Supplementary materials

Multiphysics modeling and heat distribution study in a catalytic microchannel methanol steam reformer

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Appendix-1: Physical Properties

Table A.1: The parameters to calculate the binary diffusivity of the pairs.[1]

$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$ $T^* = \frac{kT}{\varepsilon_{ij}} \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{\frac{1}{2}} \quad A = 1.06036 \quad B = 0.1561$ $C = 0.19300 \quad D = 0.47635 \quad E = 1.03587 \quad F = 1.52996$ $G = 1.76474 \quad H = 3.89411$
$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$
$M_{ij} = \frac{2}{\frac{1}{M_i} + \frac{1}{M_j}}$
Explanations: Ω_D: Diffusion collision integral [dimensionless] σ_{ij}: The characteristic length [Å] M_i, M_j: Molecular weights of i and j [g/mol] k: Boltzmann`s constant- 1.3805x10^{-23} [J/K] ε: The characteristic Lennard-Jones energy [J]

Table A.2: The characteristic length and Lennard-Jones Potentials.[1]

Substance	σ [Å]	ε/k $[K]$
CH_3OH	3.626	481.8
H_2O	2.641	809.1
H_2	2.827	59.7
CO_2	3.941	195.2
CO	3.69	91.7

Table A.3: Viscosity constants for components.[2]

Component	a	b	c	d
CH_3OH	3.0663E-7	0.69655	205	0
H_2O	1.7096E-8	1.1146	0	0
H_2	1.797E-7	0.685	-0.59	140
CO_2	2.148E-6	0.46	290	0
CO	1.127E-6	0.5338	94.7	0

Table A.4: Thermal conductivity constants for components.[2]

Component	c_1	c_2	c_3	c_4
CH_3OH	5.7992E-7	1.7862	0	0
H_2O	6.2041E-6	1.3973	0	0
H_2	0.002653	0.7452	12	140
CO_2	3.96	-0.3838	964	1860000
CO	5.9882E-4	0.6863	57.13	501.92

Table A.5: Specific heat capacity constants for components.[3]

Component	$\propto$	$\propto_1$	$\propto_2$	$\propto_3$
CH_3OH	19.0	9.152E-2	-1.22E-5	-8.039E-9
H_2O	32.24	0.1923E-2	1.055E-5	-3.595E-9
H_2	29.11	-0.1916E-2	0.4003E-5	-0.8704E-9
CO_2	22.26	5.981E-2	-3.501E-5	7.469E-9
CO	28.16	0.1675E-2	0.5372E-5	-2.222E-9

Appendix-2

a. Reaction kinetic model of Jiang *et al.*[4]

<u>Rate expression [mol kg^{-1} s^{-1}]</u>

$$r_{SR} = k_1 P_{CH_3OH}^{0.26} P_{H_2O}^{0.03} P_{H_2}^{-0.2}$$

<u>Rate constant</u>

$$k_1 = 5.307E12 \exp\left(\frac{-105000}{RT}\right) \; [mmol\ kPa^{-0.296}\ kg^{-1} s^{-1}]$$

b. Reaction kinetic model of Purnama *et al.*[5]

<u>Rate expressions [$\mathbf{mol\ g_{cat}^{-1}\ s^{-1}}$]</u>

$$r_{SR} = k_1 P_{CH_3OH}^{m} P_{H_2O}^{n}$$

$$r_{rWGS} = k_2 P_{CO_2} P_{H_2} - k_{-2} P_{H_2O} P_{CO}$$

$$m = 0.6; n = 0.4$$

<u>Rate constants</u>

$$k_1 = 8.8E8 \exp\left(\frac{-76000}{RT}\right) \; [mol\ bar^{-1} g_{cat}^{-1}\ s^{-1}]$$

$$k_2 = 6.5E9 \exp\left(\frac{-108000}{RT}\right) \; [mol\ bar^{-2}\ g_{cat}^{-1}\ s^{-1}]$$

$$k_{-2} = 4E7 \exp\left(\frac{-67000}{RT}\right) \; [mol\ bar^{-2}\ g_{cat}^{-1}\ s^{-1}]$$

c. Reaction kinetic model of Sa *et al.*[6] (model-1)

<u>Rate expression [$\mathbf{mol\ kg_{cat}^{-1}\ s^{-1}}$]</u>

$$r_{SR} = k_1 P_{CH_3OH}^{a} (\propto + P_{H_2})^{b}$$

$$a = 0.47; b = -0.55; and\ \alpha = 0.30$$

<u>Rate constant</u>

$$k_1 = 3.9E9 \exp\left(\frac{-104000}{RT}\right) \; [mol\ bar^{0.08}\ kg_{cat}^{-1}\ s^{-1}]$$

d. Reaction kinetic model of Peppley *et al.*[7]

Rate expressions [mol kg_{cat}^{-1} s^{-1}]

$$r_{SR} = \frac{k_R K^*_{CH_3O(1)} \left(\frac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right)\left(1 - \frac{P_{H_2}^3 P_{CO_2}}{K_R P_{CH_3OH} P_{H_2O}}\right) C^T_{S_1} C^T_{S_{1a}} S_C}{\left(1 + K^*_{CH_3O(1)}\left(\frac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right) + K^*_{HCOO(1)} P_{CO_2} P_{H_2}^{0.5} + K^*_{OH(1)}\left(\frac{P_{H_2O}}{P_{H_2}^{0.5}}\right)\right)\left(1 + K^{0.5}_{H(1a)} P_{H_2}^{0.5}\right)}$$

$$r_{MD} = \frac{k_D K^*_{CH_3O(2)} \left(\frac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right)\left(1 - \frac{P_{H_2}^2 P_{CO}}{K_D P_{CH_3OH}}\right) C^T_{S_2} C^T_{S_{2a}} S_C}{\left(1 + K^*_{CH_3O(2)}\left(\frac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right) + K^*_{OH(2)}\left(\frac{P_{H_2O}}{P_{H_2}^{0.5}}\right)\right)\left(1 + K^{0.5}_{H(1a)} P_{H_2}^{0.5}\right)}$$

$$r_{WGS} = \frac{k_W K^*_{OH(1)} \left(\frac{P_{CO} P_{H_2O}}{P_{H_2}^{0.5}}\right)\left(1 - \frac{P_{H_2} P_{CO_2}}{K_W P_{CO} P_{H_2O}}\right) (C^T_{S_1})^2 S_C}{\left(1 + K^*_{CH_3O(1)}\left(\frac{P_{CH_3OH}}{P_{H_2}^{0.5}}\right) + K^*_{HCOO(1)} P_{CO_2} P_{H_2}^{0.5} + K^*_{OH(1)}\left(\frac{P_{H_2O}}{P_{H_2}^{0.5}}\right)\right)^2}$$

Kinetic Parameters [7,8,9]

Kinetic Parameter	Value
k_R	$7.4E14 \exp\left(-\frac{10200}{RT}\right) [m^2\, mol^{-1}\, s^{-1}]$
k_D	$3.8E20 \exp\left(-\frac{170000}{RT}\right) [m^2\, mol^{-1}\, s^{-1}]$
k_W	$5.9E13 \exp\left(-\frac{87600}{RT}\right) [m^2\, mol^{-1}\, s^{-1}]$
K_R	$\exp\left(-\frac{50240 - 170.98T - 2.64E-02T^2}{RT}\right) [bar^2]$
K_W	$\exp\left(-\frac{-41735 + 46.66T - 7.55E-03T^2}{RT}\right)$
K_D	$\frac{K_R}{K_W} [bar^2]$
$K^*_{CH_3O(1)}$	$\exp\left(\frac{41.8}{R} - \left(-\frac{20000}{RT}\right)\right) [bar^{-0.5}]$
$K^*_{CH_3O(2)}$	$\exp\left(\frac{30}{R} - \left(-\frac{20000}{RT}\right)\right) [bar^{-1}]$

$K^*_{HCOO(1)}$	$\exp\left(\frac{179.2}{R} - \left(-\frac{100000}{RT}\right)\right)[bar^{-1.5}]$
$K^*_{OH(1)}$	$\exp\left(\frac{-44.5}{R} - \left(-\frac{20000}{RT}\right)\right)[bar^{-1.5}]$
$K^*_{OH(2)}$	$\exp\left(\frac{30}{R} - \left(-\frac{20000}{RT}\right)\right)[bar^{-1}]$
$K_{H(1a)}$	$\exp\left(\frac{-100.8}{R} - \left(-\frac{50000}{RT}\right)\right)[bar^{-1}]$
$K_{H(2a)}$	$\exp\left(\frac{-46.2}{R} - \left(-\frac{50000}{RT}\right)\right)[bar^{-1}]$
$C^T_{S_1}$	7.5E-06 $[mol\ m^{-2}]$
$C^T_{S_{1a}}$	1.5E-05 $[mol\ m^{-2}]$
$C^T_{S_2}$	7.5E-06 $[mol\ m^{-2}]$
$C^T_{S_{2a}}$	1.5E-05 $[mol\ m^{-2}]$
S_C	102,000 $[m^2\ kg^{-1}]$

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