



Hydrate Kinetics: The Main Problem in the Gas Hydrate Industrialization

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Abstract

Gas hydrates are known as one of the main problems in gas transportation lines from 1934 to now. The main researches in this field are related to the hydrate formation conditions and the effect of using inhibitors. From early 1990s, the main features of using gas hydrates in storage and transportation of natural gas and separation of gas mixtures were considered. Research shows that 1m³ of gas hydrates can reserve 170m³ of natural gas in standard conditions. Therefore, with respect to the operating conditions for production and storage, using gas hydrates for storage and transportation of natural gas with conventional methods (i.e., CNG and LNG) can be important from economic point of view. For designing gas hydrates production units, reliable kinetic and thermodynamic models for prediction of hydrate formation conditions in reactors, components composition and hydrate structure must be available. In this article, hydrates, types of its structure, formation conditions and required driving force for formation and different kinetic models are investigated. Then, kinetic models are studied and the best model is selected and simulated. Comparing the simulated results with experimental data shows that the kinetic model of Firoozabadi and Kashchiev (2003) with some modification has the best agreement with experimental data.

Keywords: Gas hydrates; Kinetic; Storage; Transportation.

Introduction

Natural gas hydrates belong to a class of solids known as clathrates. They are non-stoichiometric crystalline compounds that occur when hydrogen-bonded water molecules form cavities that can be occupied by a guest molecule. Molecules that can fit in the cavities include light hydrocarbon gases like methane, ethane, propane and etc, or light non-hydrocarbon gases like CO₂, H₂S, argon, krypton and xenon. Depending upon the guest molecules and the conditions of formation, one of four structures may form (Figure 1); structure I, structure II, structure H, and a new, currently unnamed, structure [1]. The storage of natural gas in the form of hydrate (NGH) is appealing for industrial utilization because of not only this high storage capacity, but also storage safety resulted from its higher stability at atmospheric pressure and not very low temperatures (Table 1). Some investigators performed methane hydrate dissociation experiments at low temperature, where the results indicate that at -5°C, the dissociation percentages within 24 h and 1 month after dissociation started were 7% and 50%, respectively [5,6]. Studies on the kinetics of the process of gas hydrate crystallization are, however, at a relatively early stage of development despite notable work of various authors in the last three decades [7,8]. Issues related to the nucleation and growth processes, including the supersaturation, the nucleation and growth rates and the induction time, have not been sufficiently clarified. For instance, there is considerable difference of opinion among various groups on what actually is the driving force for hydrate crystallization

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[8-13]. Skovborg and Rasmussen (1994) used the difference in gas mole fraction at the gas-liquid interface and in the liquid bulk phase as the driving force. Mullin (1993) and Kashchiev and Firoozabadi (2002) define the driving force for crystallization is supersaturation [14,15]. Nucleation is perhaps the most challenging step in understanding the process of crystallization of gas hydrates. The kinetics of gas hydrate crystallization is covered in a large number of studies in the literatures. Depending on where and how nucleation occurs and how is schematic of clusters, there are different equations. For instance, there are different equations for homogeneous nucleation (HON) or heterogeneous nucleation (HEN) and instantaneous nucleation (IN) or progressive nucleation (PN). The induction time in gas hydrate crystallization is an important characteristic of the kinetics of the process. Long induction time would allow transport of fluids through the production facilities to the processing plants without crystallization of hydrates in the system.

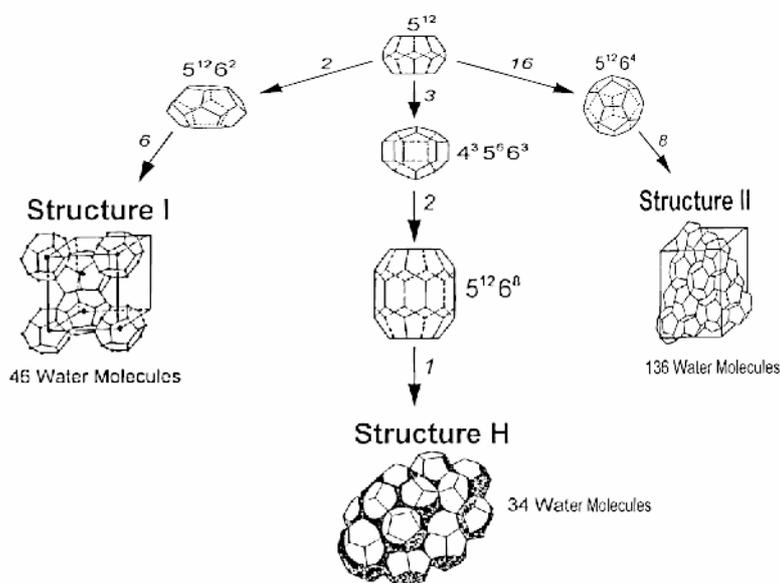


Figure 1. Hydrate structures and cavities in presence of guest molecules (Sloan, 1998).

Table 1. Geometry of cages in three hydrate crystal structures (Sloan 2003).

| Hydrate crystal Structure Cavity | I | | II | | H | | |
|--------------------------------------|----------|--------------|----------|--------------|---------------|----------|--------------|
| | Small | Large | Small | large | small | Medium | large |
| Descript | 5^{12} | $5^{12} 6^2$ | 5^{12} | $5^{12} 6^4$ | $4^3 5^6 6^3$ | 5^{12} | $5^{12} 6^8$ |
| Number of cavities/unit cell | 2 | 6 | 16 | 8 | 2 | 3 | 1 |
| Average cavity radius(nm) | 0.395 | 0.433 | 0.391 | 0.473 | 0.38 | 0.385 | 5.2 |
| Variation in radius ^a (%) | 3.4 | 14.4 | 5.5 | 1.73 | Not available | | |
| Coordination number ^b | 20 | 24 | 20 | 28 | 20 | 20 | 36 |
| Number of Waters/unit cell | 46 | | 136 | | 34 | | |

^a Variation in distance of oxygen atoms from center of cage.

^b Number of oxygen atoms at the periphery of each cavity.



Kinetic models of hydrate formation

Several researchers have measured the rate of hydrate formation after nucleation, that is, the hydrate growth stage. The rate of formation is typically expressed in terms of gas consumption rate. Studies performed under stirred conditions in liquid water, usually batch reactor studies, are reviewed in this section. Knox et al. (1961) studied the formation rate of propane hydrate for development of a desalination process [16]. They produced hydrates continuously by recycling the water phase and venting the excess gas. They observed that the liquid residence time and the subcooling affected the yield from the reactor. Also for desalination of seawater, Pangborn and Barduhn (1970) studied the formation rate of methyl bromide hydrate in a continuous stirred tank reactor (CSTR) of 3.8 liter [17]. They found that an increase in subcooling yields a higher hydrate formation rate.

Vysniauskas and Bishnoi (1983), initiated a systematic research on hydrate formation. They measured the rate of methane hydrate formation (in terms of gas consumption rate) in a semi-batch reactor, and found that the rate depends on the gas-liquid interfacial area, pressure, temperature and subcooling. Also, the effect of water memory was investigated, and it was found not to affect the gas consumption rate after nucleation. They concluded that the gas-liquid interface is the most likely place for hydrate formation to take place, because in liquid bulk, the methane concentration is too low. Experiments with ethane (Vysniauskas and Bishnoi, 1985) confirmed the observed effects. Their model is

$$q_{Vys} = Aa_s \exp\left(-\frac{\Delta E_a}{RT}\right) \exp\left(-\frac{\alpha}{\Delta T^\beta}\right) p^\gamma \quad (1)$$

Englezos et al. (1987) measured the rate of methane and ethane hydrate formation in the early growth stage before agglomeration commenced. They observed that the formation rate is a strong function of the driving force and that formation is not restricted to the interface, but also occurs in the liquid phase. For a single crystal, the following expression was proposed for the growth rate:

$$(dn/dt)_p = K^* a_p (f - f_{eq}), \quad 1/K^* = 1/k_r + 1/k_d \quad (2)$$

Some researchers have studied the rate of hydrate formation in the presence of liquid hydrocarbons. Bourgmayer et al. (1989) measured the formation rate of methane and ethane mixtures in a semi-batch reactor in the presence of a condensate. They observed that hydrates form both at the gas-water interface and at the gas hydrocarbon interface. In contrast, Skovborg (1993) discovered that a hydrocarbon liquid phase does not affect the hydrate formation rate significantly. Therefore, he suggested that the transport of gas to the water phase through a liquid water film dominates the formation rate.

On the basis of the analysis, Skovborg and Rasmussen (1994) proposed a simplified model where the gas consumption rate only depends on the transport of gas from the gas phase to the liquid bulk phase:

$$dn/dt = k_L A_{(g-l)} C_{w0} (x_{int} - x_b) \quad (3)$$

The consumption rate is a function of the gas-liquid mass transfer coefficient, the gas-liquid interfacial area and the mole fraction driving force.

On the basis of experimental results, Lekvam and Ruoff (1993) presented a reaction kinetic model for methane hydrate formation with pseudo elementary reaction steps. The initial reactants are gaseous methane and liquid water and the final product is hydrate. Reaction intermediates are dissolved methane and hydrate precursor species. The dynamic elements include gas dissolution in water phase, buildup of the precursor and growth of methane hydrate by an autocatalytic process. Rate constants were estimated for each of the five pseudo elementary reactions. The effect of stirring rate on the formation rate is modeled when gas dissolution is selected as the rate-determining step.



In 1994, Happel et al.(1994),investigated the rate of methane and nitrogen hydrate formation for development of a process for separation of nitrogen from methane. Experiments were performed in a 1 liter continuous stirred tank reactor where gas entered the CSTR upward counter currently to a recycled water stream. They found that their measured methane formation rates were much higher than those reported by Bishnoi et al.(1983, 1985) and Englezos et al. (1987a, 1987b).

As a part of the research at the Norwegian University of Science and Technology (NTNU), on NGH technology, Parlaktuna and Gudmundsson (1996) measured the formation rate of methane and natural gas mixture in a batch reactor of 0.62 liter [18]. The volumetric gas consumption rates were calculated from the initial slope of pressure drop curves. They identified the subcooling and stirring rate as important parameters, and they did not observe any water memory effect. Narita and Uchida (1996) performed comparable experiments in a 0.23 liter batch reactor with methane and observed similar effects of subcooling and stirring. As an extension of the work of Narita and Uchida, Arai (2000) performed constant pressure experiments in a 1.2 liter batch reactor. They found that the formation rate is also proportional to the system pressure.

Gaillard et al.(1996) modeled nucleation, growth and agglomeration in their hydrate loop (with liquid hydrocarbons) applying crystallization theory and methane gas consumption measurements [19]. They proposed a population balance for the hydrate crystals in the system and expressed the nucleation, growth and agglomeration rates by empirical correlations. Experiments showed no induction time and the rate of heterogeneous nucleation was expressed as:

$$J_p = k_{p0} \exp\left(-\frac{A}{RT}\right) (f - f_{eq})^m u^{m'} \quad (4)$$

For the growth rate, the following empirical correlation was adopted:

$$G = K \exp\left(-\frac{E}{RT}\right) (f - f_{eq})^m u^d L^b \quad (5)$$

In the model employed for the rate of agglomeration, the rate of agglomeration is proportional to the collision probability of two crystals and their sticking probability.

Gaillard et al. could not measure the particle size distribution due to the presence of the liquid hydrocarbon phase, but they still managed to predict consumption rates in agreement with the experimental consumption rates. Similar to the conclusion of Skovborg and Rasmussen (1994), this may indicate that the rate of hydrate formation is insignificantly affected by the particle size distribution. Gaillard et al. (1999), presented an expression for the maximum gas consumption rate without the population balance.

For their results from a semi-batch reactor, Monfort et al. (2000) proposed a semi empirical model with two driving forces for the ethane and propane gas consumption rates:

$$R_{Mon} = K(\Delta T^2 + \Delta f^2)^{b_1} \omega^{b_2} a_s^{b_3} \quad (6)$$

With an on-line particle size analyzer, Monfort et al. (2000), measured the mean growth rate of the crystals and correlated the results to driving force and stirring rate:

$$\bar{V} = K \exp\left(-\frac{\Delta E_a}{RT}\right) \omega^d \Delta f^m \quad (7)$$

Using the correlations, Monfort et al. (2000), estimated the consumption rate and the growth rate within $\pm 10\%$ of the measured value [20].

Herri et al. (1999) verified that the gas absorption follows a first-order relationship:



$$r = k_L a(C_{inp} - C_b) \quad (8)$$

Where the driving force is the difference between the methane concentration at the gas-liquid interface and in the liquid bulk [21].

The rates of primary nucleation at the interface and in the liquid bulk are calculated from two versions of the expression:

$$B_I = k_1 \exp\left(-\frac{B}{\log^2 S}\right) \quad S = \frac{C_b}{C_{int}} \quad (9)$$

The growth rate is expressed as:

$$G = k_g(C_b - C_{eq}) \quad (10)$$

Where k_g includes gas transport from the bulk to the surface and integration into the hydrate structure. Herri et al. assumed that the integration is not the rate determining step, which contradicts the conclusions by Englezos et al. (1987a). Herri et al. included an agglomeration term presented by Randolph and Larson (1988) to obtain an evolution of total number of particles in the reactor with time in accordance with the experimental results. An observed increasing rate of total number of particles with time for high stirring rates is accounted for by introducing secondary nucleation in the population balance. Four different equations for secondary nucleation were tested, and the one representing attrition was found to describe the experimental results. Later, Pic et al. (2000), presented a simplified version of the model including only primary nucleation and growth to investigate the effects of kinetic inhibitors.

The reviewed hydrate formation models strive to describe the process in terms of mass transfer concepts and crystallization theory, and to determine which step or combination of steps that are the rate-determining. Hydrate formation releases heat. Heat transfer may as well limit the formation rate, however, it is not included in any of the above models.

As far as observed, the only suggested model for the rate of hydrate formation in terms of heat transfer concepts, was recently published by Varaminian (2002). He combined an energy balance for a single crystal with an expression for the molar growth rate of a spherical particle giving the hydrate formation rate:

$$\frac{dn_{hyd}}{dt} = -\frac{4\pi h}{\Delta H} r_p^2 (T_i - T_{exp}) \quad (11)$$

The temperature difference between the temperature at the solid-liquid interface and the experimental temperature is the driving force [22]. An overall hydrate formation rate was developed by introducing a density function for the total crystal surface area. The model was fitted to the experimental data for a stirred batch reactor of Englezos et al. (1987a).

Takaoki et al. (2002) obtained a high gas consumption rate even though they used a batch reactor [23]. The reactor was especially manufactured for high rate production of hydrates and had a volume of 10 liter. No details about the reactor are reported, but it is believed that its internal geometry was designed for efficient production. A high stirring rate may also explain the high consumption rate. However, a large volume does not suffice to obtain a high rate because the reactor of Happel et al. had the same volume as the batch reactor of Herri et al. (1996b).

By Freer et al. (2001), kinetic parameters for methane hydrate formation were obtained from film growth measurements at the methane-water interface [24]. Experimental data were



collected for methane hydrate formation over the pressure and temperature ranges of 3.55–9.06MPa and 1.0–4.0 °C, respectively. The growth rate was found to be proportional to the subcooling, which indicates that crystallization proceeds by a continuous growth mechanism. A model for hydrate formation was proposed which accounts for both heat transfer and kinetics. Molecular attachment kinetics was assumed to follow Arrhenius behavior, and the heat transfer coefficient was assumed constant. The heat transfer assumption was verified using a thin wire approximation which was considered a geometric analog. The foundation of their model is derived from an energy balance at the moving boundary, which implies that the convective heat transfer cannot exceed heat generated at the moving interface. It is possible, however, to have growth kinetics that is sluggish relative to heat transport. Considering this, an overall rate constant is defined accounting for both kinetic and heat transfer resistance, and is given as:

$$\lambda_H \rho_H \frac{dX}{dt} = K(T_{eq} - T_{bulk}) \quad (12)$$

Mork and Gudmundsson (2002) investigated rate of hydrate formation in a continuous stirred tank reactor of 9 liter. Methane and natural gas hydrate formation rates measured at steady-state conditions at 70 to 90 bar and 7 to 15°C. Experimental result show that the formation rate is controlled mainly by the gas injection rate into the reactor and the pressure. The rate of hydrate formation is found to be dominated by transport processes rather than growth kinetics. A bubble-to-crystal model has been developed for the transport of gas from a gas bubble to a hydrate crystal surface [25]. Gas is transferred by molecular diffusion through a liquid film surrounding the hydrate crystal. The temperature increases across the film due to heat of hydrate formation. At the crystal surface, the dissolved gas is in equilibrium with the hydrate crystal. The gas molecules are included into the hydrate structure at the crystal surface. The inclusion of gas is modeled as a transport process where the gas is transferred across a hypothetical stagnant film at the crystal surface.

Assuming no accumulation in the liquid film around the gas bubble and neglecting the gas side mass transfer resistance, the following equation emerges for the rate of gas dissolution in liquid bulk:

$$r_1 = k_L A_g (C_{sol} - C_b) \quad (13)$$

Similar to the approach of Skovborg and Rusmussen (1994), the model can be extended to more than one hydrate-formation component by assuming that the transport rates are independent of each other:

$$r_{tot} = \sum_{i=1}^n K_i (C_{sol,i} - C_{eq,i}) X_i \quad (14)$$

By Xie et al. (2004), the hydration characteristics of a quiescent reactor with inner-placed vertical heat transfer tube were researched [26]. The growth morphology was described through the photos taken during the growth/decomposition processes. The temperatures of two points inside the reactor were also recorded and analyzed. The mass transfer mechanism was explained by surface free energy theory; the heat transfer process was also simulated. It was revealed that water can permeate into the guest phases along the surface of heat transfer tube, so massive gas hydrate can grow steadily along the vertical heat transfer tube in the guest phases without mechanical stirring. The reaction heat can be removed quickly by the coolant flowing inside the heat transfer tube. This finding will benefit gas hydrate application technologies such as natural gas storage and transportation with hydrate, or refrigerant cool



storage with gas hydrate. They suggested the flowing equation for hydrate growing along the tube:

$$\frac{dy}{dt} = (4.88 \times 10^{-9} t - 9.6 \times 10^{-6}) y + 4.23 \times 10^{-9} t + 2.41 \times 10^{-5} \quad (15)$$

Genanendran and Amin (2004), modeled hydrate formation kinetics of a hydrate promotion-water-natural gas system in a semi-batch spray reactor. The hydrate formation modeling involves two main aspects: (i) modeling hydrate nucleation and growth kinetics; and (ii) modeling the semi-batch spray reactor process [27]. The hydrate formation kinetics in a water-natural gas system in the presence of an additive chemical is modeled first, and subsequently, the hydrate formation kinetics was incorporated into a steady state, semi-batch, isobaric, isothermal reactor model. They used from correlation of Kashchiev and Firoozabadi (2002, 2003), for driving force, nucleation rate and crystal grow rate of hydrate formation kinetics.

$$\Delta\mu = kT \ln \left(\frac{\phi(P_r, T) P_r}{\phi(P_e, T) P_e} \right) + \Delta v_e (P_r - P_e) \quad (16)$$

But above equation is for gas with one component, therefore, the supersaturation of the multi-component natural gas system with 'm' hydrate forming components was approximated based on Englezos et al. (1987b) as:

$$\Delta\mu = kT \left(\sum_m x_m^h \ln \left(\frac{\phi(P_r, T)_m P_r}{\phi(P_e, T)_m P_e} \right) \right) + \Delta v_e (P_r - P_e) \quad (17)$$

And for nucleation rate:

$$J = A \exp \left(\frac{\Delta\mu}{kT} \right) \exp \left(\frac{-4c^3 v_h^2 \sigma_{ef}^3}{27kT \Delta\mu^2} \right) \quad (18)$$

And for crystal grow rate:

$$g(t) = m G^m t^{m-1} \quad (19)$$

Also they used from correlation exists about modeling process in spray reactor (Dimiccoli et al., 2000). In recent years many of authors attempted to achieve equations that describe correctly kinetics of natural gas hydrate formation. For example, Yasuhiko et al. (2004), Ohmura et al. (2005), Kobayashi et al. (2005) and Englezos et al. (2005), do many attempting to found correlation for kinetics of H structure hydrates.



Results

Investigation of various models of gas hydrate formation indicates that, in general, there is no a complete equation that describes the kinetics of gas hydrate formation, however, the kinetic model proposed by Kashchiev and Firoozabadi [15], has many advantages and can be considered as a candidate for further studying. As an example this model was extended by Genanenderan and Amin [27], for formation of hydrates in spray reactors. They gained the satisfactory results compare to experimental data (Table 2).

In this paper the kinetic model proposed by Genanenderan and Amin was simulated with MATLAB for a spray reactor and the results are shown in Table 3. It is necessary to note that, some parameters of Genanenderan and Amin model are modified for better performances. For example for calculating the equilibrium properties of hydrate, the model proposed by Anderson et al. [32] was used, because this model has the better performances (Fanaei and Nozari, 2006) [33]. For the full description of the kinetic model and parameters which are used in the simulation, refer to Navab thesis [34].

Table 2. Hydrate pilot plant experiment summary (Genanenderan and Amin (2004)).

| Case | Injection time (min) | | Injection rate (ml/min) | | Temperature (°C) | | Pressure (psig) | | HFVF (y/v) | |
|------|----------------------|-----|-------------------------|------|------------------|-----|-----------------|-----|------------|-------|
| | Value | ADD | Value | ADD | Value | ADD | Value | ADD | Value | ADD |
| I | 20.0 | 0.0 | 25.0 | 0.0 | -15.2 | 0.9 | 408 | 3 | 91.76 | 4.40 |
| II | 14.0 | 1.3 | 60.7 | 14.2 | -0.2 | 0.5 | 828 | 2 | 137.98 | 3.00 |
| III | 13.3 | 2.2 | 72.1 | 28.6 | 0.8 | 1.0 | 1248 | 16 | 156.37 | 16.40 |

Table 3. Result of simulation hydrate model (Navab (2007)).

| Model parameters | | | Case I | Case II | Case III |
|---|-----------------|--------|------------------------|------------------------|-------------------------|
| Description | Notation | Units | | | |
| <i>Input parameter</i> | | | | | |
| Pressure | P | kPa | 2913 | 5809 | 8705 |
| Temperature | T | K | 257.95 | 272.95 | 273.95 |
| Water flow rate | Q | ml/min | 25 | 60.7 | 72.1 |
| Injection time | t | min | 20 | 14 | 13.3 |
| <i>Adjustable parameters</i> | | | | | |
| Semi-batch rate component | m | — | 2.107 | 1.635 | 1.574 |
| batch rate component | n | — | 0.862 | 0.752 | 0.751 |
| <i>Output parameters</i> | | | | | |
| Equilibrium pressure in reactor temperature | P_{eq} | kPa | 414.128 | 758.628 | 849.629 |
| Compressible factor | Z | — | 0.8813 | 0.8087 | 0.7308 |
| Initial moles of gas in the reactor | M _{gi} | Mol | 30.8249 | 63.3090 | 104.5969 |
| Total mole of water injection | M _{wi} | Mol | 27.740 | 47.158 | 53.214 |
| Driving force for hydrate formation | Δm | J | 4.63×10^{-21} | 3.24×10^{-21} | 1.693×10^{-21} |
| Required energy for nucleation | W | J | 2.15×10^{-19} | 4.64×10^{-19} | 1.59×10^{-18} |
| Mole of water crystallized | M _{wc} | Mol | 14.751 | 37.860 | 47.462 |
| Mole of gas in hydrate | M _{gh} | Mol | 1.878 | 4.767 | 6.082 |
| Mole of hydrates formed | M _h | Mol | 1.878 | 4.767 | 6.082 |
| Hydrate formation volume factor at time | HFVF | — | 91.90 | 137.25 | 155.168 |



Conclusions

Investigation of various models of hydrate gas formation indicates that, in general, there is no equation that describes the kinetics of gas hydrate formation. Because, primary nucleation in hydrate can be homogeneous or heterogeneous, but homogeneous nucleation occurs more. This assumption agrees with 80% of experimental data. Kinetics of gas hydrate formation depending on reactor geometry, then results of the first experiment is not correct for the second experiment.

Kinetics of hydrate formation depended on thermodynamic of hydrate formation, for this reason, we cannot investigate kinetics of hydrate formation solely. Rate of hydrate formation is controlled by hydrodynamic condition and driving force. Generally, base of hydrate formation models is mass transfer and crystallization theory. All of the models are compared with experimental data. It means that models can be used for those systems. Hydrate formation rate increases considerably with the change of hydrodynamic conditions or by using additive materials.

Anyway, the kinetic model proposed by Kashchiev and Firoozabadi [15], has many advantages and can be considered as a candidate for further studying.

The simulated results in this paper showed that the modified Kashchiev and Firoozabadi kinetic model proposed by Genanenderan and Amin [27] has acceptable performances for spray reactors.

Notation

| | |
|-----|--|
| A | The gas-liquid interfacial area per liquid volume, Constant |
| a | Area of a particle |
| C | Concentration |
| f | Fugacity |
| G | Growth rate |
| h | Heat transfer coefficient |
| K | Thermal resistant, constant |
| k | The gas-liquid mass transfer coefficient, the methane hydrate kinetic rate coefficient |
| L | Crystal size |
| r | Gas consumption rate |
| t | The time of gas hydrate growth process |
| u | Liquid velocity |
| x | Mole fraction |
| y | The height of formed gas hydrate |

Subscripts

| | |
|--------|-------------|
| b, d | Constant |
| a | Activity |
| b | Bulk |
| eq | Equilibrium |
| g | Gas |
| int | Interface |
| L | Liquid |
| p | Particle |



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