**Comparison between 1D and 2D numerical models of a multi-tubular packed-bed reactor for methanol steam reforming**

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**Appendix. Geometrical and physicochemical properties**

**Rate constant and equilibrium constant**

Because the Langmuir-Hinshelwood macro kinetic model based on the study of Peppley et al. [1] was used for kinetic analysis in this study, the temperature dependence of such constants can be expressed either using the Arrhenius expression or the van't Hoff expression [1–3]:

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |
|  | (4) |
|  | (5) |
|  | (6) |
|  | (7) |
|  | (8) |
|  | (9) |
|  | (10) |
|  | (11) |
|  | (12) |
|  | (13) |

where the required parameters for the comprehensive kinetic model of MSR can found in Table 1 and 2.

**Table 1.** Parameters for rate constants in the comprehensive kinetic model.

|  |  |  |
| --- | --- | --- |
| Rate constants | Kinetic parameters | |
|  |  |
|  |  |  |
|  |  |  |
|  |  |  |

**Table 2.** Parameters for adsorption coefficients in the comprehensive kinetic model.

|  |  |  |
| --- | --- | --- |
| Adsorption coefficients | Kinetic parameters | |
|  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |

**Concentration of species**

|  |  |
| --- | --- |
|  | (14) |

where is the concentration of species in the fluid , is the molar fraction of species , is the partial pressure of component , is the pressure in catalyst bed .

**Superficial velocity**

The initial velocity, , of the gas mixture at the entrance of reactor is given by:

|  |  |
| --- | --- |
|  | (15) |

The gas mixture velocity, , adjusted to working pressure and temperature at every point in the reactor:

|  |  |
| --- | --- |
|  | (16) |

where is the cross-section area of reactor tube , is the molar flow rate of fluid .

**Particle effective diffusivity**

The effective diffusivity of component inside the catalyst particles is estimated based on the ordinary bulk diffusivity and the Knudsen diffusivity [4]:

|  |  |
| --- | --- |
|  | (17) |

The Knudsen diffusivity of component is calculated by:

|  |  |
| --- | --- |
|  | (18) |

where is the molar mass of component , is the ideal gas constant, is the operating temperature, is the average pore diameter.

The ordinary bulk diffusivity of component is estimated using the Maxwell-Stefan equation [5]:

|  |  |
| --- | --- |
|  | (19) |

where is the effective molecular binary diffusivity of and , is the number of components in gas mixture, is the mole fraction of specie 𝑖, is molar flux of species referred to a stationary coordinate reference frame, is the flux ratio of species to (when diffusion limits the rate of chemical reactions).

The Chapman-Enskog equation is used for the binary diffusivity at low density:

|  |  |
| --- | --- |
|  | (20) |

where is the collision integral for diffusion; is the characteristic length, which can be calculated by:

|  |  |
| --- | --- |
|  | (21) |

The collision integral for diffusion is estimated by an empirical equation:

|  |  |
| --- | --- |
|  | (22) |

where

|  |  |
| --- | --- |
|  | (23) |
|  | (24) |

To estimate the and :

|  |  |
| --- | --- |
|  | (25) |
|  | (26) |

**Table 3.** Parameters for the calculation of gas diffusivities.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Gas Components |  |  |  |  |
|  | 118.00 | 512.64 | 0.565 | 1.70 |
|  | 55.95 | 647.14 | 0.344 | 1.84 |
|  | 64.20 | 32.98 | -0.217 | 0 |
|  | 93.10 | 132.85 | 0.045 | 0.122 |
|  | 94.07 | 304.12 | 0.225 | 0 |

**The effective radial diffusion coefficient in packed bed**

The effective radial diffusion coefficient in packed bed can be calculated by[6–8]:

|  |  |
| --- | --- |
|  | (27) |

where is the diameter of catalyst particle, is the inner diameter of reactor tubes.

**The radial thermal conductivity in packed bed**

The radial heat transfer in the packed bed can be evaluated by the effective radial thermal conductivity as the following expression [9]:

|  |  |
| --- | --- |
|  | (28) |

where is the effective stagnant thermal conductivity due to molecular heat conduction in the fluid and the solid phase, which is independent of the fluid velocity, and is the effective thermal conductivity due to fluid convection.

Correlation (28) is usually expressed in a dimensionless form by using a molecular Peclet number:

|  |  |
| --- | --- |
|  | (29) |

where is the thermal conductivity of the fluid, and can be calculated as:

|  |  |
| --- | --- |
|  | (30) |
|  | (31) |

where is the aspect ratio, or the number of particles on the tube diameter:

|  |  |
| --- | --- |
|  | (32) |

The volume-equivalent particle diameter is used in this work. For a cylinder catalyst with a diameter and a height , the can be calculated by:

|  |  |
| --- | --- |
|  | (33) |

The correlation for the stagnant thermal conductivity in packed beds is given by [9,10]:

|  |  |
| --- | --- |
|  | (34) |
|  | (35) |
|  | (36) |

where is the ratio of the thermal conductivity of the solid catalyst particle and the gas fluid:

|  |  |
| --- | --- |
|  | (37) |

The thermal conductivity of catalyst particles can be assumed as linear dependent on temperature based on the study of Bert Koning [9], where the CuO/Al2O3 cylinder catalyst with a particle diameter of was used:

|  |  |
| --- | --- |
|  | (38) |

The effect of particle size on effective thermal conductivity of packed beds is approved to be insignificant [11,12].

The thermal conductivity of gas mixture can be calculated by:

|  |  |
| --- | --- |
|  | (39) |
|  | (40) |

where is the thermal conductivity of the component , which can be calculated by:

|  |  |
| --- | --- |
|  | (41) |

where the constants for thermal conductivities can be found in Table 4.

**Table 4.** Thermal conductivity constants for components

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Gas Component | a | b | c | d | e |
| CO2 | 0.6395 | 0.0190 | 1.5214e-04 | -1.1666e-07 | 7.8815e-05 |
| CO | 0.0185 | 0.0918 | -3.1038e-05 | 8.1127e-09 | 9.7460e-07 |
| H2 | -11.9000 | 0.8870 | -9.2345e-04 | 5.6111e-07 | -0.0026 |
| CH3OH | 8.0364e-05 | 0.0130 | 1.4250e-04 | -2.8336e-08 | 1.2646e-09 |
| H2O | 0.4365 | 0.0529 | 1.0053e-05 | 4.8426e-08 | 2.3506e-05 |

**Overall heat transfer coefficient**

For heat exchange between the tube and shell sides, there are three regions, where the temperature varies sharply, corresponding to three resistances to heat transfer: 1) the fluid film of the inner side of the tube, 2) the tube wall and 3) the fluid film outside the tube. The cross section of a single tube and the radial temperature profile are represented in Figure 1. Assuming the steady-state heat transfer, the overall heat-transfer coefficient on the shell side and the tube side can be described by [13]:

|  |  |
| --- | --- |
|  | (42) |
|  | (43) |

Diagram

Description automatically generated with low confidence

**Figure 1.** Cross section of single tube and radial temperature profile.

According to the study of Mears et al. [14], the heat transfer resistance between the tube wall and the catalyst bed isn’t negligible with a small ratio of tube to particle diameter (). Furthermore, the major cause of the heat transfer resistance between the tube wall and the catalyst bed could be regard as the gas film [15]. The heat transfer resistance can be considered as the heat transfer coefficient of the inner film , which is estimated as:

|  |  |
| --- | --- |
|  | (44) |

where is the void fraction of the catalyst bed, is the Prandtl number, is the average thermal conductivity of the gas mixture inside tubes, is the Reynolds number. For packed beds, the Reynolds number is defined by:

|  |  |
| --- | --- |
|  | (45) |

A picture containing text, weapon

Description automatically generated

**Figure 2.** Arrangement of tubes and baffles in the shell of reformer.

The Donohue equation is generally used to estimate the heat transfer coefficient in the shell-side film in a shell-tube heat exchanger:

|  |  |
| --- | --- |
|  | (46) |
|  | (47) |
|  | (48) |
|  | (49) |
|  | (50) |
|  | (51) |

where is the mass velocity of gas mixture, is the mass velocity through the baffle window, is the mass velocity for crossflow perpendicular to the tubes, is the area available for shell-side fluid flow through the baffle window, is the interstitial area available for crossflow perpendicular to the bank of tubes at the widest point in the shell, is average thermal conductivity of shell-side gas, is the mass flow rate of shell-side gas, and is the average viscosity of shell-side burner gas.

**Density of gas mixture**

The density of gas mixture is mathematically expressed as:

|  |  |
| --- | --- |
|  | (52) |

where is the total pressure of the gas mixture, is the mole fraction of gas component , is the molar mass of gas component .

**Specific heat capacity**

The specific heat capacity of the gas mixture is computed by:

|  |  |
| --- | --- |
|  | (53) |

is the specific heat capacity of the multicomponent mixture, is the number of components in gas mixture, is the specific heat capacity of component , which can be calculated using the following relationship and data for parameters :

|  |  |
| --- | --- |
|  | (54) |
|  | (55) |

**Table 5.** Specific heat capacity constants for components

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Gas Component | a | b | c | d | e |
|  | 33.066178 | -11.363417 | 11.432816 | -2.772874 | -0.158558 |
|  | 30.92000 | 6.832514 | 6.7934356 | -2.534480 | 0.0821398 |
|  | 24.99735 | 55.18696 | -33.69137 | 7.948387 | -0.136638 |
|  | 25.56759 | 6.096130 | 4.054656 | -2.671301 | 0.131021 |
|  | 13.93945 | 111.30774 | -41.59074 | 5.482564 | 0.052037 |

**Reaction enthalpy**

The temperature dependence of reaction enthalpies can be presented as:

|  |  |
| --- | --- |
|  | (56) |
|  | (57) |
|  | (58) |

**Gas mixture viscosity**

The gas mixture viscosity was calculated by Wilke’s method described by the following correlation [16]:

|  |  |
| --- | --- |
|  | (59) |
|  | (60) |

where is the viscosity of fluid mixture, is the viscosity of component , is the molecular weight. The first-order solution for viscosity of pure gas can be expressed [17]:

|  |  |
| --- | --- |
|  | (61) |
|  | (62) |
|  | (63) |
|  | (64) |
|  | (65) |
|  | (66) |

where , , , , and .

**Table 6**. Basic constants values for the calculation of viscosity of gases

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Gas Components |  |  |  |  |
|  | 118.00 | 512.64 | 0.565 | 1.70 |
|  | 55.95 | 647.14 | 0.344 | 1.84 |
|  | 64.20 | 32.98 | -0.217 | 0 |
|  | 93.10 | 132.85 | 0.045 | 0.122 |
|  | 94.07 | 304.12 | 0.225 | 0 |

**Nomenclature**

|  |  |
| --- | --- |
|  | cross-sectional area of a reactor tube, |
|  | specific heat capacity, |
|  | concentration of species , |
|  | effective radial diffusion coefficient, |
|  | effective diffusivity of species inside catalyst particles, |
|  | inner diameter of reactor tube, |
|  | outer diameter of reactor tube, |
|  | diameter of catalyst particle, |
|  | volume-equivalent particle diameter, |
|  | activation energy for rate constant of reaction , |
|  | molar flow rate of species , |
|  | superficial mass velocity, |
|  | heat transfer coefficient in the shell-side film, |
|  | heat transfer coefficient in the tube-side film, |
|  | adsorption coefficient of surface species |
|  | reaction equilibrium constant of reaction |
|  | rate constant for reaction, |
|  | molecular weight of species , |
|  | number of baffles |
|  | number of tubes |
|  | operating pressure, |
|  | Peclet number |
|  | Prandtl number |
|  | partial pressure of species , |
|  | tube pitch, |
|  | universal gas constant, |
|  | Reynolds number |
|  | operating temperature, |
|  | heat transfer coefficient between tube and shell sides, |
|  | superficial velocity, |
|  | mole fraction of species |
|  | thickness of tube wall, |
| *Greek symbols* | |
|  | viscosity of species , |
|  | heat of reaction for formation of species , |
|  | entropy of adsorption for species , |
|  | effective radial thermal conductivity, |
|  | thermal conductivity of gas mixture, |
|  | thermal conductivity of species , |
|  | thermal conductivity of catalyst particles, |
|  | density, |
|  | void fraction |

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