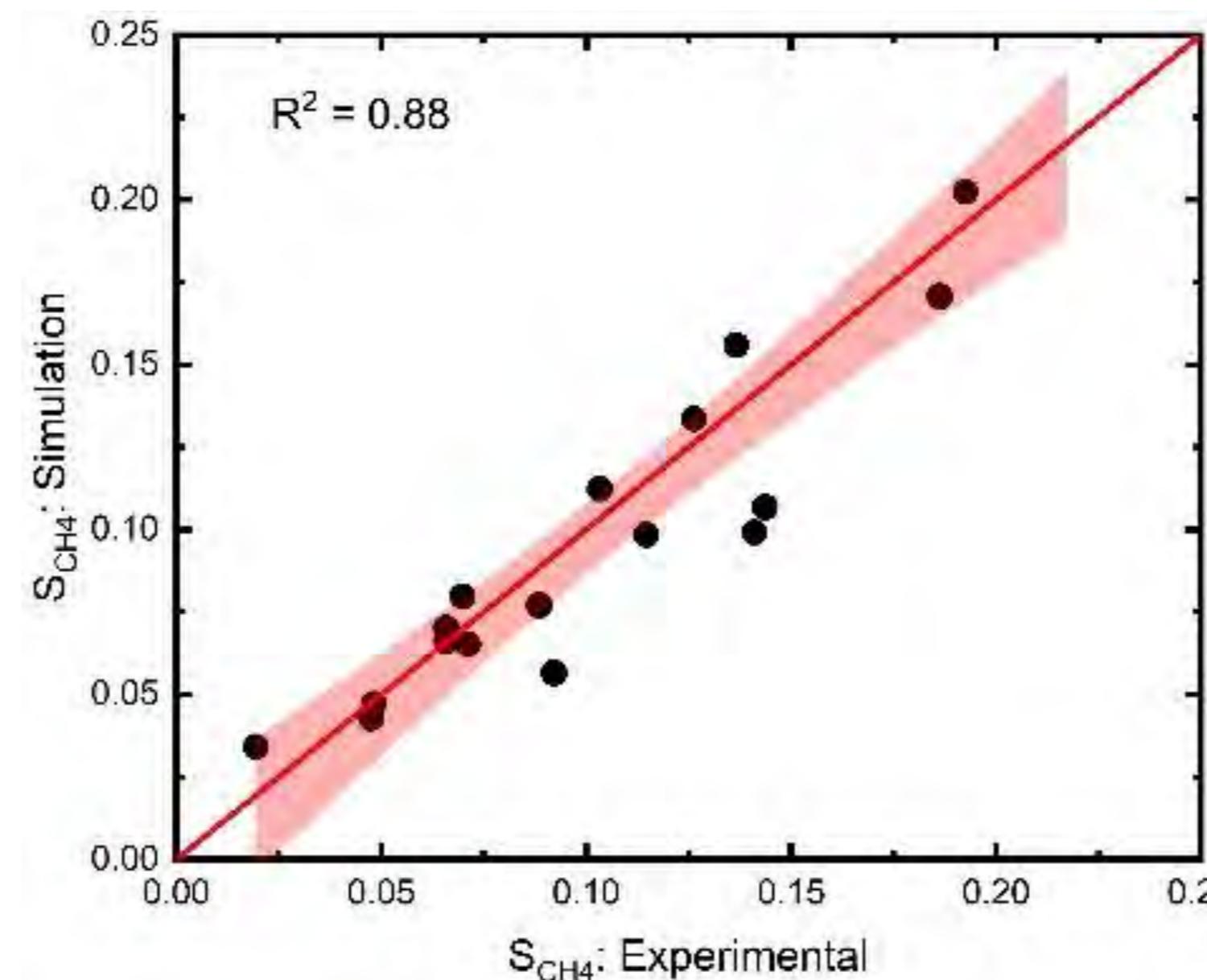
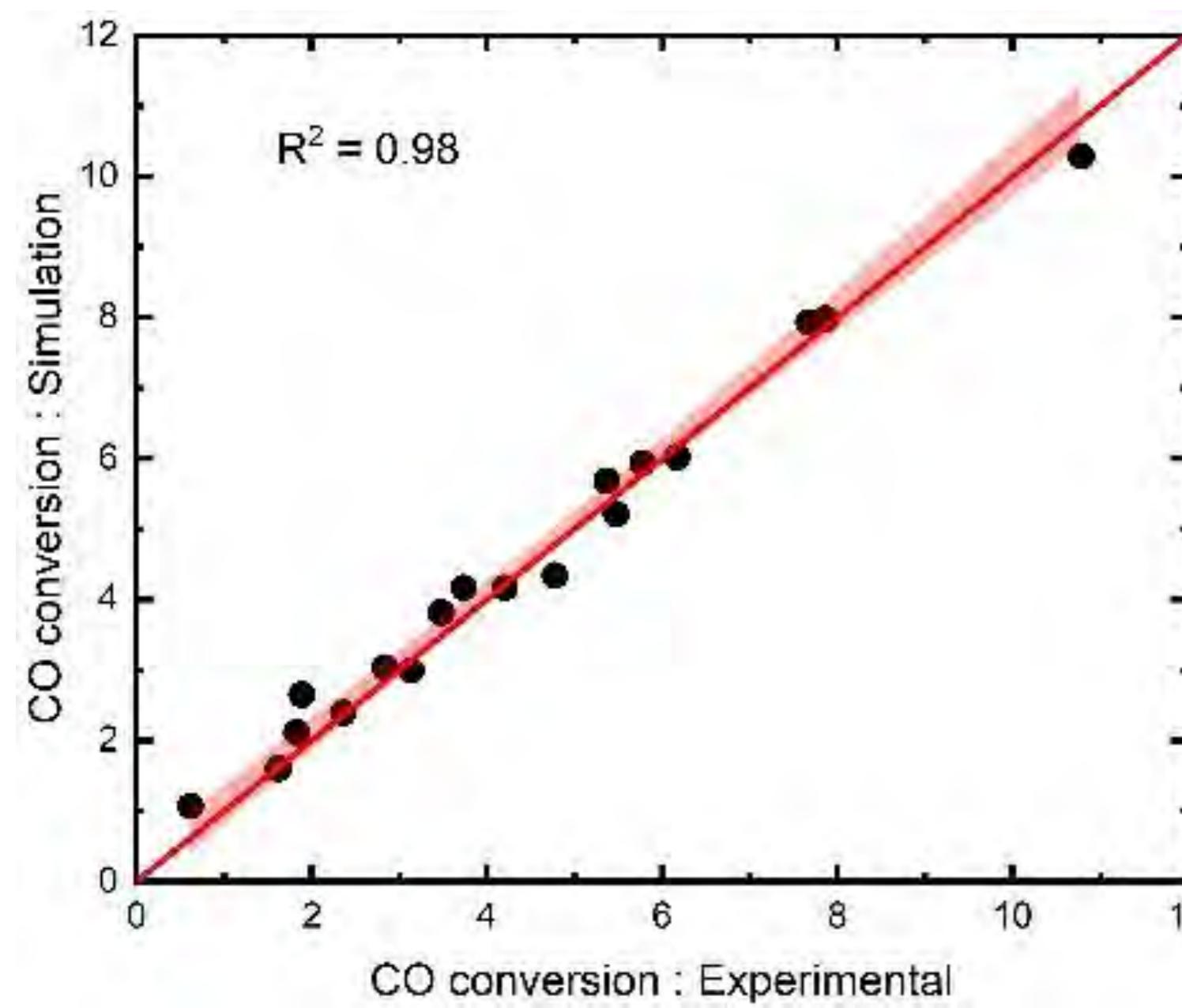
$$R = \frac{a P_{CO} P_{H_2}}{(1 + b P_{CO})^2} \quad a = a_0 \exp\left(\frac{-E_a}{RT}\right) \quad b = b_0 \exp\left(\frac{\Delta H_b}{RT}\right)$$

$$\alpha = \frac{1}{1 + k_\alpha \left(\frac{C_{H_2}}{C_{CO}}\right)^\beta \exp\left[\frac{\Delta E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right]}$$

4. RESULTS

Reactor model

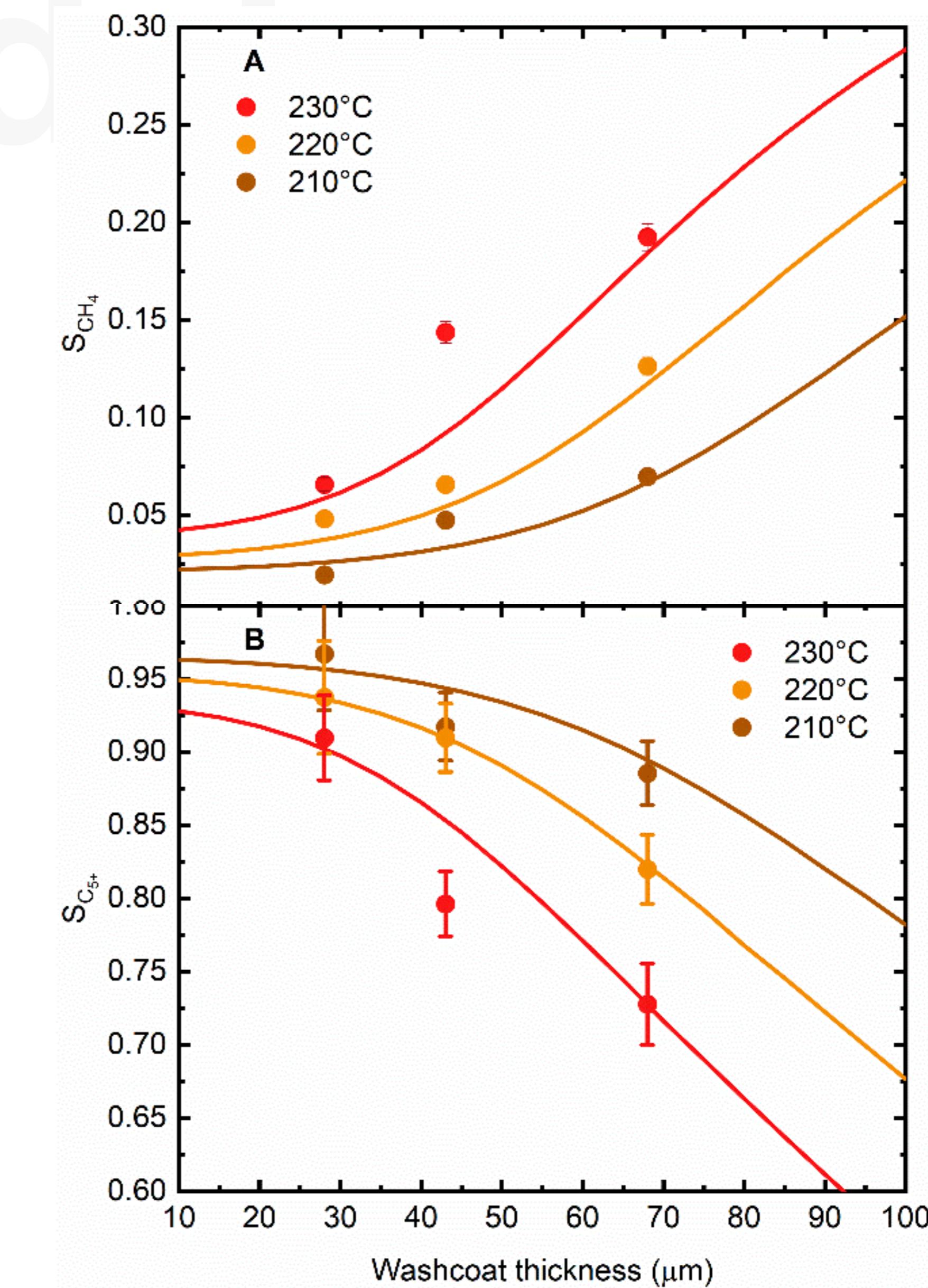
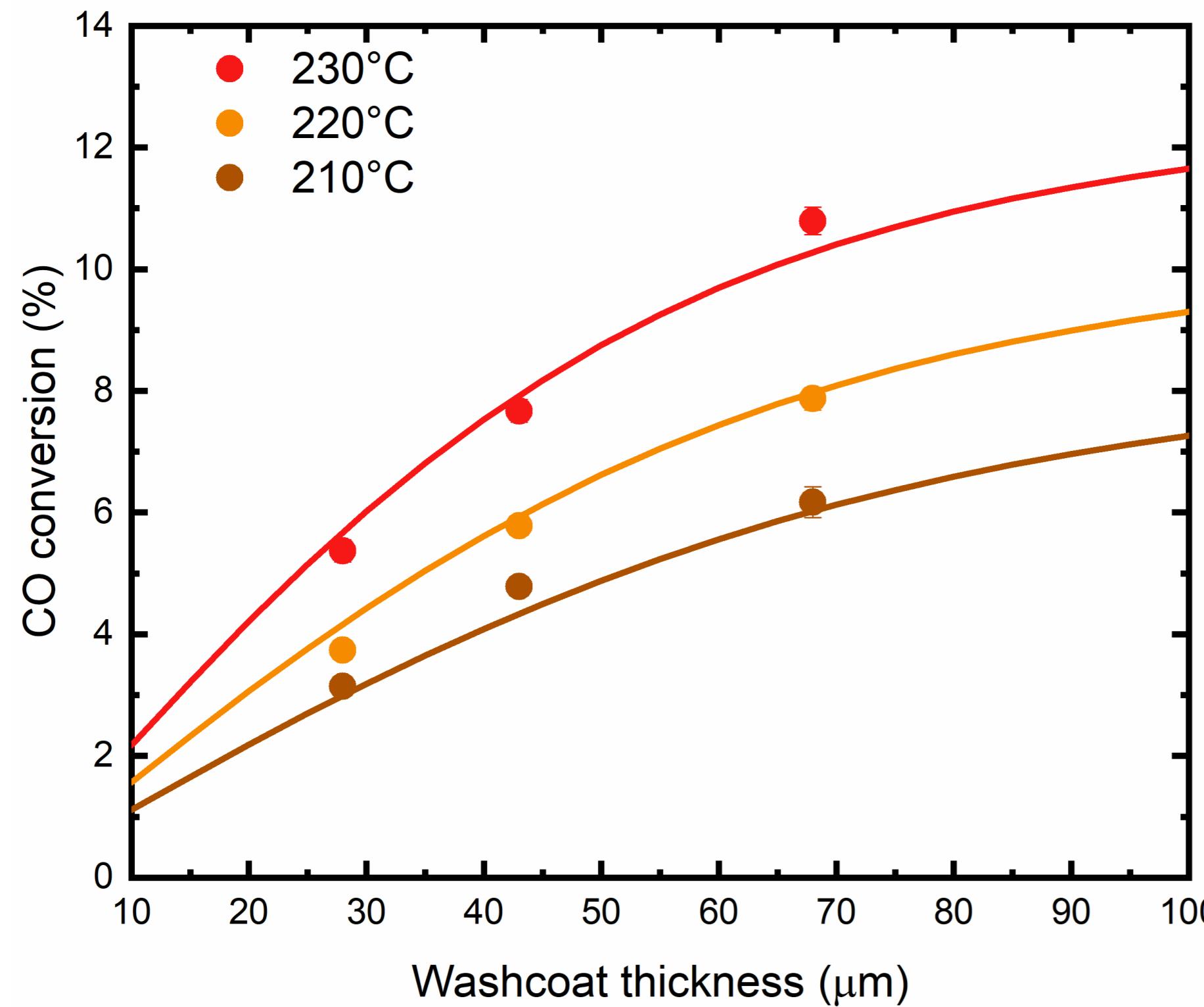
Parameter estimation



4. RESULTS

Reactor model

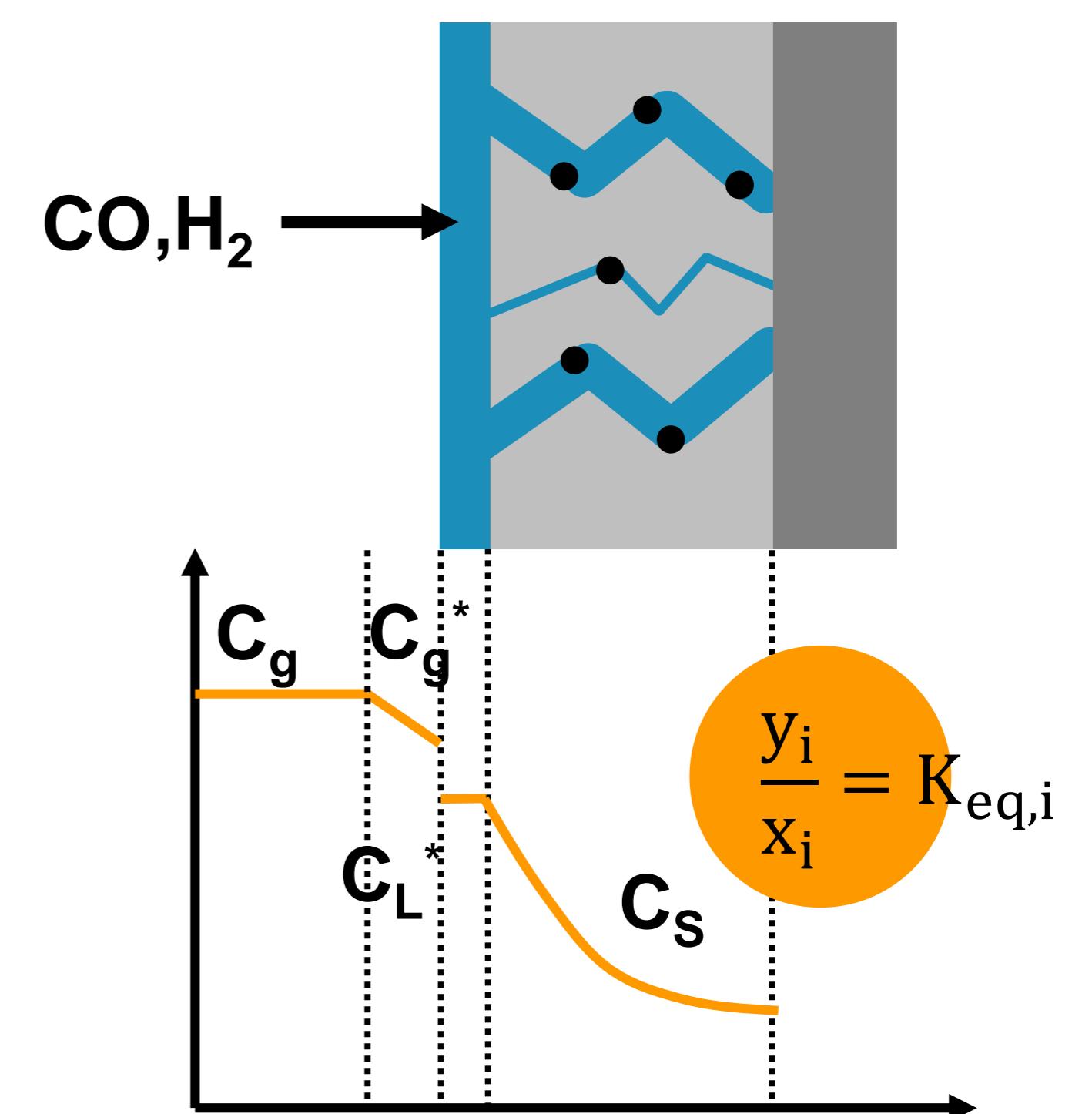
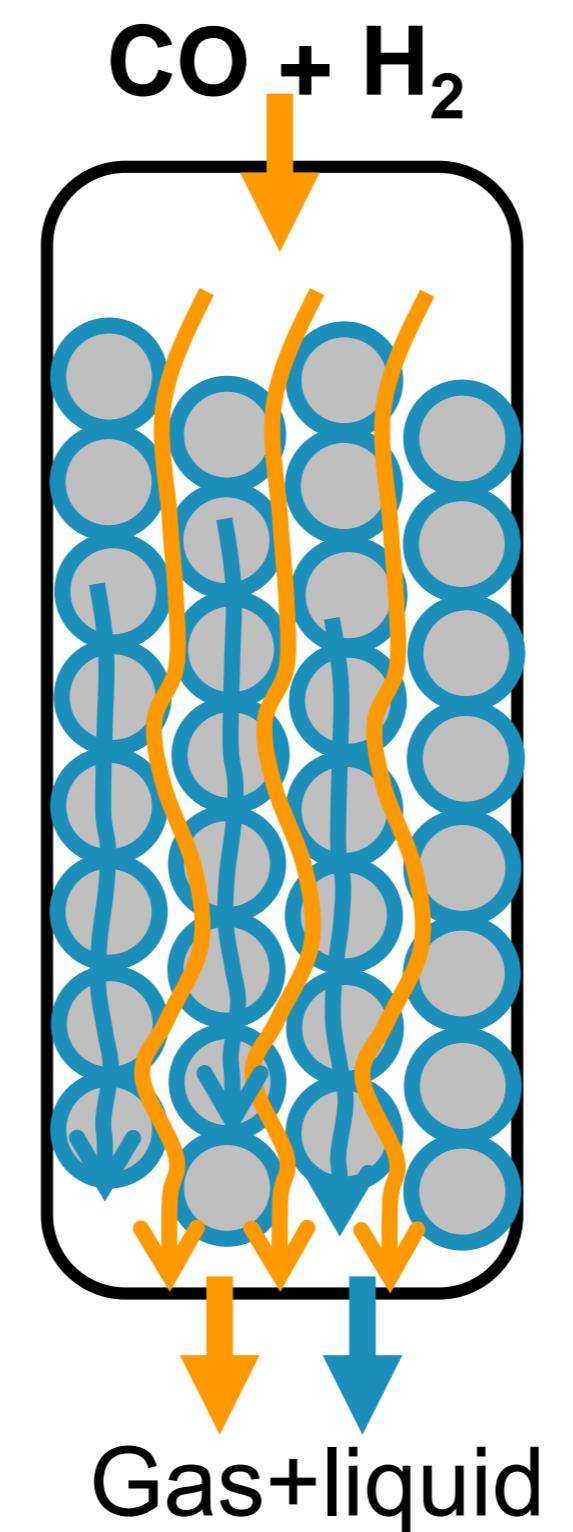
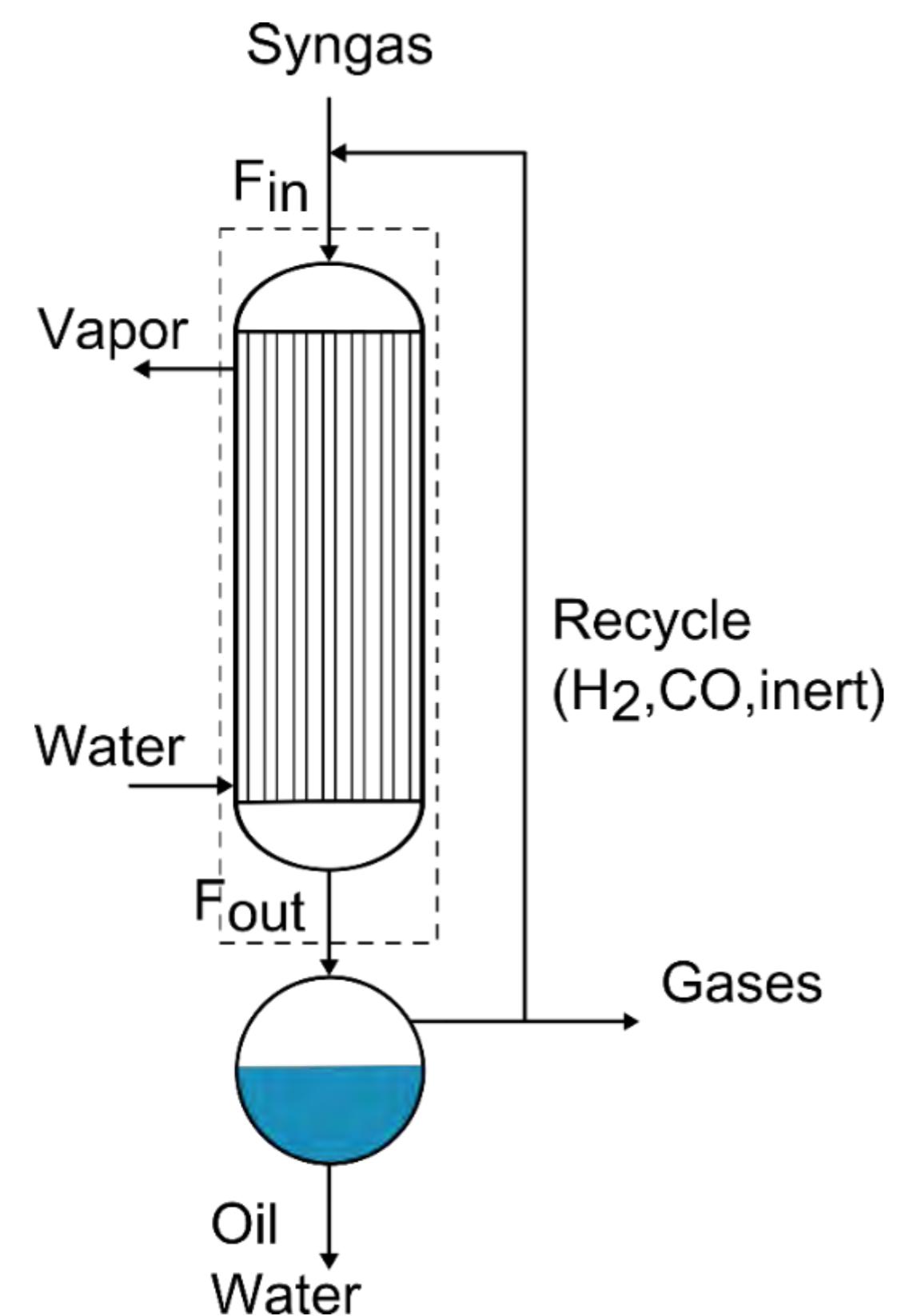
Parameter estimation



The model describes the experiments with acceptable level of accuracy

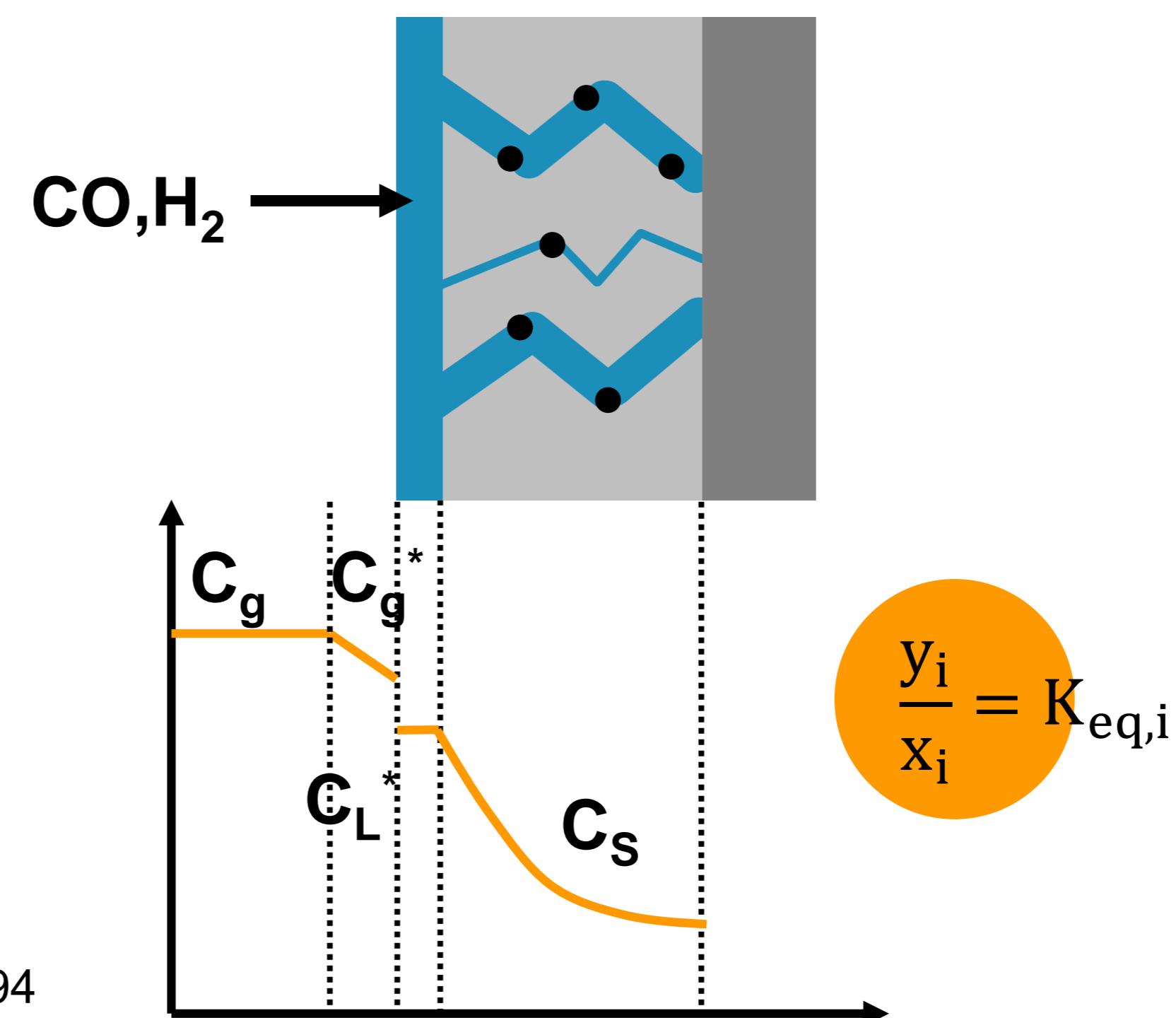
5. SIMULATIONS

Reactor model



Influence of the VLE

How important is the effect of the **vapor-liquid equilibria** in the predicted reactor performance and product distribution

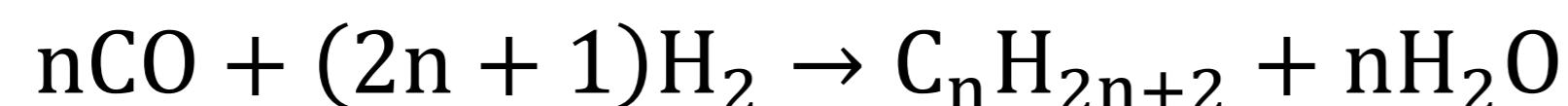


Model assumptions

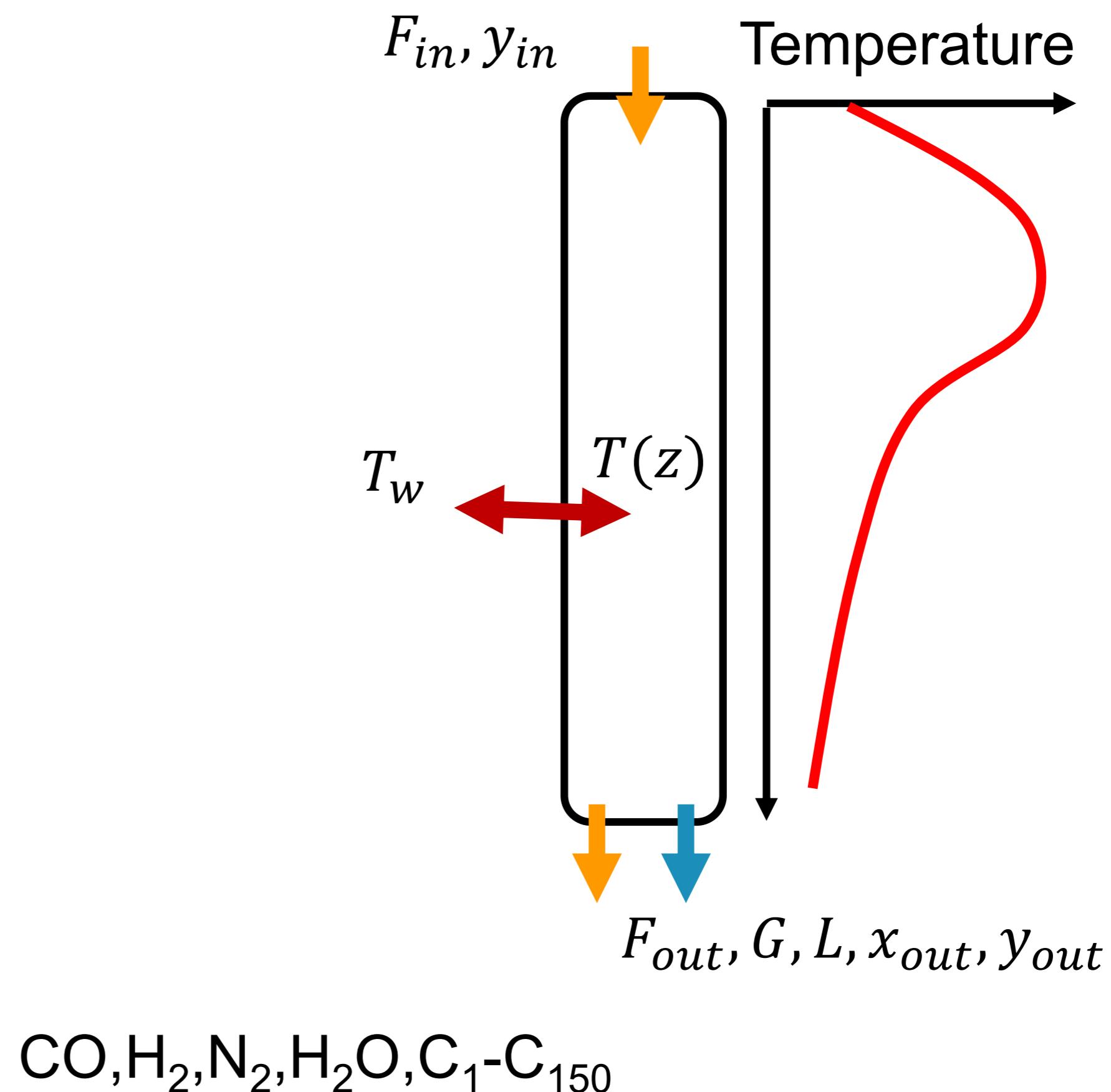
1-D Model, pseudohomogeneous, plug-flow

No mass and heat transfer limitations

Only n-paraffin formation



The gas and the liquid phase are in equilibrium



5. SIMULATIONS

Model equations

Kinetic

$$r_{CO} = \frac{a C_{CO} C_{H_2}}{(1 + b C_{CO})^2}$$

$$b = b_0 \exp\left(\frac{\Delta H_b}{RT}\right)$$

$$a = a_0 \exp\left(\frac{E_a}{RT}\right)$$

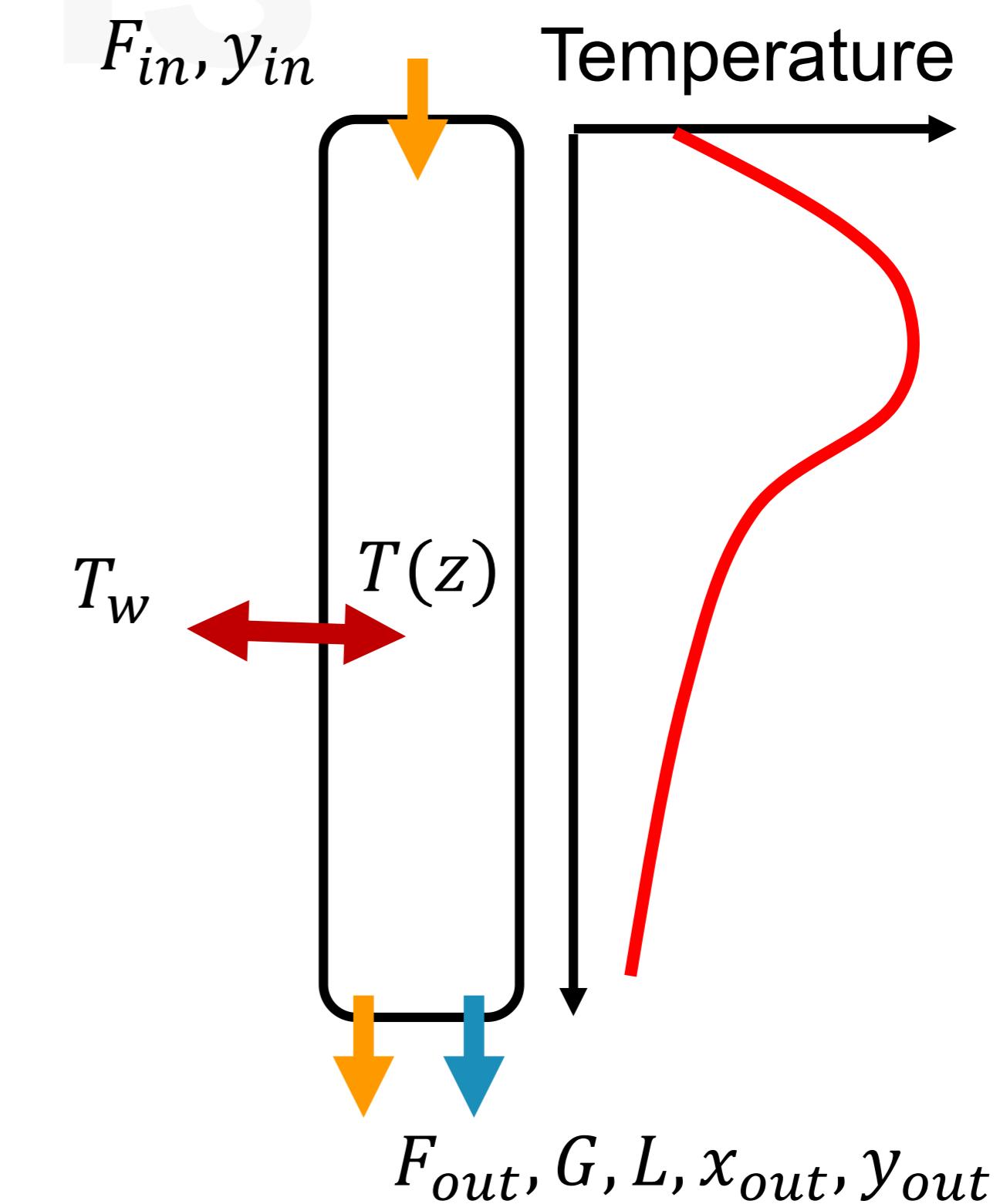
Mass balance

$$\frac{dF_i}{dV} = v_i r_{CO} \rho_b$$

$$v_n = \frac{S_n}{n}$$

Energy balance

$$(F_i c_{p_i}) \frac{dT}{dV} = -\Delta H r_{CO} \rho_b + U a_e (T_w - T)$$



Selectivity

$$S_n = n(1 - \alpha)^2 \alpha^{n-1}$$

$$\alpha = \frac{1}{1 + k_\alpha \left(\frac{C_{H_2}}{C_{CO}}\right)^\beta \exp\left[\frac{\Delta E_a}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]}$$

Model equations

Vapor-Liquid equilibria

$$F_i = Lx_i + Gy_i$$

$$y_i = \quad x_i = 1$$

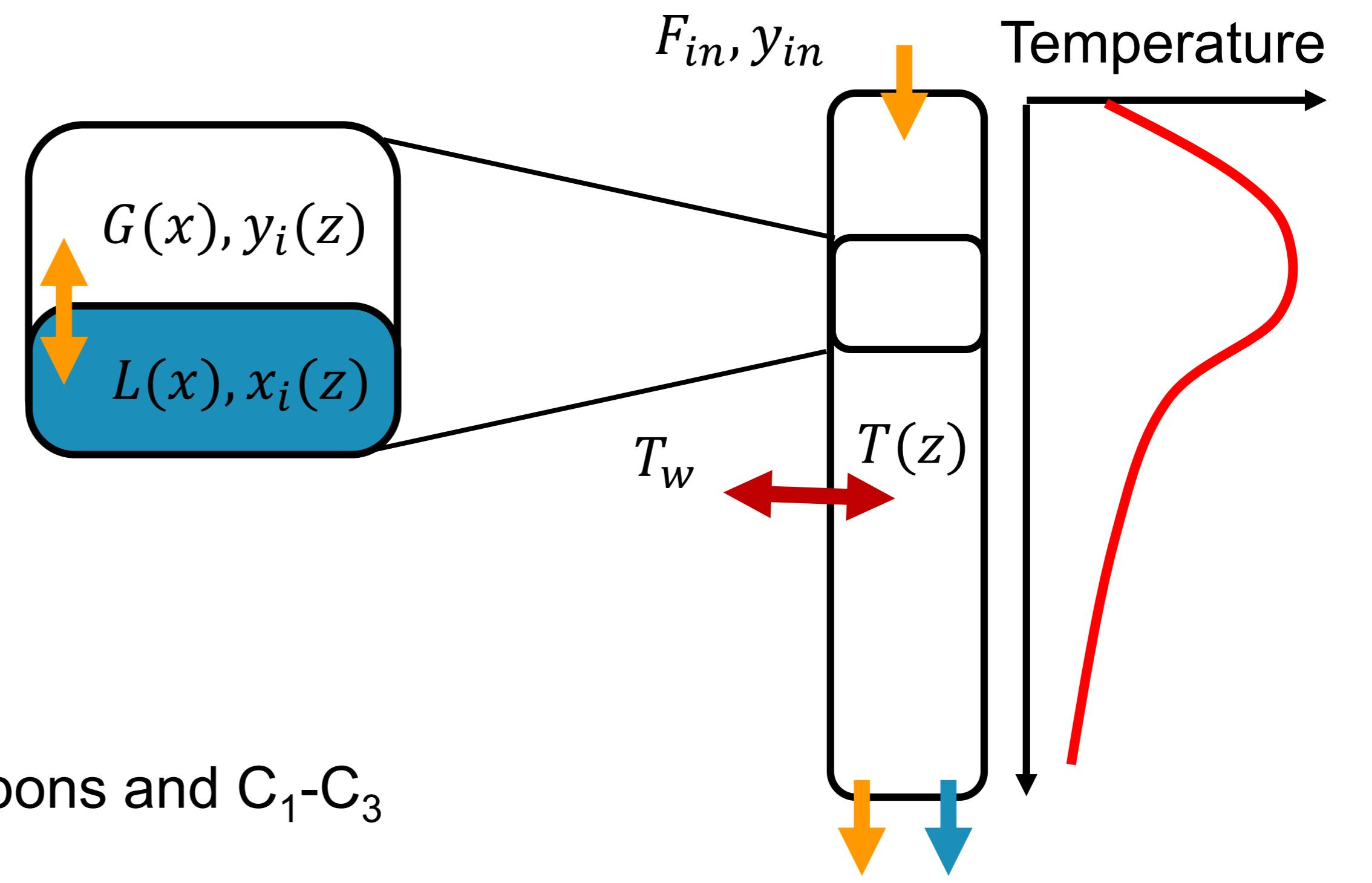
$$y_i = x_i K_{eq,i}$$

$$K_{eq,i} = \frac{H_i^\infty \Phi_i}{\phi_{i,v} P}$$

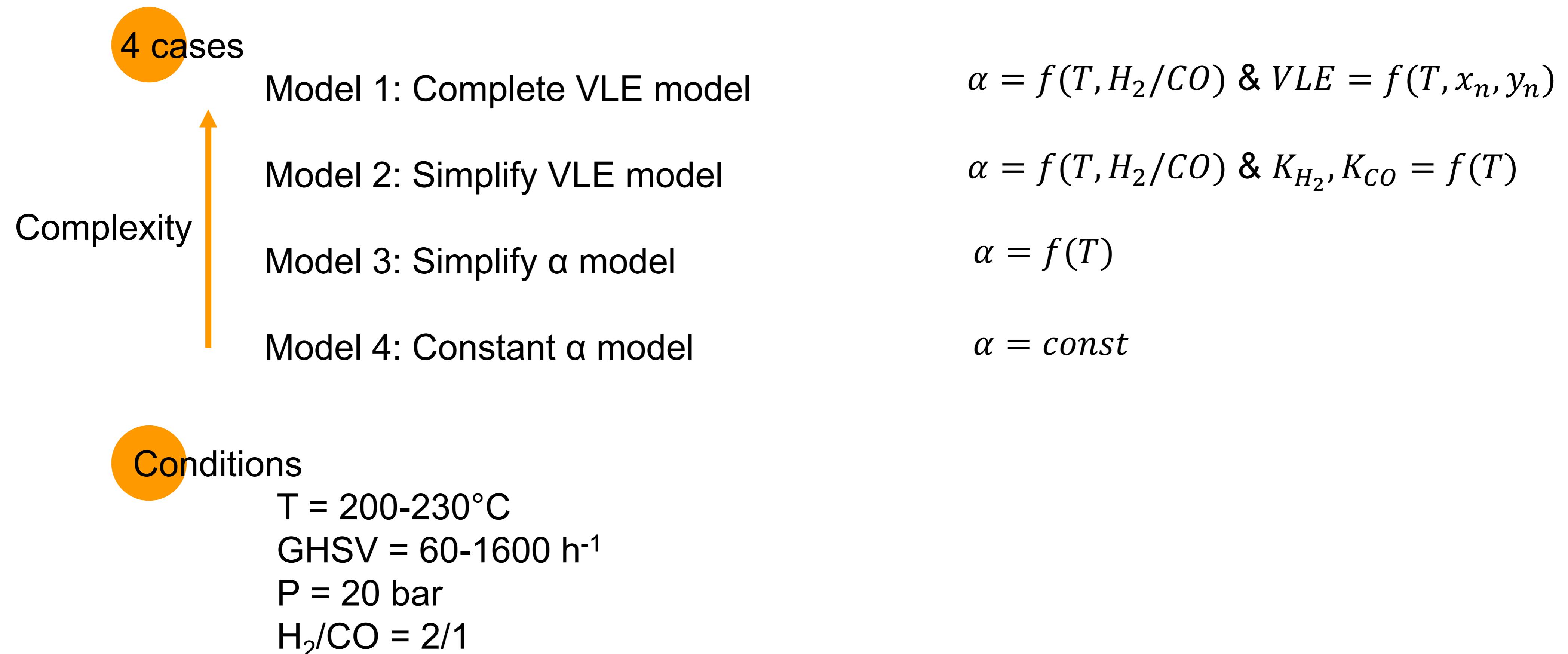
$$K_{eq,i} = \frac{\gamma_i^\infty P_{i,sat} \Phi_i}{\phi_{i,v} P}$$

Non-hydrocarbons and C₁-C₃

Hydrocarbons C_n ≥ C₄



Parametric study



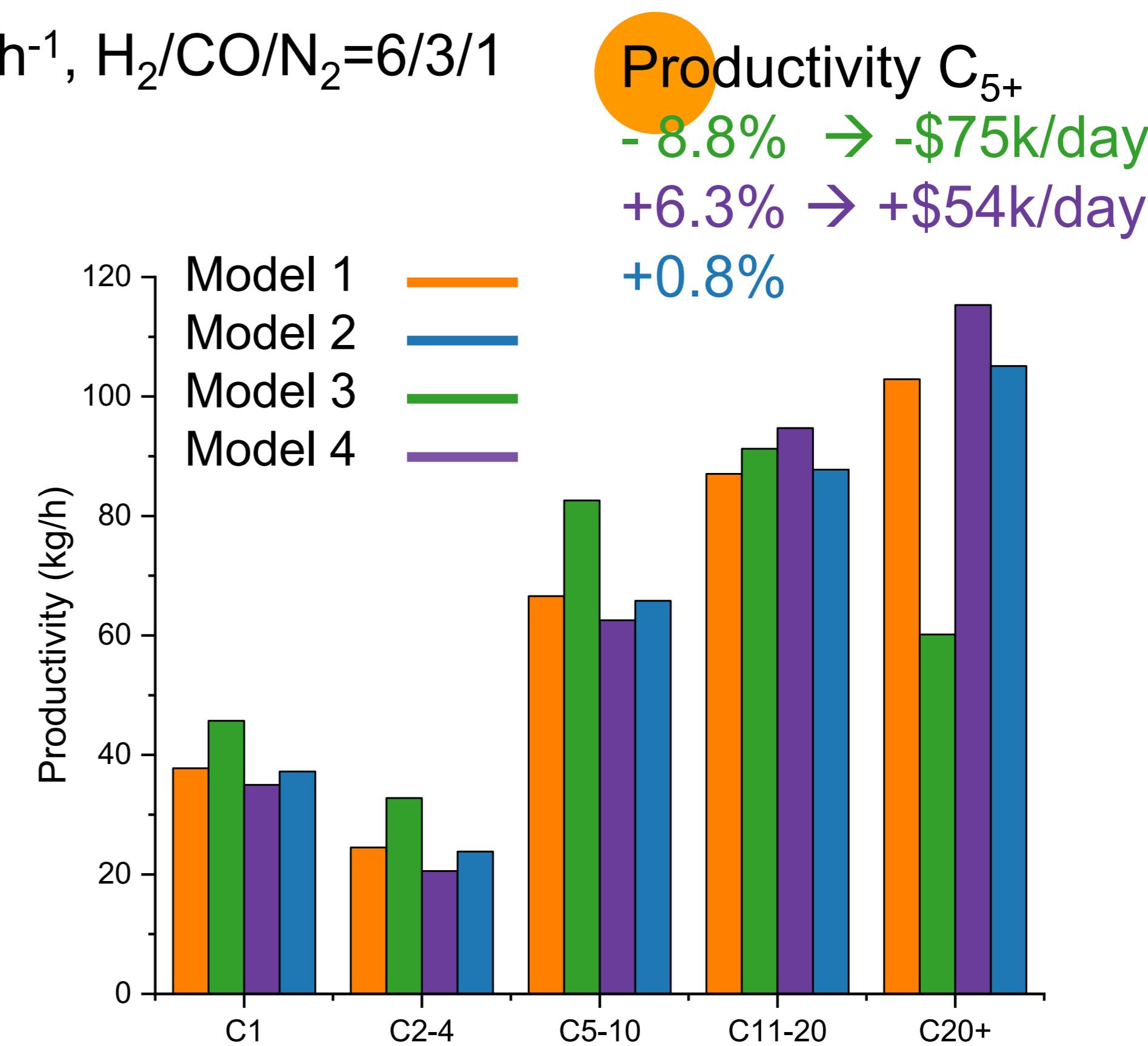
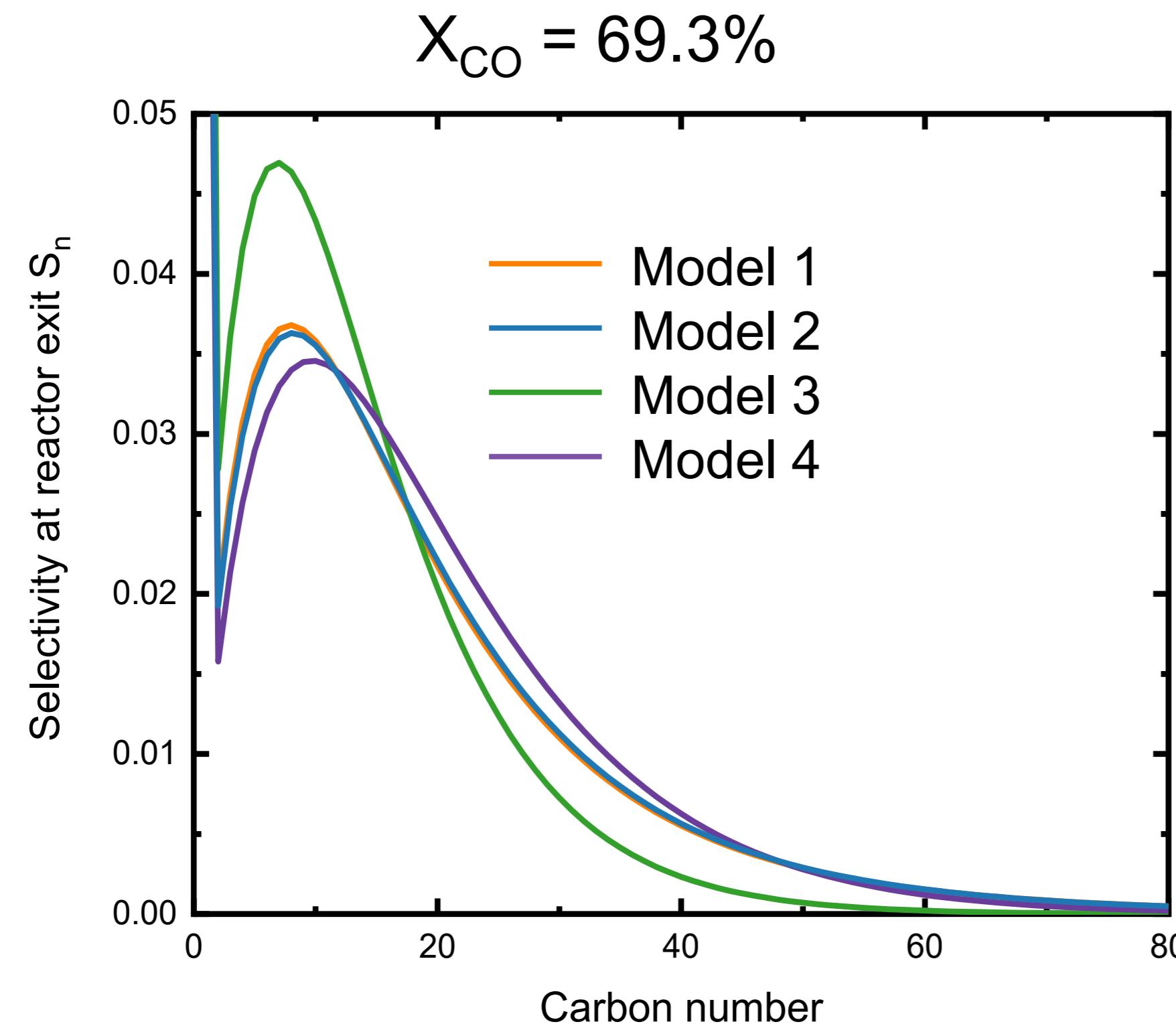
5. SIMULATIONS

Example 1

Complexity ↑

- Model 1: Complete VLE model $\alpha = f(T, H_2/CO) \& VLE = f(T, x_n, y_n)$
- Model 2: Simplify VLE model $\alpha = f(T, H_2/CO) \& K_{H_2}, K_{CO} = f(T)$
- Model 3: Simplify α model, without VLE $\alpha = f(T)$
- Model 4: Constant α model, without VLE $\alpha = const$

Conditions: 220°C, 20 bar, GHSV = 795 h⁻¹, H₂/CO/N₂=6/3/1



The simplify VLE model gives similar results to the complete model

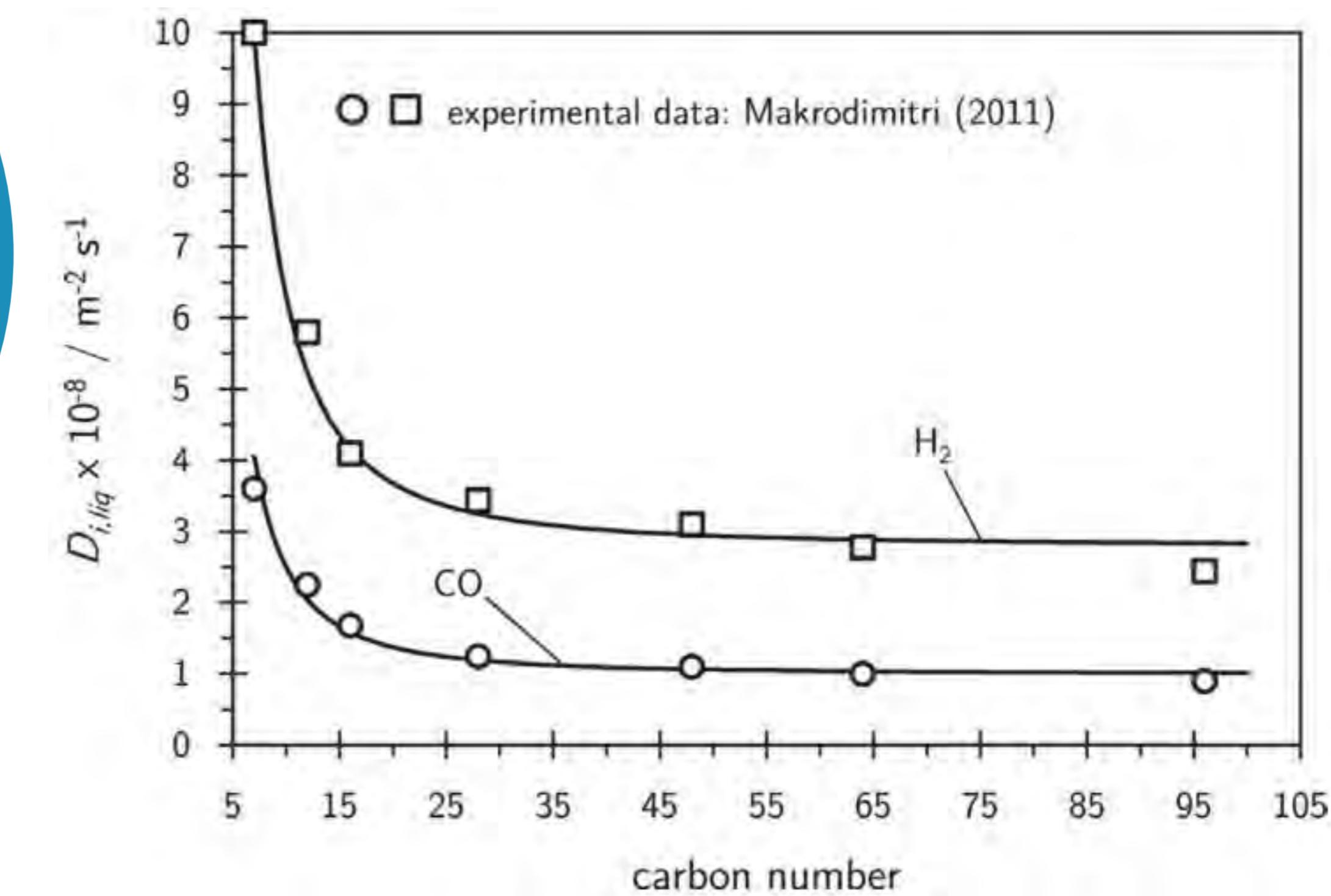
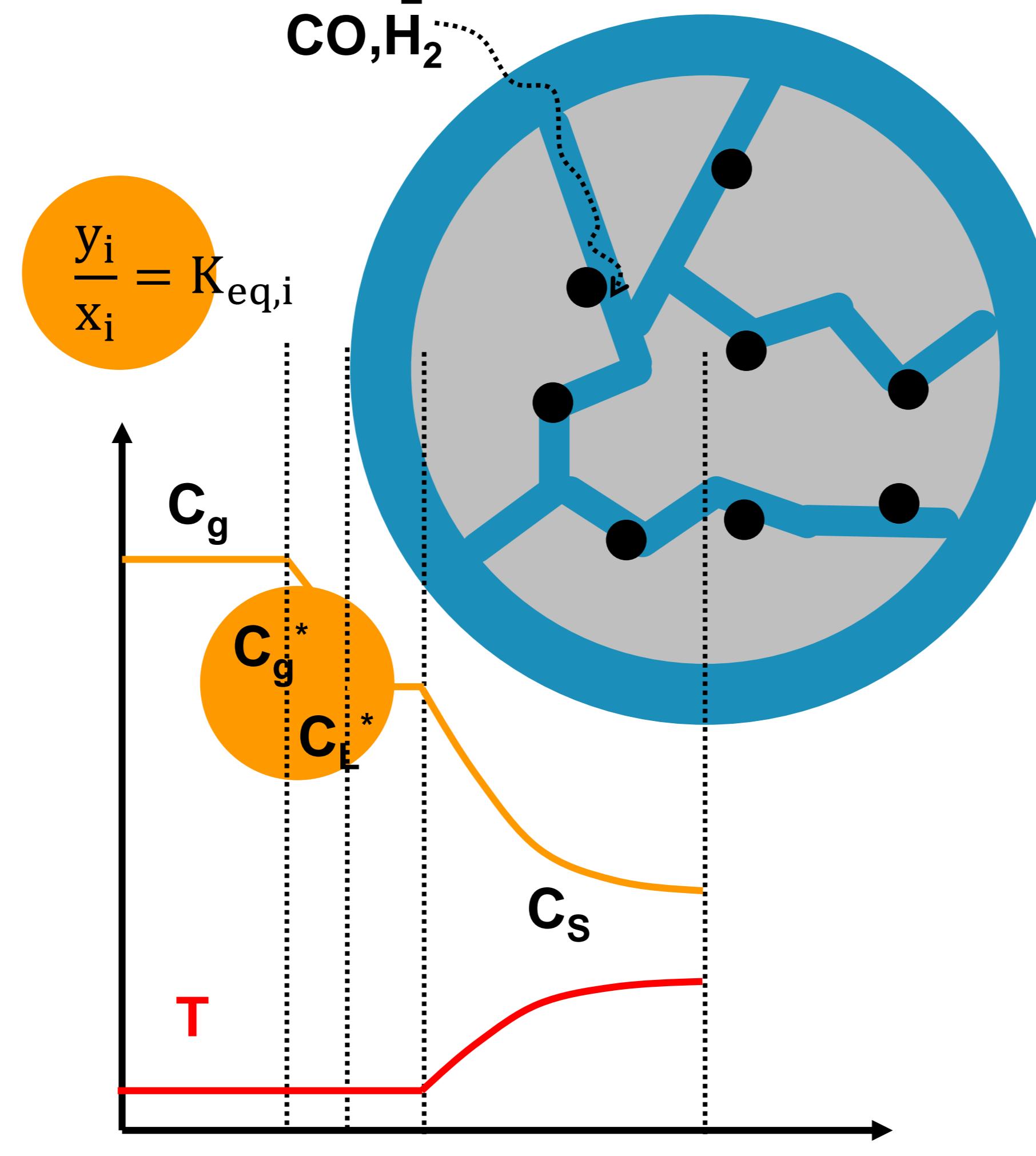
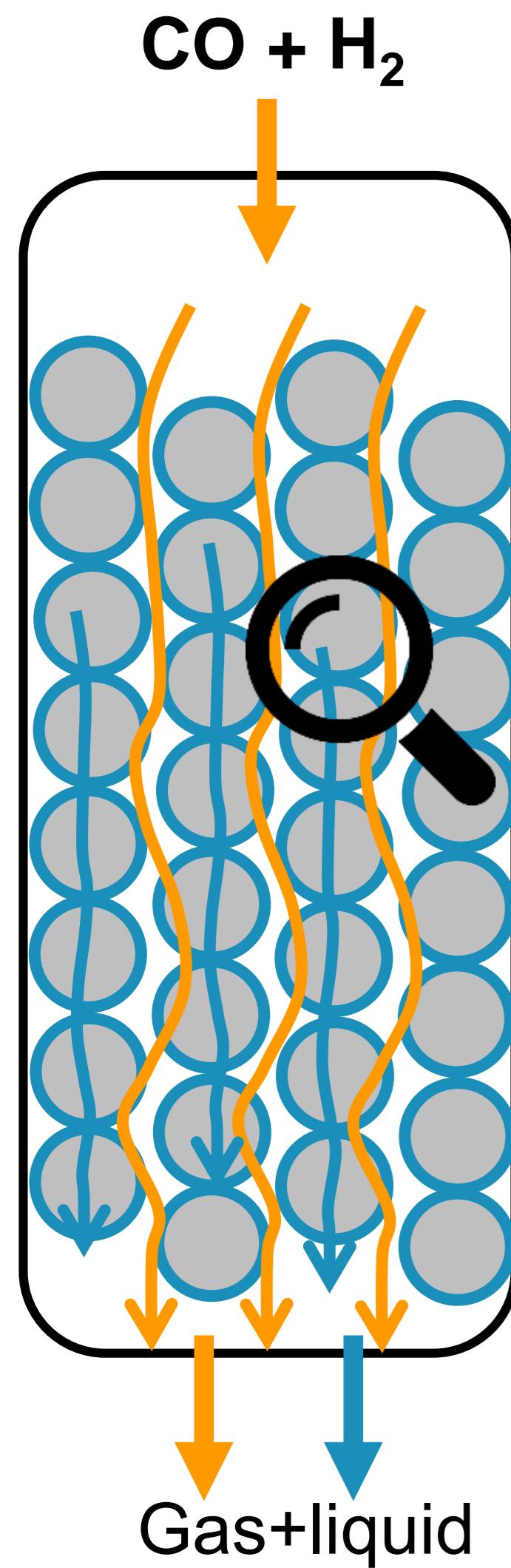
Liquid composition

The simplified VLE model gives similar results to the complete model, but...

The liquid composition... will affect the reactor performance?

5. SIMULATIONS

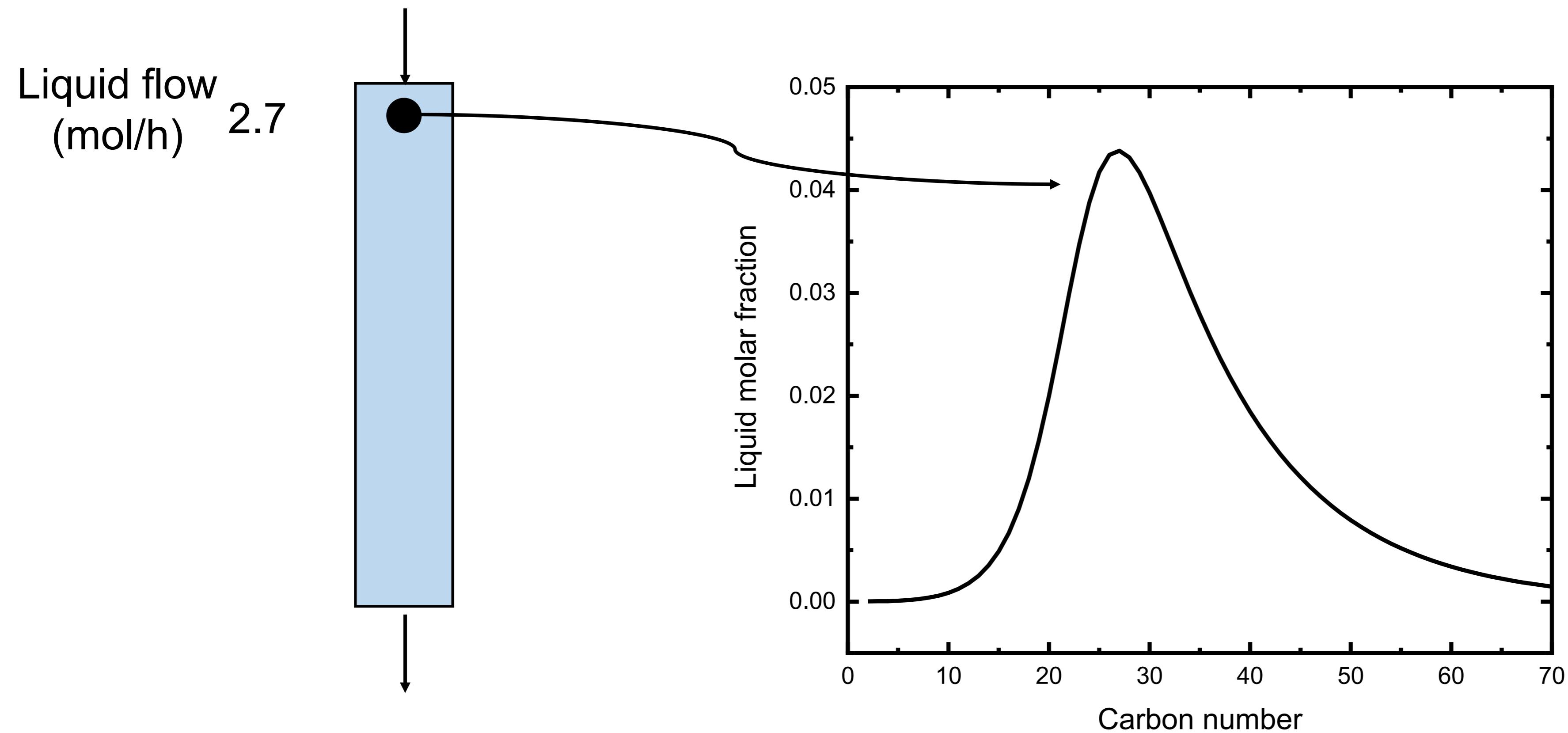
Liquid composition



6. MODELLING RESULTS

Liquid composition

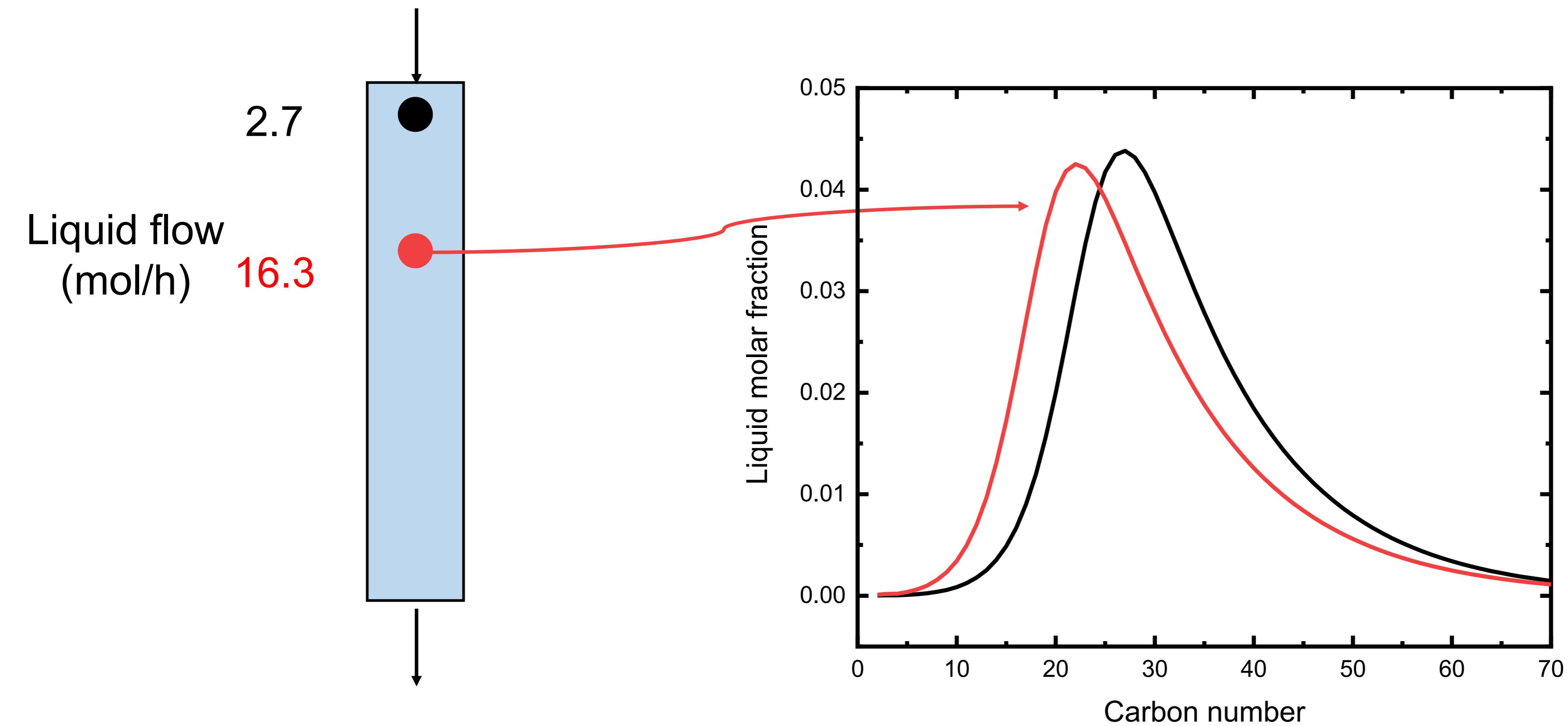
Conditions: 210°C, 20 bar, GHSV = 795 h⁻¹, H₂/CO/N₂=6/3/1, X_{CO} = 68.3%



6. MODELLING RESULTS

Liquid composition

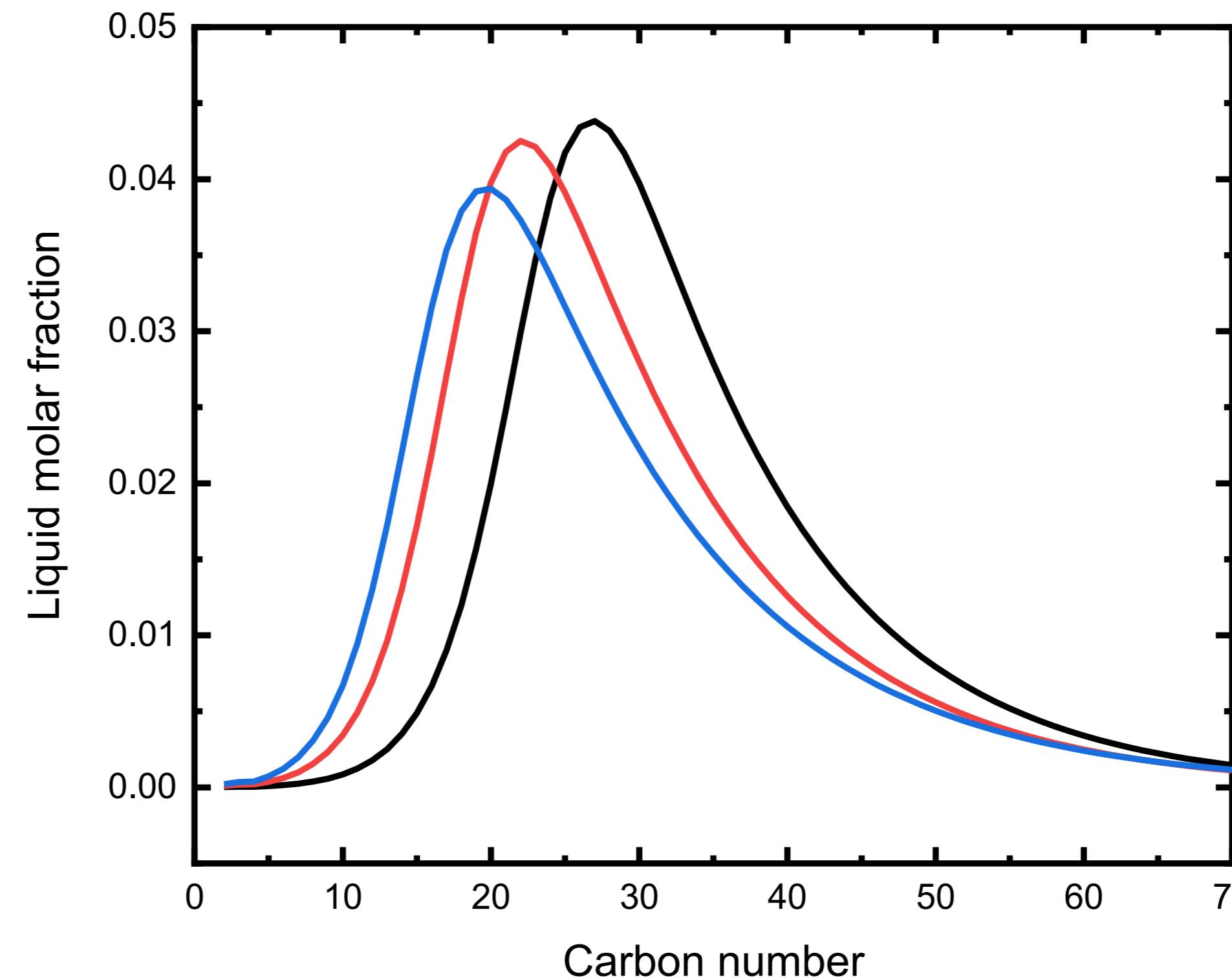
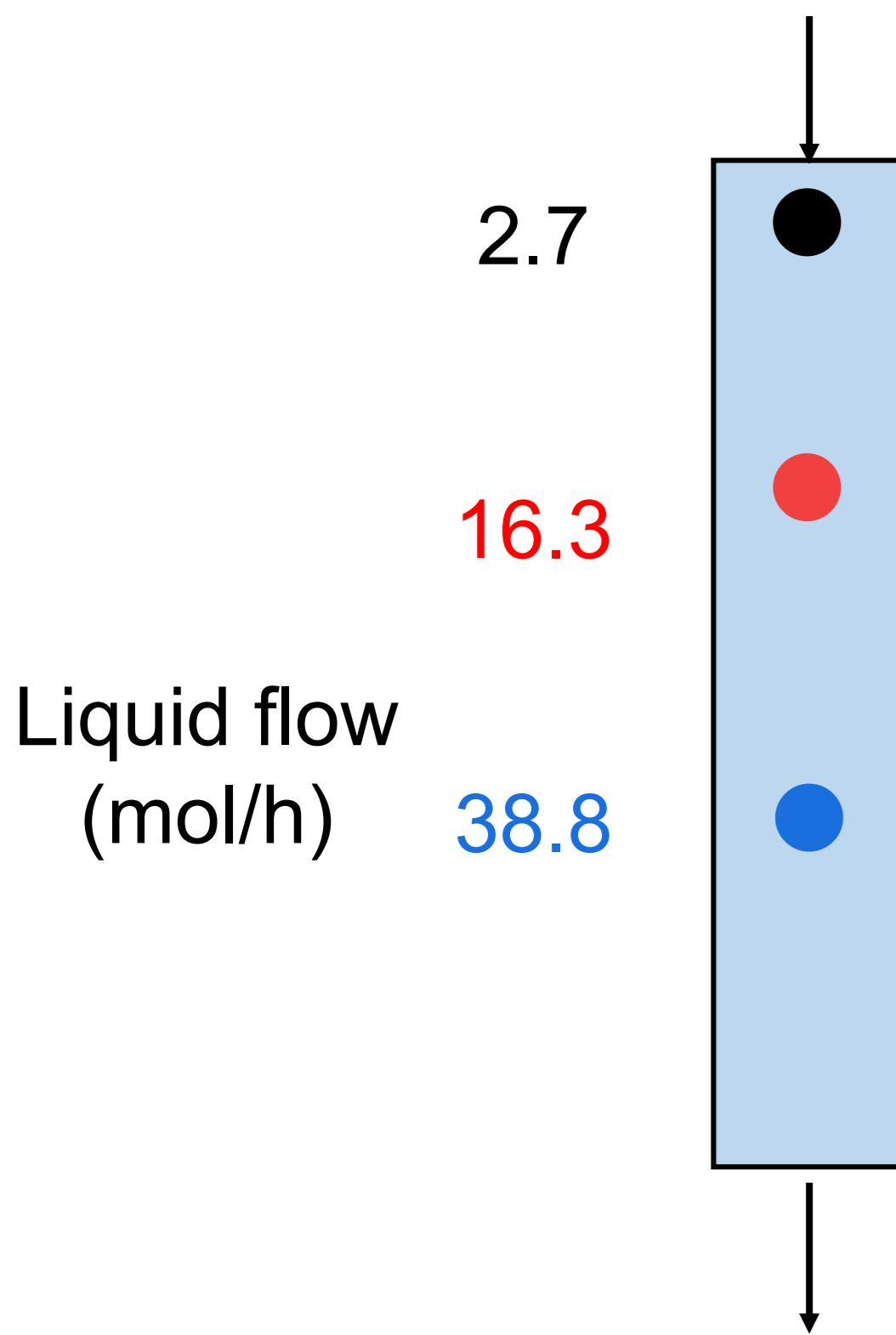
Conditions: 210°C, 20 bar, GHSV = 795 h⁻¹, H₂/CO/N₂=6/3/1, X_{CO} = 68.3%



6. MODELLING RESULTS

Liquid composition

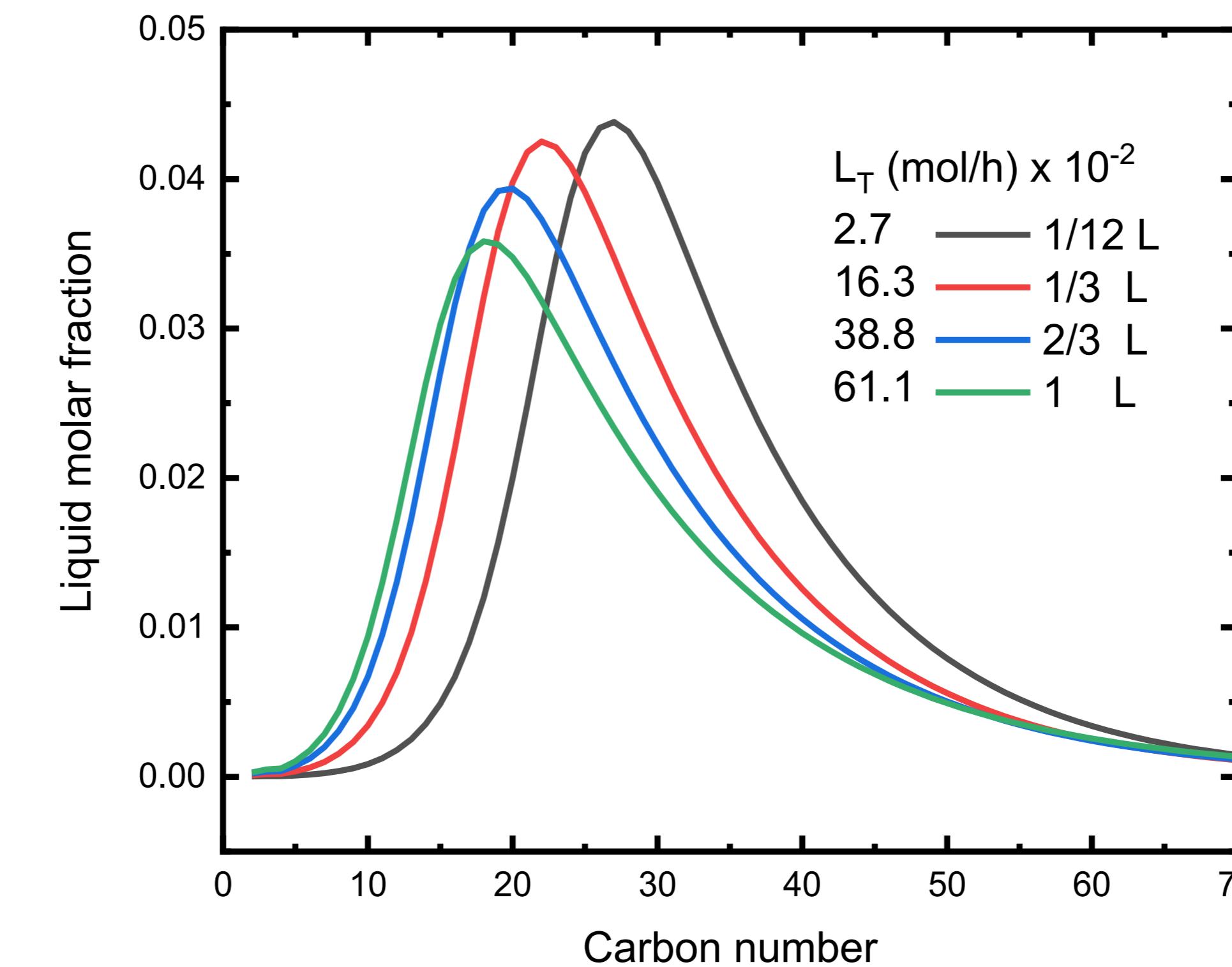
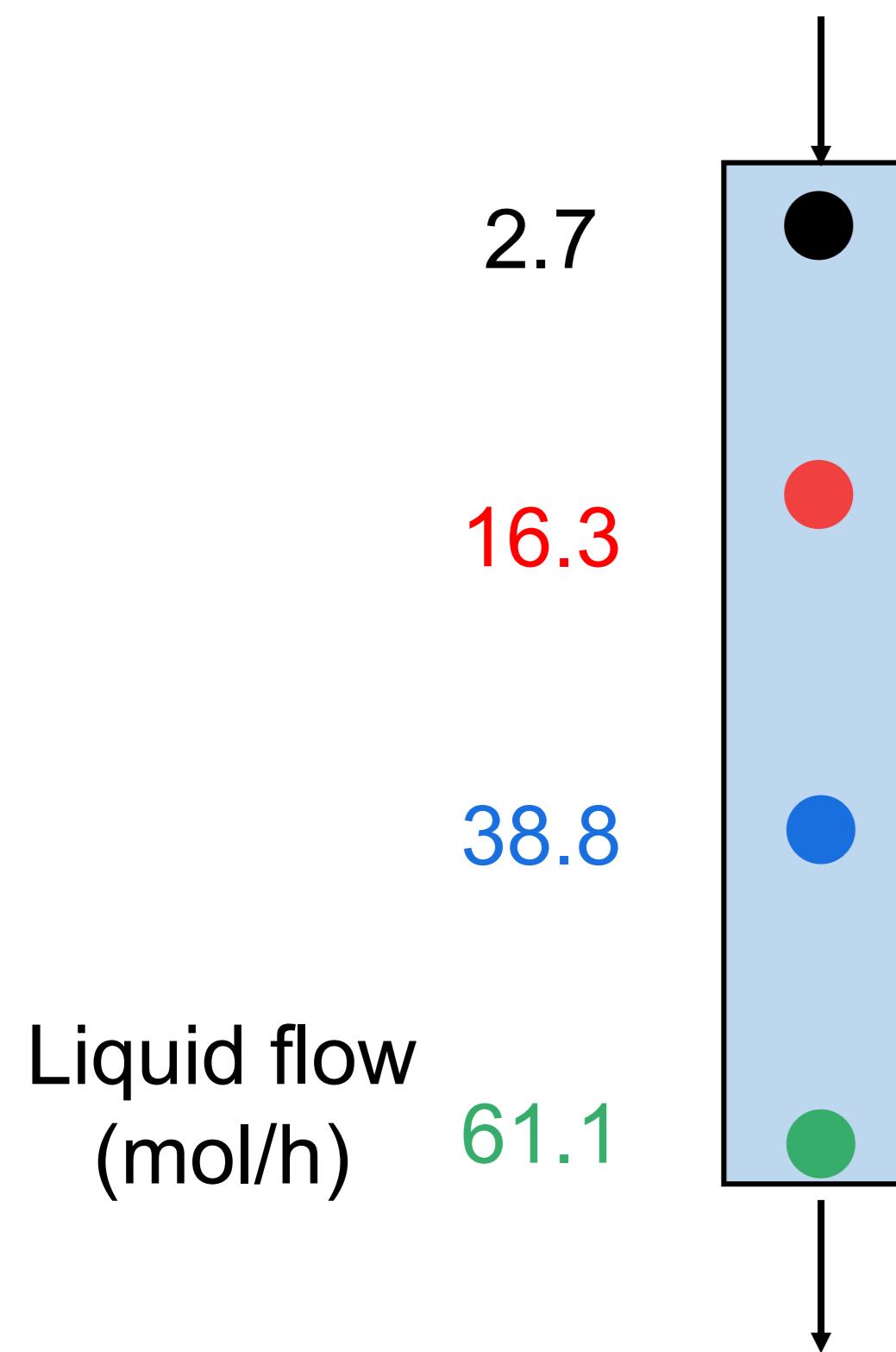
Conditions: 210°C, 20 bar, GHSV = 795 h⁻¹, H₂/CO/N₂=6/3/1, X_{CO} = 68.3%



6. MODELLING RESULTS

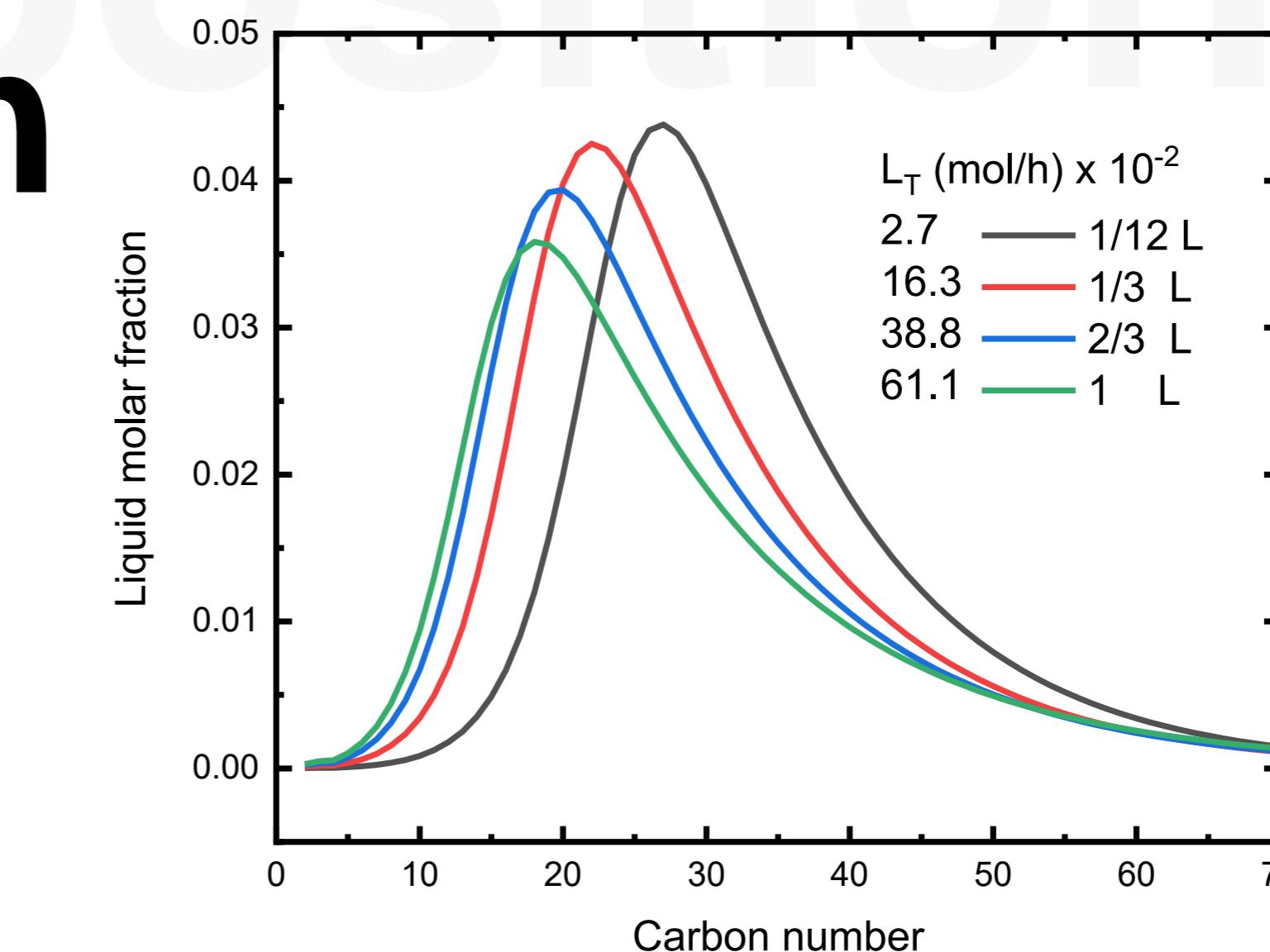
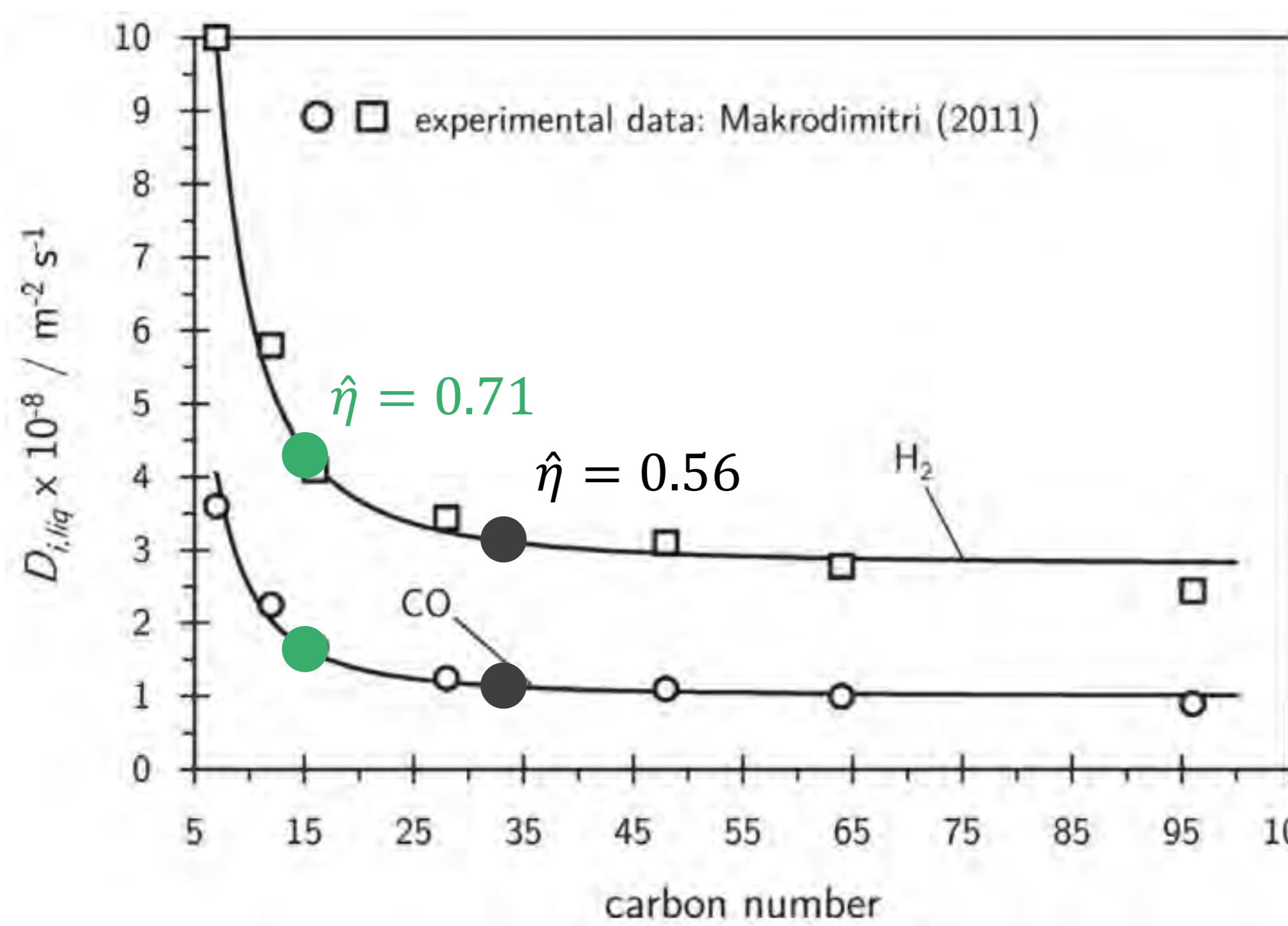
Liquid composition

Conditions: 210°C, 20 bar, GHSV = 795 h⁻¹, H₂/CO/N₂=6/3/1, X_{CO} = 68.3%

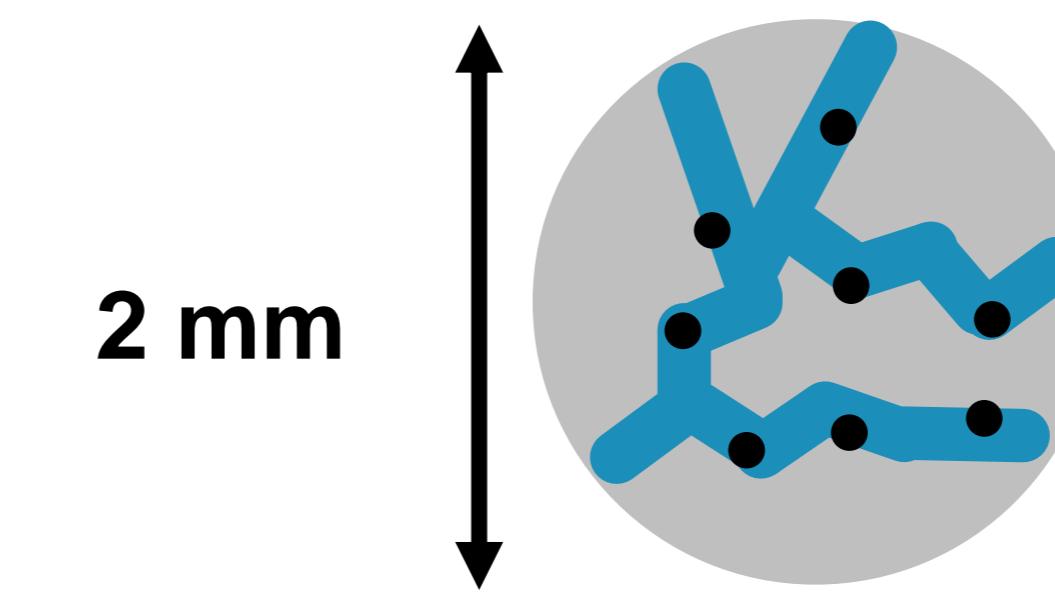


6. MODELLING RESULTS

Liquid composition

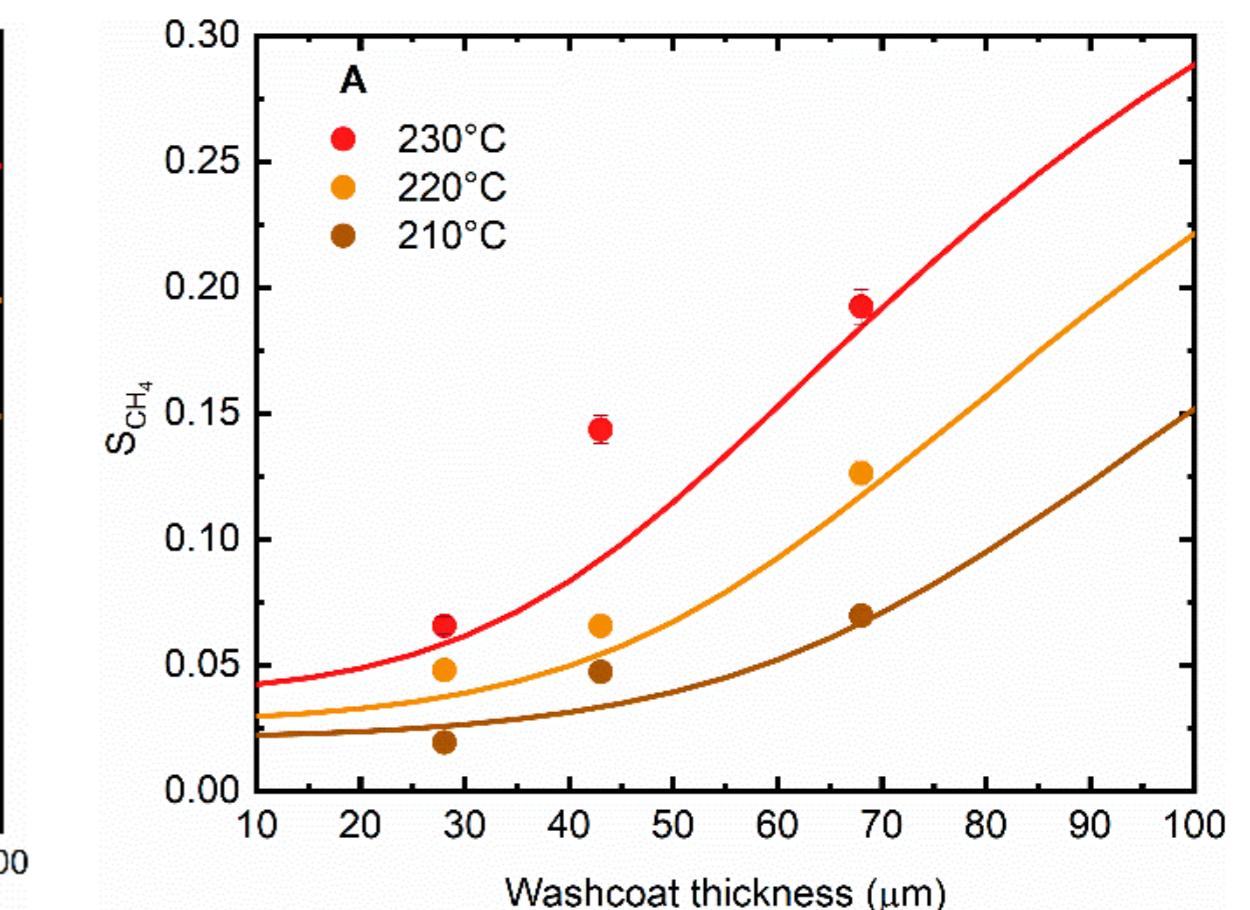
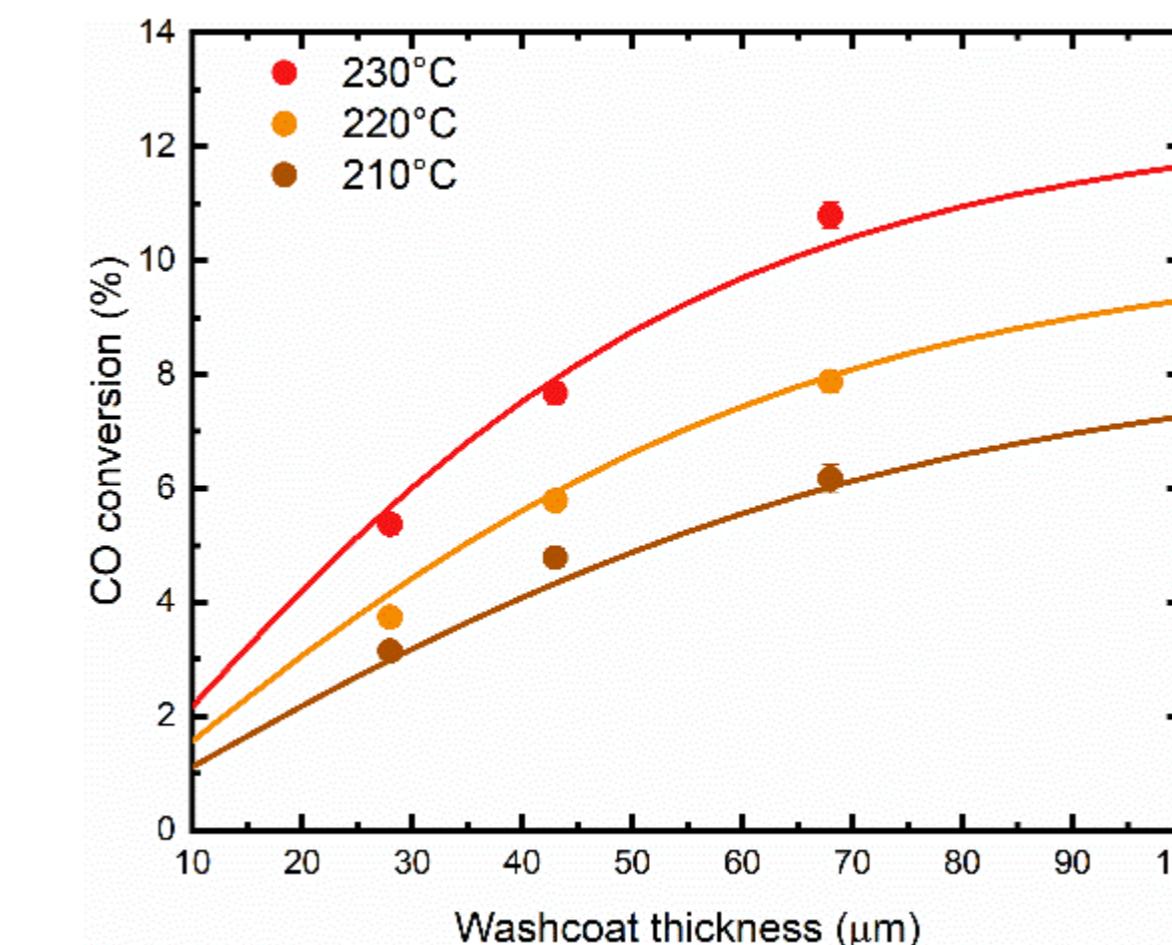
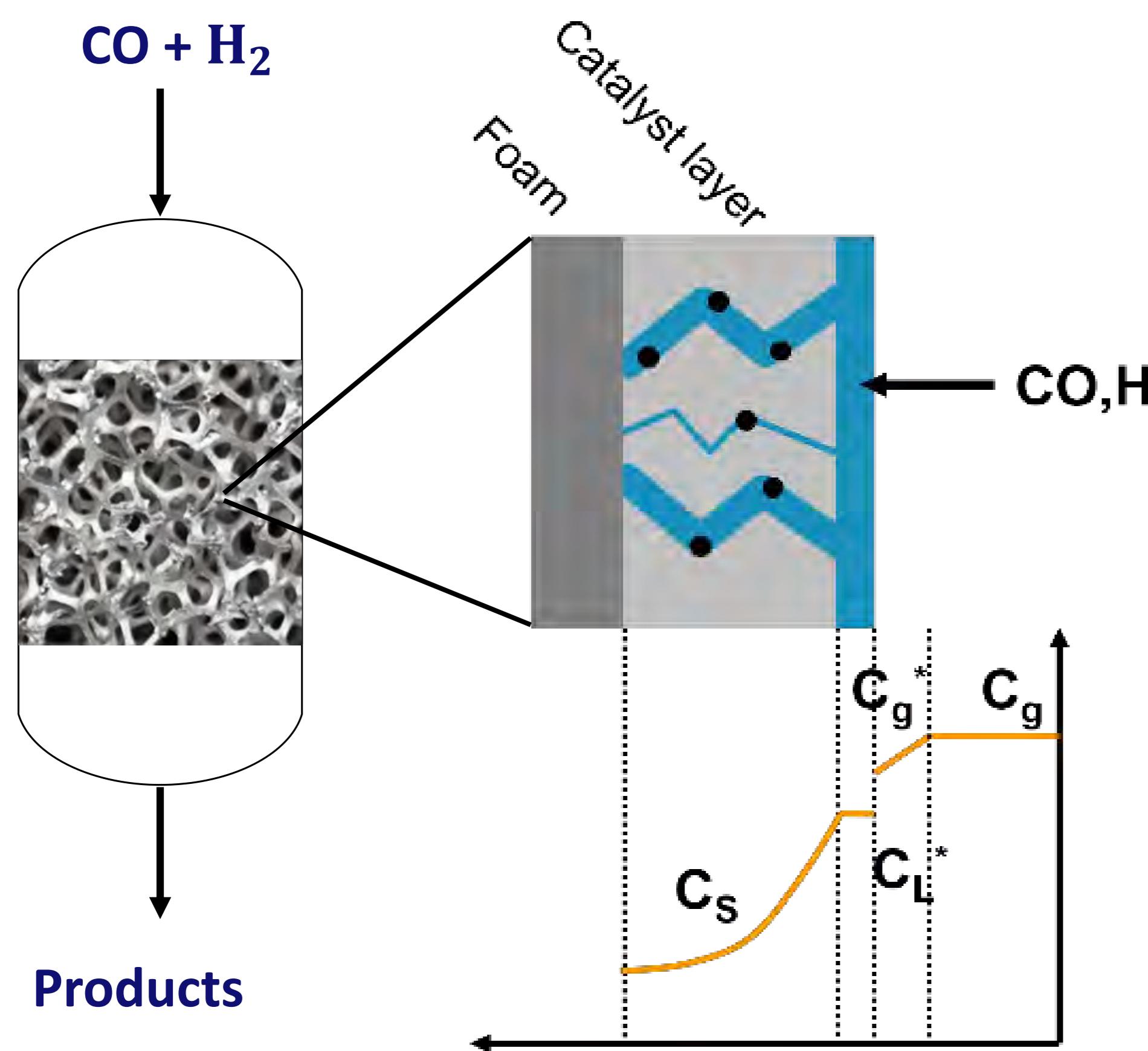


$$\hat{\eta} = \frac{\text{rate of reaction with pore diffusion resistance}}{\text{reaction rate at surface conditions}}$$



The liquid composition will affect the reactor performance

CONCLUSIONS



- High surface area
- Low washcoat layer thickness
- Simplify VLE model at a first stage
- Estimation of liquid composition (complete VLE model)