

Calculations of effectiveness factors and the criteria of mass transfer effect for high-temperature methanation (HTM) catalyst

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Abstract

Natural gas is an extremely important bridge fuel to a low-carbon energy economy for improving local air quality. Coal to synthetic natural gas (SNG) is an effective way to convert the high-carbon energy (coal) into the low-carbon energy with rich hydrogen (natural gas). For the modern coal to SNG industry, the high-temperature methanation (HTM) catalyst plays an important role, and the advanced evaluation process should necessitate the elimination of mass transfer effect. Some simple but effective model catalysts, such as slab and sphere, can be very helpful in defining the reaction conditions, and thus facilitating the evaluation process for real HTM catalysts. In this work, slab and sphere model catalysts were adopted to derive mass transfer and reaction-coupled equations, the numerical methods were used to solve the coupled equations for the concentration profiles in catalysts, and the effectiveness factors were accordingly calculated. By taking advantage of the Thiele module φ and the Weisz–Prater module Φ , the criteria for the elimination of mass transfer effect in the HTM catalyst evaluation process were successfully defined. This work also complements the Weisz–Prater criterion by incorporating ‘negative reaction orders’.

Keywords: high-temperature methanation; catalyst; effectiveness factor; synthetic natural gas

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1 INTRODUCTION

Natural gas, composed mainly of methane, is known as a quality clean-and-low-carbon energy. However, natural gas is very limited in many parts of the world [1]. With rapid urbanization and increasing living standard, the demand for natural gas is huge, and the short supply will get even worse in future without unconventional input.

Coal reserves are abundant, and therefore coal to synthetic natural gas (SNG) has been seriously considered as one of the solutions for natural gas shortage. The H/C ratio in coal can be raised four to six times higher by converting into natural gas. The total thermal efficiency for coal to SNG can be as high as 62–65%, by comparison, coal to oil is 40–50% and coal to electricity is as low as 36–38% [2]. The high efficiency of coal to SNG process reduces relatively the CO_2 emission, and the CO_2 gets highly concentrated in the process for treatment or utilization. In addition, pollutants such as sulfur can be reclaimed as useful byproducts in the coal to SNG process.

The high-temperature methanation (HTM) catalyst is crucial for the modern coal to SNG industry, and is of much superior hydrothermal stability at high temperatures to the conventional methanation catalysts [3, 4]. Usually, there are two evaluation processes applied. By comparison, the process for ‘activity change’ measurement has been regarded most favorable for the evaluation of the HTM catalyst [4]. To apply the process, the measurement conditions must be carefully defined. Only under the conditions of the elimination of mass transfer effect, can intrinsic reactions occur, and the measured reaction rates can be used to quantify the activities of catalyst.

Mass transfer in porous catalysts has been of great interest for a very long time, and the first papers appeared in the late 1930s [5]. Due to the ubiquitous nature of mass transfer, the concentrations of reactants are always higher on the surfaces than in the interior of catalyst particles. The effectiveness factor η has been defined as ‘the ratio of the real reaction rate of the catalyst particle to the imaginary reaction rate when the whole particle is

assumed to bathe in the surface reactant concentration' [6, 7]. Numerous efforts have been directed to the approximate solution of model catalyst systems for the effectiveness factor η changing with complex reaction kinetics. In contrast, the Weisz–Prater criterion, which was introduced in 1954 [8], has been widely applied in reaction kinetics measurements since it dictates the conditions for the elimination of mass transfer effect.

The Weisz–Prater criterion has been derived by analyzing a model catalyst with 'zero and positive reaction orders' and by using the general assumption for mass transfer elimination if $|\eta - 1| \leq 0.05$ [8]. However, the methanation reaction has been known to proceed via a negative order of -0.5 with respect to CO in high concentrations [9, 10], for which the Weisz–Prater criterion could not give definite answers for the mass transfer effect. Therefore, detailed investigation, including positive to negative reaction orders, should be made of the effectiveness factor η in relation with the Thiele module φ and the Weisz–Prater module Φ , so that the effect of mass transfer can be evaluated and eliminated in the advanced evaluation process of 'activity change' measurement for the HTM catalyst.

2 CATALYST MODELS AND CALCULATION METHODS

Catalyst models, mass transfer and reaction-coupled equations and the solving methods and the equation for effectiveness factor η calculations will be discussed successively in this section.

2.1 Slab and sphere catalyst models

The shapes of real catalysts are very complicated and can vary from particles to particles. However, it was shown that some simple model catalysts could be very effective in defining the reaction conditions for real catalysts [6, 7]. In fact, the Weisz–Prater criterion has been derived by assuming sphere model represents the general case [8], because it was observed that the effectiveness factor responds similarly to the change of Thiele module φ for various catalyst shapes [8]. The Weisz–Prater criterion gives safe answers for mass transfer effect without any knowledge of kinetics, and great success has been achieved in many fields related to mass transfer, such as catalysis, chemical engineering and biochemistry [11]. Later, it was shown that sphere and slab could be the two extremes in catalyst shape [12], and numerous investigations were accordingly made for the two models to give an insight into the real systems.

Therefore, it can be said that sphere and slab models represent the most reasonable choices for our study. For slab and sphere catalysts, the concentration profiles are 1D, according to Figure 1. For slab catalyst (left), the side far away from reactants is denoted as the zero point (0), and the thickness is L . For sphere catalyst (right), the center is denoted as the zero point (0), and the diameter is R . The arrows in Figure 1 for slab and sphere catalysts all point to directions for concentration increase, and the concentration on catalyst surfaces is denoted as C_0 .

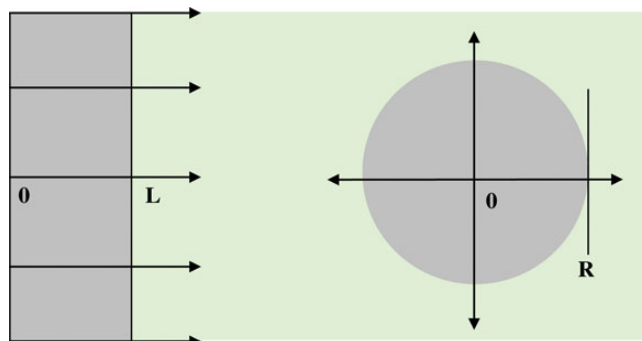


Figure 1. Slab and sphere catalyst models with 1D concentration profile.

2.2 Mass transfer and reaction-coupled equations

Assuming the system is in an isothermal and steady state and the reaction follows a power order, the mass transfer and reaction-coupled equations can be derived for slab and sphere catalysts [6, 7, 13]. Assuming further a concentration C for a position X in slab and sphere catalysts, let $y = C/C_0$, $x = X/L$ (slab) = X/R (sphere), x and y can be taken into the coupled equations to obtain:

$$\frac{d^2 y}{dx^2} = \varphi^2 y^n \quad (\text{slab}) \quad (1)$$

$$\frac{d^2 y}{dx^2} + \frac{2}{x} \frac{dy}{dx} = \varphi^2 y^n \quad (\text{sphere}) \quad (2)$$

Constrained by slab and sphere catalyst models (1D), the boundary conditions for equations (1) and (2) are the same: $x = 0$, $dy/dx = 0$; $x = 1$, $y = 1$. In addition, n is the power order, and φ is the Thiele module. For the slab and sphere catalysts, φ can be defined as

$$\varphi = L \sqrt{\frac{k_v C_s^{n-1}}{D_e}} \quad (\text{slab}) = R \sqrt{\frac{k_v C_s^{n-1}}{D_e}} \quad (\text{sphere}) \quad (3)$$

In equation (3), D_e is the effective diffusion coefficient of reactant in catalysts, k_v is the volumetric intrinsic reaction rate constant and C_s is the reactant concentration on surfaces.

The pores in the catalyst models can be of any shape, including the classical cylinder pore, which may lead to different D_e values [7]. It has also to be said that the reaction kinetics of real systems may be very complicated in the whole concentration range, which cannot be fitted by the above simple power-order kinetics. Nevertheless, the interested range is usually limited, and the power order should still be accurate enough for practical considerations [14].

2.3 Solution of equations and calculation of effectiveness factors

For zero- and first-order reactions, analytic solutions have been available by solving equations (1) and (2) [7, 13, 15]. However, for fractional or negative orders, analytic solutions may not exist or are hard to obtain. In such cases, numerical method is helpful.

Equations (1) and (2) should be properly modified for numerical solution by Matlab programming. In addition to equation modifications, the Thiele module φ should be varied stepwise to calculate the corresponding concentration profile in catalysts.

With the concentration profile being known, the effectiveness η can be obtained by equation (4) derived from the definition.

$$\eta = \int_0^1 y^n dx (\text{slab}) = \int_0^1 3x^2 y^n dx (\text{sphere}) \quad (4)$$

3 RESULTS AND DISCUSSIONS

By applying Matlab programming to equations (1) and (2), the concentration profiles in slab and sphere catalysts were firstly obtained for zero- and first-order reactions. Equation (4) was used to calculate the effectiveness factors for first-order reaction.

Calculation were then extended to more orders of 0, ± 0.25 , ± 0.50 , ± 0.75 , ± 1.00 , ± 1.50 , ± 2.00 and ± 3.00 for equations (1) and (2), and by varying Thiele module φ , the concentration profiles in catalysts were obtained and the corresponding effectiveness factors were calculated. The criteria for mass transfer effect were finally defined by using the Thiele module φ and the Weisz–Prater module Φ .

3.1 Concentration profile in catalysts for $n = 0$ and 1.00

According to Figure 2, for slab catalysts with $n = 0$ and 1.00, and by varying the Thiele module φ in an order of magnitude, the

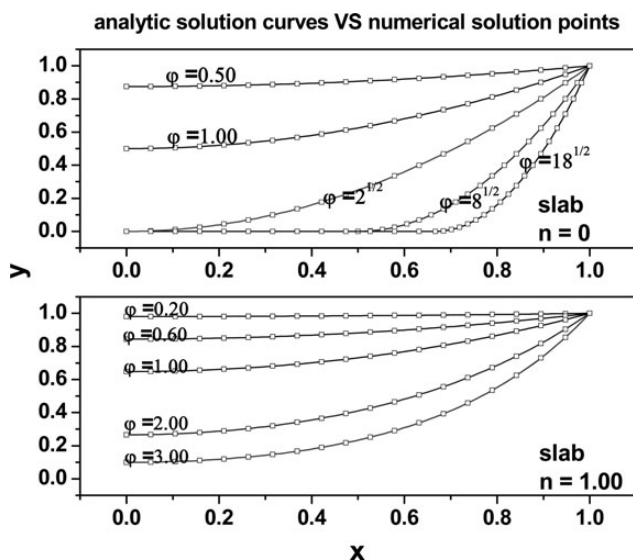


Figure 2. Comparisons of analytic and numerical solutions for the reactant concentration profiles in slab catalysts with $n = 0$ and 1.00. Analytic solution curves are drawn by thin lines, and numerical solution points are given by open circles, which fall exactly on the thin lines.

numerical solution points of equation (1) obtained by Matlab programming are located precisely on the analytic solution curves [7, 15].

This shows Matlab programming is nicely fit for slab catalyst model, and the perfect superposition of two solutions indicates the method can generate accurate results for the n orders outside 0–1.00, and the Thiele module φ varying in greater range.

Similar observations for analytic and numerical solutions have also been made of sphere catalysts with $n = 0$ and 1.00 (not shown). These results indicate Matlab programming can indeed provide reliable numerical results for the concentration profiles in slab and sphere catalysts, even if analytic solutions do not exist for equation (1) and (2), or the analytic solutions are hard to obtain.

3.2 Calculation of effectiveness factors for $n = 1.00$

With the concentration profiles obtained by Matlab programming, equation (4) can be used to calculate effectiveness factors. In Figure 3, the numerical solution points of effectiveness factors for $n = 1.00$ were displayed, as well as the analytic solution curves. The perfect coincidence between the two solutions can be observed.

For the same effectiveness factor η , it has been found that the Thiele module φ for sphere catalysts is about three times that for slab catalysts [7, 16]. By multiplying the Thiele module φ with 1/3, it is apparent that the η – $\varphi/3$ curve for sphere catalysts moves close to the η – φ curve for slab catalyst. The biggest difference occur at about $\varphi = 1$.

As discussed in above, for slab and sphere catalysts, the numerical solutions are in good agreement with the analytic solutions with regard to concentration profiles and effectiveness factors. These results validate the numerical method of Matlab

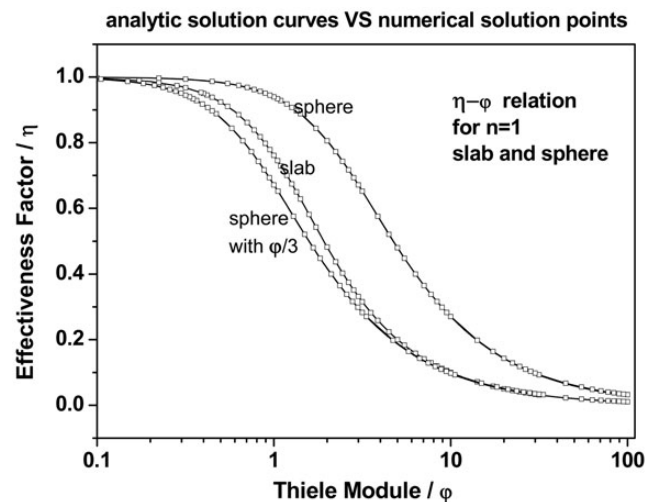


Figure 3. Comparisons of the effectiveness factor η as a function of the Thiele module φ for slab and sphere catalysts with $n = 1.00$. Analytic solution curves are drawn by thin lines, and numerical solution points are given by open circles, which fall exactly on the thin lines. The η – $\varphi/3$ curve for sphere catalysts is close to the η – φ curve for slab catalysts.

programming for the solution of mass transfer and reaction-coupled equations (1) and (2), and equation (4) for effectiveness factor calculations.

3.3 Mass transfer criteria derived from the Thiele module

According to Figure 3, the effectiveness factor η is a function of the Thiele module φ that is clearly defined in equation (3), which has been previously investigated for the effect of mass transfer [7]. For the heterogeneous systems with known constants to define the Thiele module φ , the effectiveness factor η can be obtained by calculating the Thiele module φ and then referring to the η - φ curve.

By using the catalyst models and the numerical methods in this work and by varying the Thiele module φ , the concentration profiles were obtained and the effectiveness factors calculated for the reactions with orders of 0, ± 0.25 , ± 0.50 , ± 0.75 , ± 1.00 , ± 1.50 , ± 2.00 and ± 3.00 . According to Figure 4, the η - φ curves for positive and negative curves are not very symmetrical with respect to the line $\eta = 1$. By comparison, the η - φ curves for the reactions with negative orders change much more rapidly with the increase of φ . Reactions with a zero order can retain $\eta = 1$ for a wide range of φ . In particular, the region for $|\eta - 1| \leq 0.05$ should

get more attention, because the mass transfer effect can be neglected due to the small variations of η .

The intersection φ values in Figure 4 between the η - φ curves and the lines $\eta = 0.95$ and $\eta = 1.05$ are summarized in Table 1. According to Figure 4 and Table 1, for the reactions with non-negative power orders, the mass transfer effect cannot be neglected for φ bigger than 1.49 and 2.91 for slab and sphere catalysts, respectively, and can be neglected for φ smaller than 0.28 and 0.64 for the reactions with a second-order kinetics. For the reactions approximated by a third-order kinetics, φ is lowered further to 0.23 and 0.52 to eliminate the mass transfer effect.

Till now, few investigations of mass transfer effect have been made for the reactions with negative orders, and the results in this work can be applied in the evaluation of the HTM catalyst. According to Figure 4 and Table 1, for the methanation reaction with a negative order of -0.5 with respect to CO in high concentrations, the corresponding φ values for mass transfer negligence are 0.51 and 1.12 for slab and sphere catalysts, respectively. The effect of mass transfer on the reactions with negative orders other than -0.5 can be evaluated in terms of φ according to Figure 4 and Table 1.

3.4 Mass transfer criteria derived from the Weisz-Prater module

According to the definition, to calculate φ for the evaluation of mass transfer effect, the volumetric intrinsic reaction rate constant k_v has to be known. However, k_v is desired in a study of intrinsic reaction kinetics, which requires the elimination of mass transfer effect. Under such circumstance, the Thiele module criteria are not fit for a proper evaluation of mass transfer effect. Due to this difficulty, Weisz and Prater developed the module Φ [6, 7, 11, 14, 16].

$$\Phi = \mathfrak{R}_v \frac{L^2}{C_s D_e} (\text{slab}) = \mathfrak{R}_v \frac{R^2}{C_s D_e} (\text{sphere}) \quad (5)$$

In equation (5), \mathfrak{R}_v is the real volumetric reaction rate, all other parameters being the same as discussed in above. In contrast to the Thiele module φ , the Weisz-Prater module Φ precludes the utilization of volumetric intrinsic reaction rate constant k_v , and can be directly calculated from the experimental observables.

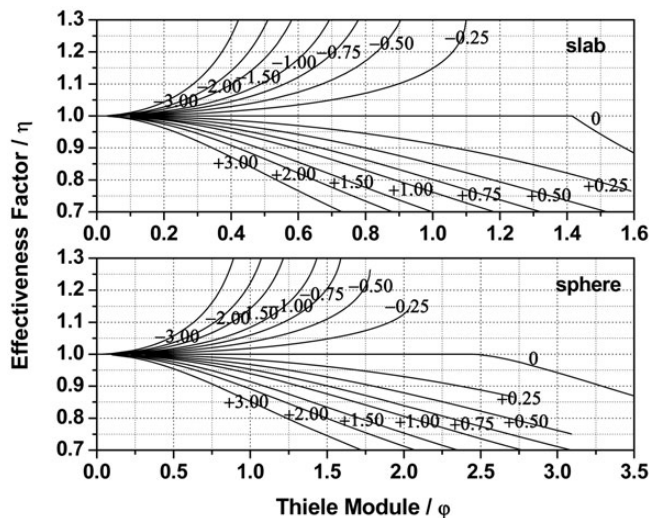


Figure 4. The effectiveness factor η as a function of the Thiele module φ for slab and sphere catalysts.

Table 1. The intersection φ values between the η - φ curves and the lines $\eta = 0.95$ and $\eta = 1.05$ in Figure 4.

Power order, n	+3.00	+2.00	+1.50	+1.00	+0.75	+0.50	0.25	0	-0.25	-0.50	-0.75	-1.00	-1.50	-2.00	-3.00
Slab															
$\eta = 0.95$	0.23	0.28	0.33	0.40	0.45	0.55	0.76	1.49							
$\eta = 1.05$									0.70	0.51	0.42	0.37	0.30	0.26	0.21
Sphere															
$\eta = 0.95$	0.52	0.64	0.75	0.89	1.02	1.24	1.70	2.91							
$\eta = 1.05$									1.53	1.12	0.92	0.81	0.66	0.57	0.48

Generally, for the reactions with power orders, it can be proved:

$$\Phi = \varphi^2 \eta \tag{6}$$

As a result, for the reactions with orders of 0, ±0.25, ±0.50, ±0.75, ±1.00, ±1.50, ±2.00 and ±3.00, equation (6) can be used to calculate effectiveness factor η as a function of Weisz–Prater module Φ , and the results are given in Figure 5 for slab and sphere catalysts. Similar patterns like those in Figure 4 can also be observed, the η – Φ curves are not symmetrical with respect to the line $\eta = 1$, and the η values for the reactions with negative orders change more rapidly with the increase of Φ than the reactions with positive orders.

The intersection Φ values in Figure 5 between the η – Φ curves and the lines $\eta = 0.95$ and $\eta = 1.05$ are summarized in Table 2. According to Figure 5 and Table 2, for the reactions with non-negative power orders, the mass transfer effect cannot be neglected for Φ bigger than 2.11 and 8.06 for slab and sphere catalysts, respectively, and can be neglected for φ smaller than 0.08 and 0.39 for the reactions fitted by a second-order kinetics. For the reactions approximated by a third-order kinetics, Φ is further lowered to 0.05 and 0.26 to eliminate the mass transfer effect. These calculations are consistent with the Weisz–Prater criterion [8].

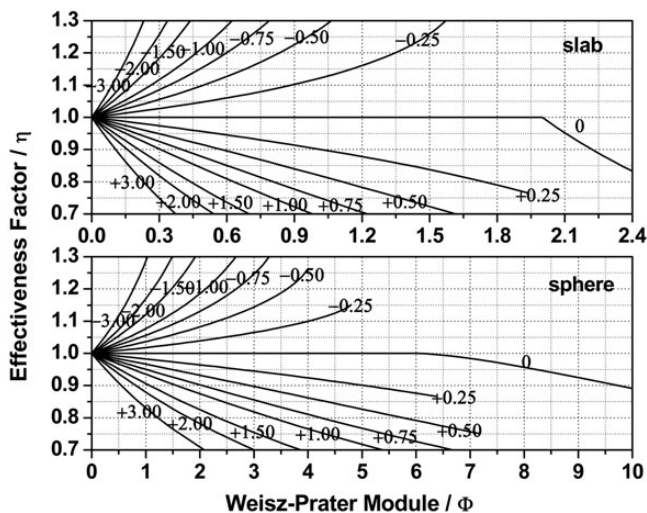


Figure 5. The effectiveness factor η as a function of the Weisz–Prater module Φ for slab and sphere catalysts.

Table 2. The intersection Φ values between the η – Φ curves and the lines $\eta = 0.95$ and $\eta = 1.05$ in Figure 5.

power order, n	+3.00	+2.00	+1.50	+1.00	+0.75	+0.50	0.25	0	-0.25	-0.50	-0.75	-1.00	-1.50	-2.00	-3.00
Slab															
$\eta = 0.95$	0.05	0.08	0.10	0.15	0.19	0.28	0.55	2.11							
$\eta = 1.05$									0.51	0.27	0.18	0.14	0.09	0.07	0.05
Sphere															
$\eta = 0.95$	0.26	0.39	0.52	0.76	1.00	1.50	2.75	8.06							
$\eta = 1.05$									2.47	1.31	0.89	0.68	0.47	0.34	0.24

As discussed in above, the Weisz–Prater module Φ should be much more conveniently applied than the Thiele module φ in the evaluation of the HTM catalyst, because it requires only the input of the real volumetric reaction rate R_v , instead of the volumetric intrinsic reaction rate constant k_v , which needs to be known in advance. According to Figure 5 and Table 2, for the methanation reaction with a negative order of -0.5 with respect to CO in high concentrations, the corresponding Φ values for mass transfer negligence are 0.27 and 1.31 for slab and sphere catalysts, respectively. The effect of mass transfer on the reactions with negative orders other than -0.5 can be evaluated in terms of Φ according to Figure 5 and Table 2.

4 CONCLUSIONS

Natural gas is highly desired as a clean-and-low-carbon energy in this world for environmental protections, and coal to SNG can add to the limited natural gas supply. The modern coal to SNG industry highlights the role of the HTM catalyst, for which the mass transfer effect has to be eliminated in the advanced evaluation process.

The Weisz–Prater criterion has been derived by considering only ‘zero and positive reaction orders’. Because the methanation reaction has been known to proceed via a negative order of -0.5 with respect to CO in high concentrations, the criterion could not give definite answers for the mass transfer effect in the HTM catalyst evaluation, which has to be dealt with in this work.

By using slab and sphere catalyst models, numerical method, the Thiele module φ and the Weisz–Prater module Φ , the mass transfer effect has been investigated in detail. For the methanation reaction with high CO concentrations, it has been found to eliminate the mass transfer effect, the Thiele module φ should be smaller than 0.51 and 1.12, and the Weisz–Prater module Φ should be smaller than 0.27 and 1.31 for slab and sphere catalysts, respectively.

While providing definite answers for the HTM catalyst evaluation, this work has also complemented the Weisz–Prater criterion by incorporating ‘negative reaction orders’. A complete criterion for the elimination of mass transfer effect is helpful for developing experiments for catalyst evaluation and kinetics study.

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