Kinetic studies of methane hydrate formation in porous media based on experiments in a pilot-scale hydrate simulator and a new model

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HIGHLIGHTS

- A new kinetic model is established for hydrate formation in porous media.
- The intrinsic reaction rate constant k_0 is obtained.
- The validity of the proposed model is verified with the experimental data.
- The new model performs better than the other kinetic models.

ARTICLE INFO

ABSTRACT

A new kinetic model is established to investigate into the characteristics of methane hydrate formation in the porous media. In this model, the hydrate formation is mainly controlled by the mass transfer at the gas–water contact area, which is formed between the liquid and the "gas bubbles" in the pores. Six experimental formation runs are carried out in a three-dimensional pressure vessel, the Pilot-Scale Hydrate Simulator (PHS). The experimental data for four of the six runs are correlated with the kinetic model, and the intrinsic reaction rate constant k_0 and the activation energy ΔE_a are determined to be approximately 8.06 kg/(m² Pa s) and 8.09×10^4 J/mol, respectively. The system pressures, the hydrate formation rates, and the amount of the remaining free methane gas at other conditions are predicted from the obtained k_0 and ΔE_a. Compared with the experimental data from other two runs, the predicted results are in good agreement, which verifies the reliability of the proposed kinetic model for the prediction of methane hydrate formation in porous media. Sensitivity analysis indicates that the hydrate formation is strongly dependent on the kinetic parameters of k_0 and the reduction exponent β.

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1. Introduction

Natural gas hydrates are crystalline solid compounds in which gas molecules are bound in the hydrogen-bonded lattices formed by another several water molecules when the environmental conditions are favorable for their formation. The hydrate-forming gases are usually small and light molecules, such as CH_4, C_2H_6 and CO_2, and they can exist with water in the form of structure I, II and H hydrate, depending on the gas species and the formation conditions (Sloan and Koh, 2008). The transition process can be simply presented using the following reversible reaction equation:

$$G + N_H H_2O \Leftrightarrow G \cdot N_H H_2O + \Delta H \tag{1}$$

where G is the hydrate-forming gas, N_H is the hydration number, $G \cdot N_H H_2O$ represents the solid hydrate, and ΔH is the enthalpy of hydrate formation or dissociation. The enthalpy is dependent on the temperature (Moridis et al., 2009). The methane gas is prevalently agreed to be the major gas component in the majority of gas hydrates found in nature, and the estimated amount is such large that it may solve the global problem of energy shortage in the future as a kind of clean and reliable new energy resource.

The hydrate formation is a complex kinetic process that is controlled by many factors. Vysniauskas and Bishnoi (1983) firstly investigated the methane hydrate formation kinetics in a semi-batch stirred tank reactor, and found that the formation kinetics were determined by the gas–water contact area, pressure, temperature and degree of supercooling. After the classical Kim-Bishnoi model was

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proposed for describing the kinetic characteristics of methane hydrate dissociation in pure water system (Kim et al., 1987), Englezos et al. (1987a, 1987b) further established a kinetic model that was similar to the Kim-Bishnoi model to define the formation processes of methane and ethane gas hydrates. Their model was based on the crystallization theory, and the mass transfer at the gas–water interface was calculated using the two-film theory. It was concluded that the hydrate formation rate was proportional to the surface area of the hydrate particles and the deviation of the dissolved gas fugacity from the hydrate equilibrium fugacity. Skovborg and Rasmussen (1994) performed an analysis of the kinetic model of Englezos et al. (1987b) and further proposed a simplified model that considered the mass transportation rate from gas phase to aqueous phase as the dominating factor in determining the hydrate formation rate. Accounting for both heat transfer and kinetic resistance, Freer et al. (2001) proposed a kinetic model in which the difference between the equilibrium temperature and the bulk temperature was the driving force for methane hydrate growth, and kinetic parameters such as the formation rate constant and the activation energy were measured at the methane–water interface. Generally, both of the formation and dissociation kinetic models can be formulated as follows:

$$\frac{\partial m_H}{\partial t} = kA_S(f_g - f_{eq}) \tag{2}$$

where m_H is the mass of the present hydrate in the system (kg); k is the kinetic rate constant of hydrate formation or dissociation (kg/(m^2 Pa s)); A_S is the surface area involved in the reaction (m^2); f_g and f_{eq} are the local fugacity and the equilibrium fugacity of methane gas under the local temperature, respectively (Pa). The kinetic constant k is usually written in an Arrhenius-type equation as $k = k_0 \exp(-\Delta E_a/RT)$, in which k_0 is the intrinsic reaction rate constant (kg/(m^2 Pa s)), ΔE_a represents the activation energy (J/mol), R is the gas constant (8.314 J/(mol K)), and T is the local temperature (K). In this kinetic model, A_S is generally thought to be equivalent to the surface area of the solid hydrate particles during its formation or dissociation (Vysniauskas and Bishnoi 1983; Englezos et al., 1987a, 1987b). Recently, Mohebbi et al. (2012) carried out two kinds of hydrate formation experiments under isochoric and isobaric conditions in a stirred vessel. The results showed that the consumed gas rates were very close with these two methods, which indicated the independence of gas consumption rate on the total surface area of the existing hydrate particles. It was concluded that the gas uptake rate was mainly controlled by the mass transfer at the gas–liquid contact area. This was in accordance with the results of Skovborg and Rasmussen (1994), which also demonstrated that the mass transfer in the liquid side of the contact area of gas–liquid controls the gas consumption during the methane hydrate formation. That is, the reaction surface area A_S in Eq. (2) should be treated differently during hydrate formation and dissociation processes. In addition, there are few reports about the kinetic constant measurements. These facts cause many uncertainties to the application of the kinetic model.

The kinetic studies mentioned above are all focused on pure water system, where the effects of mass transfer and heat transfer on hydrate formation can be easily controlled by regulating the stirring speed in a semi-batch stirred tank reactor. Up to now, few efforts have been made in investigating the kinetic characteristics of hydrate formation or dissociation in porous media due to the difficulties of (i) visualizing hydrates directly in the pores and (ii) precisely controlling the heat and mass transfer in the black box of the porous media. Jung et al. (2012a, 2012b) carried out hydrate formation and dissociation experiments in porous media, and found that hydrate nucleated at the interface between the gas and water phases in capillary tubes in the pores, and that the increased interfacial area between water and gas can trigger and/ or facilitate the hydrate formation. Through the morphology observation, Babu et al. (2013) found that the hydrate crystals

tended to form in the interstitial pore space between the sand grains. The hydrate formation and dissociation are actually coupled with the complex mass and heat transfer processes, making it an arduous task for direct measurements of the hydrate kinetics in porous media. The numerical simulation will be a useful method in indirectly comprehending the kinetic behaviors of hydrate formation and dissociation. Sun et al. (2006) have developed a numerical simulator and investigated the hydrate formation and dissociation kinetics using the experimental data of Yousif and Sloan (1991). The Kim-Bishnoi model is employed to describe the intrinsic kinetics, and the reaction surface area is estimated using two conceptual models in which $k_0 = 5.875 \times 10^{-12}$ kg/(m^2 Pa s) (Englezos et al., 1987a) and the A_S is assumed to be proportional to the hydrate saturation S_H. The TOUGH+HYDRATE (T+H) code is developed especially for the simulation of hydrate formation and dissociation in geological media (Moridis et al., 2009). Both an equilibrium and a kinetic model are included in this code. It has been widely used to estimate the production potential of the large-scale hydrate deposits in both permafrost and marine sediments (Li et al., 2010, 2012c; Moridis et al., 2011). Under the equilibrium model, hydrate dissociates spontaneously and immediately when the pressure or temperature drops below the equilibrium level. Recently, Li et al. (2012a, 2012b) have completed the validation of the equilibrium model through the history match of the gas production data from a pilot-scale hydrate simulator (PHS). Under the kinetic regime, the hydrate formation and dissociation rates are also computed using the Kim-Bishnoi model, and the reaction surface area A_S is calculated by assuming a uniform distribution of hydrate particles in the voids of the porous media. Up to now, few studies have been published about the kinetic option of the T+H code because of its uncertainties mentioned above and the enormous computational demands of the kinetic model.

In this study, we establish a new model to describe the characteristics of methane hydrate formation in porous media. According to the experimental results of Mohebbi et al. (2012), the methane gas is assumed to exist in the form of small spherical "gas bubbles" in the voids of porous media, and the A_S is calculated to be the total surface area of these gas bubbles. Then the original kinetic model in the T+H code is replaced with the new proposed one, and the experimental data of hydrate formation in the PHS are used for numerical simulation to verify the precision of the kinetic model. The reaction rate constant is obtained by fitting the experimental data with time, and the sensitivity of hydrate formation rate to the kinetic parameters is also assessed. Furthermore, the formation behaviors of methane hydrate are predicted using different kinetic models, and they are compared with the experimental data to determine which model is the most appropriate for the accurate description of hydrate kinetic formation in porous media.

2. Experimental apparatus and procedure

2.1. Apparatus

The PHS shown in Fig. 1 is especially designed for the investigation of hydrate formation and dissociation characteristics in porous media. It is a cylindrical stainless steel that can sustain a maximum pressure of 30 MPa. With an effective length of 0.60 m and a diameter of 0.50 m, the inner volume is 117.8 L. The low-temperature conditions desired for hydrate formation is realized by (i) sealing the PHS in a water jacket (−15 to 30 °C, ±0.1 °C) and (ii) placing the whole system in a cold refrigeration room (−8 to 30 °C, ±2 °C). A complex well system composed of various vertical and horizontal wells is included in the PHS. A detailed description of the well distribution can be found in previous studies (Li et al., 2012a, 2012d). There are nine vertical wells and three horizontal