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Short Communication

Effectiveness factor correlations for spherical nickel catalyst pellets used in small-scale steam methane reformers

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ABSTRACT

A simple method is devised for determining the effectiveness factors of spherical nickel catalyst pellets used for steam methane reforming (SMR) processes; specifically, the factors are determined for reforming conditions relevant to small-scale hydrogen production systems (1–3 bar pressure, 600–800 °C temperature, 2–4 steam/carbon ratio). The effectiveness factors are plotted with respect to a newly proposed effective Thiele modulus that considers the mass transfer limitation near the equilibrium methane conversion. Then, a modified Thiele modulus is introduced to make the effectiveness factors for various reforming conditions and structural parameters fall on a single correlation curve. The results indicate that the proposed method can properly describe the effectiveness factors of nickel catalyst pellets for the SMR conditions considered in this study.

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Introduction

Residential fuel cell systems rely on on-site, small-scale reforming of methane for hydrogen production by utilizing well-developed city gas supply infrastructures [1–3]. In these systems, steam methane reforming (SMR) processes are commonly performed at near-atmospheric pressures, which differ from the high reforming pressures of 20–40 bar used in industrial hydrogen production plants [4–6]. In addition, small spherical or cylindrical catalyst pellets are commonly used to obtain higher efficiencies in those small-scale reformers.

Catalyst effectiveness factors are essential data for accurately simulating reforming processes, as well as for properly optimizing reactor design. However, previous numerical studies have commonly used a constant catalyst effectiveness factor between 0.03 and 0.07 [7–9], primarily due to a lack of reference studies. Accordingly, Baek et al. [10] solved the detailed reaction/diffusion problem corresponding to SMR processes in spherical nickel catalyst pellets and presented the obtained catalyst effectiveness factors as a function of methane conversion and the effective Thiele modulus.

However, the effective Thiele modulus proposed by Baek et al. [10] overestimated the mass transport rate of methane

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under reforming conditions near the equilibrium methane conversion. Thus, the effectiveness factor curves showed incorrect behavior with respect to the effective Thiele modulus near equilibrium. In this study, the mass transport limitation near the equilibrium methane conversion is fully considered in evaluating the effective Thiele modulus. The simulation cases used in Baek et al. [10] are thoroughly repeated to calculate this new effective Thiele modulus. Then, a modified Thiele modulus is introduced to make the effectiveness factors for various reforming conditions and structural parameters fall on a single correlation curve. Finally, the correlation error is estimated by comparing the proposed correlation curves and the effectiveness factor data.

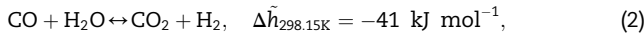
Theory and calculation

Following the work of Baek et al. [10], the detailed SMR processes inside spherical catalyst pellets are calculated by considering the distributed reaction, multi-component diffusion and permeation, and conductive and convective heat transfer in the porous media. Three global chemical reactions are considered for steam methane reforming processes:

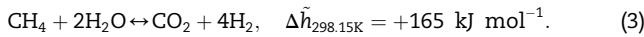
I. steam reforming (SR):



II. water-gas shift (WGS):



III. reverse methanation (RM):



The intrinsic kinetics for these three reactions are calculated based on the rate equations proposed by Xu and Froment [11,12]:

$$r_{\text{I}} = \frac{k_{\text{I}}}{p_{\text{H}_2}^{2.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2}^3 p_{\text{CO}}}{K_{\text{eq,I}}} \right) / \text{DEN}^2 \text{ kmol kg}_{\text{cat}}^{-1} \text{ h}^{-1}, \quad (4)$$

$$r_{\text{II}} = \frac{k_{\text{II}}}{p_{\text{H}_2}} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2} p_{\text{CO}_2}}{K_{\text{eq,II}}} \right) / \text{DEN}^2 \text{ kmol kg}_{\text{cat}}^{-1} \text{ h}^{-1}, \quad (5)$$

$$r_{\text{III}} = \frac{k_{\text{III}}}{p_{\text{H}_2}^{3.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_{\text{eq,III}}} \right) / \text{DEN}^2 \text{ kmol kg}_{\text{cat}}^{-1} \text{ h}^{-1}, \quad (6)$$

where DEN is defined as

$$\text{DEN} = 1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}. \quad (7)$$

Detailed information regarding the numerical calculation can be found in Baek et al. [10].

After simulating the SMR processes in the catalyst pellets, the effectiveness factors for the SR reaction (I) and RM reaction (III) are evaluated as the ratio of the actual reaction rate in the catalyst pellet to the maximum reaction rate

corresponding to the bulk flow stream condition. For example, the effectiveness factor for reaction I, η_{I} , is expressed as

$$\eta_{\text{I}} = \int_0^{r_{\text{cat}}} \rho_{\text{cat}} r_{\text{I}}(p_{i|i=1\dots 5}; T) \cdot 4\pi r^2 dr / \rho_{\text{cat}} \frac{4\pi r_{\text{cat}}^3}{3} r_{\text{I}}(p_{i|i=1\dots 5}; T_{\infty}), \quad (8)$$

where ρ_{cat} and r_{cat} are the apparent density and radius of the catalyst pellets, respectively. Here, $r_{\text{I}}(p_{i|i=1\dots 5}; T)$ denotes the local reaction rate inside the catalyst pellets, whereas $r_{\text{I}}(p_{i|i=1\dots 5}; T_{\infty})$ denotes the maximum reaction rate corresponding to the bulk flow stream condition.

In Baek et al. [10], the calculated effectiveness factors were plotted with respect to the methane conversion ratio, β_{CH_4} , which is defined as

$$\beta_{\text{CH}_4} = 1 - \frac{n_{\text{CH}_4}^{\circ}}{n_{\text{CH}_4}^{\circ}} \quad (9)$$

Here, $n_{\text{CH}_4}^{\circ}$ denotes the molar amount of methane supplied and n_{CH_4} denotes the current amount of methane remaining. Thus, methane conversion is a good measure of the progress of SMR processes. Depending on the reforming conditions, there may exist an equilibrium methane conversion ratio, $\beta_{\text{CH}_4}^{\text{eq}}$, less than one. In this case, β_{CH_4} cannot be increased above $\beta_{\text{CH}_4}^{\text{eq}}$, indicating that complete conversion of methane is impossible under these reforming conditions.

In Baek et al. [10], the calculated effectiveness factors were also plotted with respect to the effective Thiele moduli, ϕ_{I} and ϕ_{III} , defined as

$$\phi_{\text{I}} = \sqrt{\frac{R_{\text{p,I}}}{M_{\text{p,CH}_4}}} \quad \text{and} \quad \phi_{\text{III}} = \sqrt{\frac{R_{\text{p,III}}}{M_{\text{p,CH}_4}}}, \quad (10)$$

where $R_{\text{p,I}}$ and $R_{\text{p,III}}$ denote the nominal reaction rates for reaction I and III, and $M_{\text{p,CH}_4}$ denotes the methane diffusion rate in the pellet. The nominal reaction rates are defined as

$$R_{\text{p,I}} = r_{\text{I},\infty} \rho_{\text{cat}} \frac{4}{3} \pi r_{\text{cat}}^3 \quad \text{and} \quad R_{\text{p,III}} = r_{\text{III},\infty} \rho_{\text{cat}} \frac{4}{3} \pi r_{\text{cat}}^3. \quad (11)$$

In Baek et al. [10], the methane diffusion rate, $M_{\text{p,CH}_4}$, was defined as

$$M_{\text{p,CH}_4} = 12\pi r_{\text{cat}} D_{\text{CH}_4} \frac{p_{\text{t},\infty}}{R_g T_{\infty}} x_{\text{CH}_4,\infty}, \quad (12)$$

where D_{CH_4} is the effective diffusion coefficient of methane in the pellet and $p_{\text{t},\infty}$, T_{∞} , and $x_{\text{CH}_4,\infty}$ are total pressure, temperature, and methane mole fraction in the bulk gas stream, respectively. However, Eq. (12) tends to overestimate the methane diffusion rate under conditions near the equilibrium methane conversion because it ignores the possible existence of an equilibrium methane conversion, $\beta_{\text{CH}_4}^{\text{eq}}$, less than one. In this study, $M_{\text{p,CH}_4}$ is more accurately defined by considering the equilibrium methane mole fraction, $x_{\text{CH}_4}^{\text{eq}}$, as follows:

$$M_{\text{p,CH}_4} = 12\pi r_{\text{cat}} D_{\text{CH}_4} \frac{p_{\text{t},\infty}}{R_g T_{\infty}} (x_{\text{CH}_4,\infty} - x_{\text{CH}_4}^{\text{eq}}). \quad (13)$$

The equilibrium methane conversion, $\beta_{\text{CH}_4}^{\text{eq}}$, and the equilibrium methane mole fraction, $x_{\text{CH}_4}^{\text{eq}}$, are summarized in Tables 1 and 2 for a pressure range of 1–3 bar pressure, temperature range of 600–800 °C, and steam to carbon (S/C) ratio range of 2–4. The data in Tables 1 and 2 can be easily obtained by calculating of the equilibrium composition, as explained in

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