SUPPLEMENTARY MATERIAL FOR

ENERGY TECHNOLOGY PAPER:

Model based Optimal Sabatier Reactor Design for

Power-to-Gas Applications

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2. Optimal reactor design

2.1 Level 1

The rate equation and the parameter values for the methanation reaction were taken from Koschany *et al*.[1]

The rate equation for the CO_2 methanation:

$$r = k\, p_{H_2}^{0.5}\, p_{CO_2}^{0.5} \left(1 - \frac{p_{CH_4} p_{H_2O}^2}{K_{eq} p_{H_2}^4 p_{CO_2}}\right) / DEN^2 \times 10^3 \qquad \text{(S1)}$$

where $DEN = 1 + K_{OH}\dfrac{p_{H_2O}}{p_{H_2}^{0.5}} + K_{H_2}\, p_{H_2}^{0.5} + K_{MIX}\, p_{H_2}^{0.5}$ (S2)

According to the Arrhenius equation and van't Hoff equation, the rate and adsorption constants are calculated respectively as follows:

$$k = k_{o,ref}\,\exp\left(\frac{E_A}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \qquad \text{(S3)}$$

where

$k_{o,ref} = 3.4\text{e-}4 \pm 4.1\text{e-}5 \text{ mol bar}^{-1}\text{ s}^{-1}\text{ g}_{cat}^{-1}$ and

$E_A = 77.5 \pm 6.9 \text{ kJmol}^{-1}$ at $T_{ref} = 555$ K.

For the adsorption constants the equation (S4) was used:

$$K_i = A_{i,ref}\,\exp\left(\frac{\Delta H_i}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \qquad \text{(S4)}$$

where $i \in \{OH, H_2, mix\}$

Table S1 lists the pre-exponential parameters A_i and the adsorption enthalpies ΔH_i for the adsorption constants.

Table S1 Parameters of the adsorption constants at T= 555K as reported by [1]

i	A_i [bar$^{0.5}$]	ΔH_i [kJ/mol]
OH	0.5 ± 0.05	22.4 ± 6.4
H_2	0.44 ± 0.08	-6.2 ± 10.0
mix	0.88 ± 0.10	-10.0 ± 5.7

2.1.1 Model Formulation

Equation (S5) defines the energy balance:

$$\sum_i n_i \hat{C}_{pi} \frac{dT}{dt} = -(q_{ex} + \Delta H_{rxn} \, r_{rxn} \, \rho_c \frac{(1-\varepsilon)}{\varepsilon} V_g) \tag{S5}$$

where $\hat{C}_{pi}$ is the molar heat capacity of component i. It is estimated using temperature dependent formulas reported in Yaws.[2]

2.2 Level 2

2.2.1.1 Model Formulation of the Reactors

The composition of the different compounds is calculated using the component mass balance equation:

$$\frac{1}{n_{int}} \frac{d(\rho_i v_{int})}{dt} = v_i r_{rxn} \rho_c \frac{(1-\varepsilon)}{\varepsilon} M_i \tag{S6}$$

The interstitial velocity profile is calculated using the conservation of the total mass flow rate:

$$v_{int} = \frac{\rho_{g,in} v_{int,in}}{\rho_g} \tag{S7}$$

The superficial velocity is calculated from the interstitial one using:

$$v_s = \varepsilon v_{int} \tag{S8}$$

The same assumptions made for the energy balance in Level 1 applies in Level 2 too:

$$\rho_g C_p \frac{dT}{dt} = -\left(\frac{4}{\varepsilon D_t} q_{ex} + \Delta H_{rxn} r_{rxn} \rho_c \frac{1-\varepsilon}{\varepsilon} \right) \tag{S9}$$

In Level 2 the heat exchange between the reaction segment and the coolant section is limited by the following transport kinetic equation:

$$q_{ex} = \alpha_w (T_g - T_c) \tag{S10}$$

where T_c is the coolant (bounded between 422 and 613 K). The heat transfer coefficient across the wall of the reactor is calculated using the correlation given by Yagi *et al.* [3]:

$$a_w = 0.2\,\text{Re}_p^{-0.2}\,C_p\,\text{Pr}^{-2/3}\,r_g v_s \tag{S11}$$

The specific heat capacity of the gas mixture is calculated using:

$$C_p = \sum_{i=1}^{4} y_i \frac{\hat{C}_{pi}}{M_i} \tag{S12}$$

The pressure drop inside the reactor is calculated using Ergun equation:

$$\frac{dp}{dt} = -\left[150 m_g \frac{(1-e)^2}{D_p^2 e^3} + 1.75 \frac{v_s r_g (1-e)}{D_p e^3}\right] \frac{v_s^2}{e} 10^{-5} \tag{S13}$$

The equation reported by Jeschar et al. [4] is used to calculate the bed porosity:

$$e = 0.375 + 0.34 \frac{D_p}{D_t} \tag{S14}$$

<u>Criteria for the limitation-free inter and intra heat and mass transport:</u>

In order to ensure that the catalyst is fully utilized ($h_c \geq 0.95$), criteria for inter and intra heat and mass transport limitations are enforced as constraints. These are:

1. Mears criterion for the limitation free particle interphase heat transport [5]:

$$\frac{-\Delta H_{rxn} r_{rxn} r_p D_p}{a_p T} < \frac{0.3 RT}{E_a} \tag{S15}$$

where a_p is the heat transfer coefficient between the particle and the fluid. It is calculated using the correlation provided for spherical particles by Wakao et al.[6].

2. Hudgins criterion for limitation free particle interphase mass transport [7]:

$$\frac{D_p \left| r'_{rxn} \right| r_c}{k_c} < 0.3 \tag{S16}$$

where k_c [m/s] is the mass transfer coefficient and is calculated using the Sherwood correlation of Wakao et al.[6] and $\left| r'_{rxn} \right|$ is the absolute value of

derivative of the reaction rate with respect to concentration. The advantage of this criterion is its applicability to all forms of kinetic expressions.

3. Anderson criterion for absence of temperature gradient inside the catalyst[8]:

$$\frac{-\Delta H_{rxn} r_{rxn} r_c D_p^2}{T \lambda_p} < \frac{3RT}{E_a} \qquad (S17)$$

4. Hudgins criterion for absence of concentration gradient inside the catalyst [7]:

$$\frac{D_p^2 \left| r_{rxn}' \right| r_c}{D_{im}} < 3 \qquad (S18)$$

D_{im}, which is the diffusion coefficient of component i diffusing in a mixture of gases forming a stagnant film, is calculated using the equation proposed by Wilke[9]:

$$D_{im} = \frac{1 - x_i}{\displaystyle\sum_{j=1, j \neq i}^{4} \frac{x_j}{D_{ij}}} \qquad (S19)$$

The binary diffusion coefficient D_{ij} is calculated using the empirical correlation.[10] For a most conservative design, the lowest value of D_i is considered in the equation of Hudgins criterion.

In order to ensure a plug flow, the following constraint is enforced:

$$\frac{D_t}{D_p} \geq 10 \qquad (S20)$$

2.2.2 Membrane Reactor

2.2.2.1 Model for Membrane Packed Bed Reactor

The equations for the component mass balance, the mass flux through the membrane and the interstitial velocity profile are:

$$\frac{1}{n_{int}} \frac{d(r_i v_{int})}{dt} = \frac{4 D_{ti}}{\varepsilon \left(D_{to}^2 - D_{ti}^2 \right)} j_i M_i + J_i r_{rxn} r_c \frac{(1 - \varepsilon)}{\varepsilon} M_i \qquad (S21)$$

The mass flux is described by a phenomenological transport kinetic model where the water molar flux is proportional to the permeance, the variable with which the water flux is controlled, and to the partial pressure difference across the membrane:

$$j_{H_2O} = 10^5 \times Perm(p_{H2O} - p_{H2O,s})$$ (S22)

The *Perm* is set to vary within realistic bounds: $10^{-8} < Perm < 10^{-6}$ (molm^{-2} Pa^{-1} s^{-1}). These bounds were chosen based on the permeance values of the state-of-the-art hydrophilic membranes reported in literature.[11] It is assumed that the flow rate of the sweep gas (e.g. air) is so high that its water mole fraction is considered negligible. This will allow a maximum driving force for the permeation, and thus the determination of the maximum potential of this proposed reactor concept.

The interstitial velocity profile is determined by solving the continuity equation:

$$\frac{1}{n_{int}}\frac{d(r_g v_{int})}{dt} = \frac{4D_{ti}}{e(D_{to}^2 - D_{ti}^2)}\sum_{i=1}^{4} j_i M_i$$ (S23)

The energy balance for the reaction channel is defined as:

$$r_g C_p \frac{dT}{dt} = -\left(\frac{4D_{to}}{e(D_{to}^2 - D_{ti}^2)}q_{ex} + \Delta H_{rxn} r_{rxn} r_c \frac{1-e}{e}\right)$$ (S24)

The energy balance in the permeate side is not considered at this level. The modeling of the permeate side becomes important in Level 3 where a detailed reactor design is made.

The void fraction of the reaction side is calculated using the equation reported by Dutoit et al. [12]:

$$e = 0.3517 + 0.387\frac{D_p}{D_{to} - D_{ti}}$$ (S25)

2.3 Level 3:

The same equations and bounds of Level 2 are applied in Level 3. However, the balance equations are formulated in the Eularian formulation:

$$\frac{d(r_i v_{int})}{dz} = J_i r_{rxn} r_c \frac{(1-e)}{e} M_i$$ (S26)

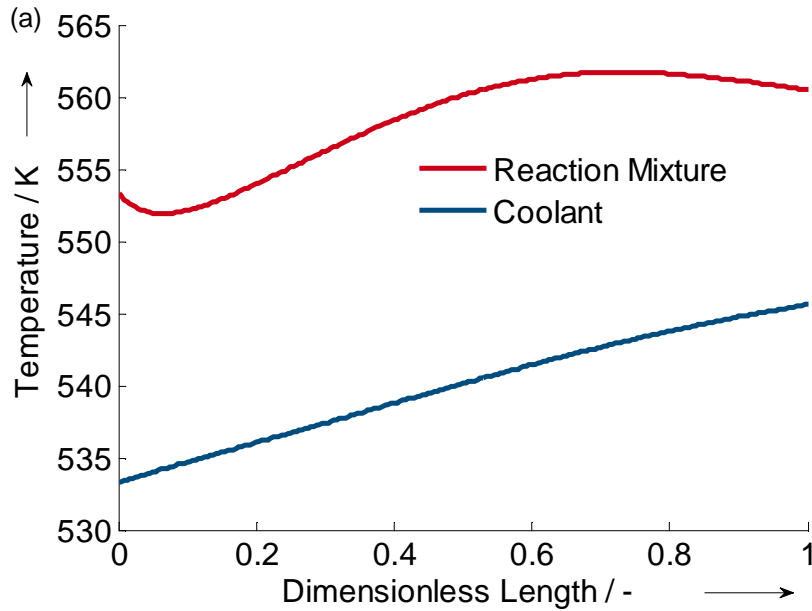$$r_g C_p \frac{dT}{dz} = -\left(\frac{4}{e\,D_t} q_{ex} + \Delta H_{rxn} r_{rxn} r_c \frac{1-e}{e}\right) \frac{1}{v_{int}} \tag{S27}$$

$$\frac{dp}{dz} = -\left(150 m_g \frac{(1-e)^2}{D_p^2.e^3} + 1.75 \frac{v_s.r_g(1-e)}{D_p.e^3} v_s\right) \times 10^{-5} \tag{S28}$$

The energy balance of the coolant is described by Eq. (S29). The mass flow rate of the coolant, $\dot{m}_c$, is an optimization variable. The heat capacity of the coolant is $C_{p,c}=1.5616$ kJkg^{-1}K^{-1}.

$$\dot{m}_c C_{p,c} \frac{dT_c}{dz} = p D_t q_{ex} \tag{S29}$$

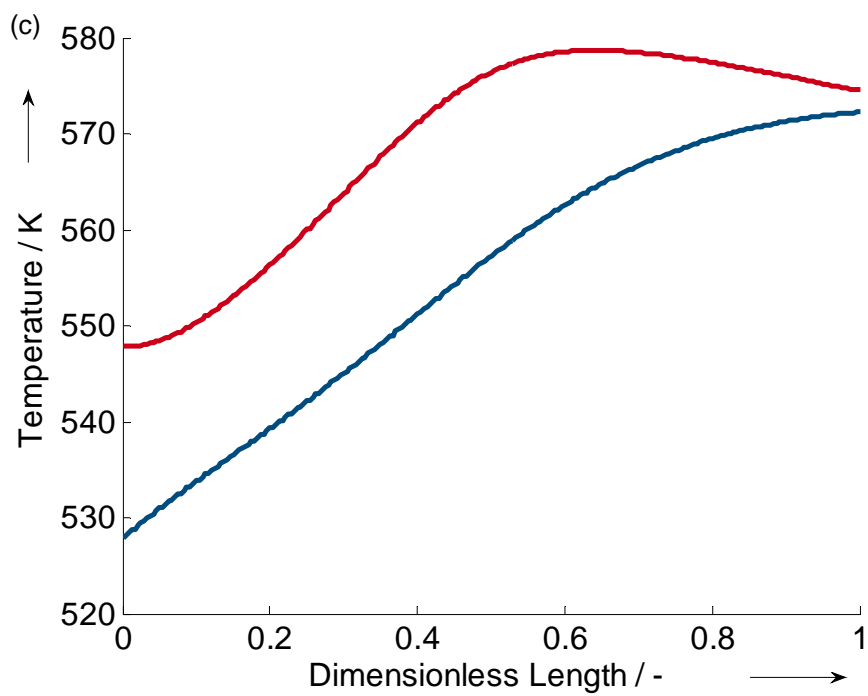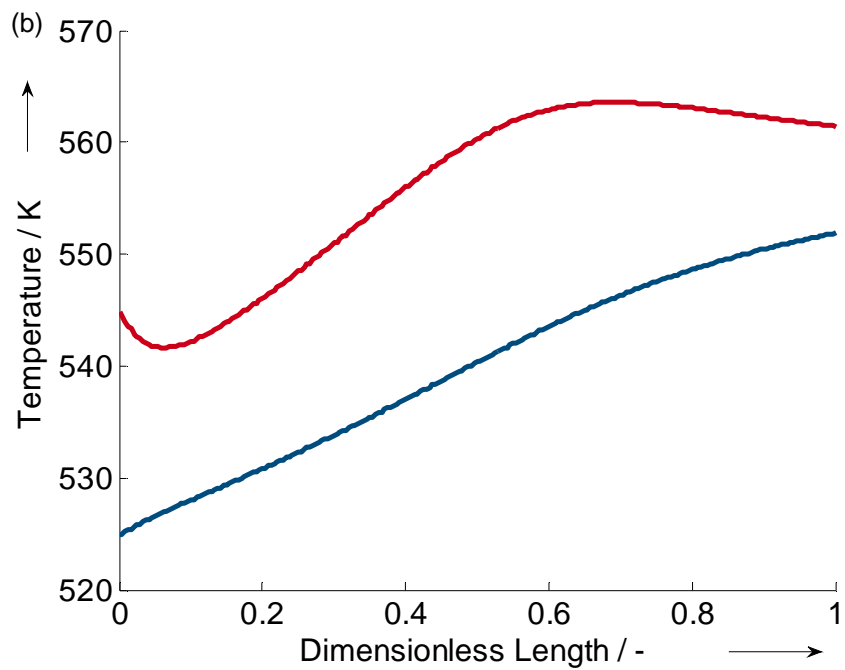### 2.3.2 Result and Discussion

(a)

Figure S1 Results of 2CS cascade of level 3, coolant and reaction mixture temperature profile (a) in the 1st reactor (R1), (b) in the 2nd reactor (R2), (c) in the 3rd reactor (R3)

Nomenclature

Latin symbols

C	concentration, kg/m^3
C_p	mass heat capacity, J/(mol K)
$\hat{C}_p$	molar heat capacity, J/(mol K)
D_t	tube diameter, m
D_p	catalyst particle diameter, m
D	binary molecular diffusion coefficient, m^2/s
E_a	activation energy, J/(mol K)
j	component flux, mol/(m^2 s) or mol/s for level 1
k	rate constant
k_c	mass transfer coefficient, m/s
K	adsorption constant
L	reactor length, m
m	mass flow rate, kg/s
M	molecular weight, kg/mol
n	moles in fluid element, mol
$\dot{n}$	molar flow rate, mol/s
$\dot{m}$	mass flow rate, kg/s
p	pressure, atm
$Perm$	permeance of the membrane, mol/(m^2 Pa s)
q_{ex}	heat flux, W/m^2 or W for level 1
r	reaction rate, mol/(kg s)
$\left|r'_{rxn}\right|$	absolute derivative of the reaction rate with respect to concentration
R	gas constant, J/(mol K)
S	selectivity, -
STY	space time yield, mol/(m^3 s)
T	temperature, K
t	time, s
v_{int}	interstitial velocity, m/s
v_s	superficial velocity, m/s
V	volume, m^3
x	mole fraction, -
y	mass fraction, -
z	axial coordinate, m

Greek symbols

a_p heat transfer coefficient between the fluid and catalyst particle, W/(m^2 K)

a_w wall heat transfer coefficient, W/(m^2 K)

a_i selection variable to indicate the component fluxes involved,-

e porosity, -

DH enthalpy, J/mol

h_c catalyst efficiency,-

l thermal conductivity, W/(m K)

m dynamic viscosity, kg/(m s)

J stoichiometric coefficient

r mass density, kg/m^3

t residence time, s

X split factor,-

Suffices

c coolant side, or catalyst

cond   condenser

g gas phase

f final/outlet value

i component index, or inner tube

j component index

in   inlet

out   outlet

o outer tube

prod   produced

rxn   reaction

m mixture

s sweep gas

p particle

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