Kinetics of Gas Hydrate Formation from Pyrolysis Gas in Water-In-Oil Emulsion System

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Abstract

The experiments on gas hydrate formation kinetics of ethylene pyrolysis gas in the water-in-oil emulsion were carried out in a batch stirred reactor at pressures of 4 MPa and 5 MPa and temperatures of 270.15 K and 274.15 K. The influence of temperature and pressure on hydrate formation rate was studied, respectively. The kinetic model by Firoozabadi et al. coupled with the Chen-Guo hydrate model was used to predict the rate of gas hydrate formation for the gas mixtures by using pure gas data. The kinetic algorithm of absorption-hydration for the gas mixture in the water-in-oil emulsion was developed, which involved vapor-liquid-liquid-hydrate four phase equilibrium. The study revealed that the hydrate formation rate is much faster in the emulsion than that in pure water. The experimental data and the modeling work are of value for the design of hydrate separation reactor.

Keywords: Hydrate, Ethylene Pyrolysis Gas, Separation, Emulsion

Nomenclature

A Parameter in kinetic model
A' Parameter in kinetic model [MPa]
$A_{ij}$ Binary interaction parameter in Chen-Guo hydrate model [K]
$a_w$ Activity of water
$B'$ Parameter in Chen-Guo hydrate model [K]
$C$ Parameter in Chen-Guo hydrate model [K]
$C_l$ Langmuir constant [MPa⁻¹]
f Fugacity [MPa]
$K$ Parameter in kinetic model [kmol·m⁻³·min⁻¹]
P Pressure [MPa]
r gas consumption rate [kmol·m⁻³·min⁻¹]
T Temperature [K]
V volume [m³]
$X$ Constant in equation (10) [MPa⁻¹]
$x_i$ Mole fraction of component i
$x_i^*$ Mole fraction of basic hydrate component i formed by hydrate former i
$Y$ Constant in equation (10) [K]
$Z$ Constant in equation (10) [K]
$α$ Hydrate structure parameter
$β$ Hydrate structure parameter
$θ_j$ Fraction of linked cavities occupied by gas component j
$λ_1$ Number of small cavities per water molecule
$λ_2$ Number of large cavities per water molecule

Subscripts

i, j, k Component i, j, k
w Water

Introduction

The ethylene industry is the basis of the petrochemical industry. The demand for the ethylene is increasing rapidly with the development of the economy. However, the refrigeration system is the bottleneck for extending the production capacity using the existing equipments because of its large amount of energy consumption. Currently, the separation of methane from ethylene and ethane is implemented by the distillation at high pressure and the temperature below -110 degree Celsius, which needs high facility investments and operation costs in the

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separation of the ethylene pyrolysis gas. However, the separation of low boiling gas mixture by forming hydrate could be performed around the ice point and avoid deep cooling. Therefore applying hydrate technique to the ethylene production could reduce the costs of production.

Gas hydrates, also called clathrate hydrate is a sort of nonstoichiometric crystalline compound composed of water and gases with small-sized molecules \([1]\), such as \(\text{CH}_4, \text{C}_2\text{H}_6, \text{CO}_2, \text{H}_2\text{S}\), etc. The hydrate-based technique for separating gas mixtures is based on the difference of hydrate formation characteristics of various gas species. Study of gas hydrate formation kinetics is of significance in designing the separation equipment and enhancing the process rate and separation efficiency.

Several studies on hydrate formation kinetics have been published in the literature. The study can be divided into two categories: the primary nucleation process and the crystal growth process. Gas hydrate nucleation and growth have been investigated by various experimental and modeling methods. Before 1980s, the studies were mainly focused on the non-hydrocarbon systems. And then more and more researches on the hydrocarbon systems were reported, such as the study on the hydrate growth of methane and ethane by Vysniauskas et al. \([2,3]\), Englezos et al. \([4,5]\) and Skovborg et al. \([6]\) or the study on the induction time and driving force of crystallization of methane and ethane hydrates by Kashichiev and Firoozabadi et al. \([7-9]\).

The most researches reported in the literature are focused on the simple gas hydrate formation kinetics, such as one component or binary systems. Nevertheless, the gas mixtures involved in the practical ethylene production are almost multi-component systems. The hydrate technique has not been applied to the practical industrial production at the present time. The limiting factors are mainly as follows: The natural formation rate of hydrate is so slow that it could not meet the need of industrial production; the single-stage separation efficiency is very low; the hydrates naturally formed tend toward aggregation and plugging the facilities. We found that if the gas mixture contacted with the water-in-oil emulsion, the hydrate formation rate and the separation efficiency could be enhanced enormously due to the combined contributions of absorption and hydration. Furthermore, the hydrate crystals would disperse into the emulsion in small particles without aggregation and growing up. In this work, the experimental data of hydrate formation rate from the ethylene pyrolysis gas in the water-in-oil emulsion were obtained in a batch reactor. The kinetic model by Firoozabadi et al. \([7-9]\) was modified and coupled with the Chen-Guo hydrate model \([10]\) to calculate the gas consumption rate. An algorithm of kinetics of absorption and hydration process was developed, which involved the coexistence of vapor-liquid-liquid-hydrate four phases.

**EXPERIMENTAL EQUIPMENT AND PROCEDURE**

Analytical grade hydrogen and hydrocarbon gases supplied by Beifeng Gas Industry Corporation, Ltd., China, were used in preparing the simulated gas mixtures. Water used in the experiments was de-ionized and distilled. Referring to the typical pyrolysis gas mixture, a gas mixture was prepared.

The experimental apparatus used in this study has been described in detail in previous articles from this laboratory \([11-15]\). The apparatus consisted of a cylindrical transparent sapphire cell (2.54 cm in diameter, effective volume of 60 cm\(^3\)) installed in an air bath and equipped with a magnetic stirrer for accelerating the formation of hydrate. The formation of the hydrate crystals in the emulsion were observed directly through the transparent cell wall. The accuracy of temperature and pressure measurement was \(\pm 0.2\) K and \(\pm 0.025\) MPa, respectively.

A typical experiment started by washing the sapphire cell with water and prepared emulsion three times, respectively. Air was removed from the reactor by a vacuum pump. Then, 10 cm\(^3\) of emulsion composed of 50 w% water and 50 w% decane was added into the cell which was installed in an air bath. The air-bath temperature was then tuned to the required temperature, and then the cell was charged with feed gas until the required pressure was reached. The liquid phase was stirred with a magnetic stirrer, and a pressure drop would begin due to the hydrate formation. Drive the manual pump to reduce the cell volume for keeping the pressure constant. The volume was recorded at regular intervals until the system pressure was kept stable for 4 hours.
MODELING STUDY

Rate of Gas Hydrate Formation

The rate of gas hydrate formation could be expressed in terms of the gas consumption rate, which could be given as follows [7,8]

\[ r = G^n J \]  
\[ G = K_1 \left( e^{\frac{\Delta w}{RT}} - 1 \right) \]  
\[ J = K_2 e^{\frac{-\Delta \mu}{RT}} \exp \left( \frac{-A}{RT \Delta \mu^2} \right) = K_2 e^{\frac{-A}{RT \Delta \mu^2}} \]  

where \( r \) is the gas consumption rate, kmol·m⁻³·min⁻¹; \( G \) is the time-independent growth rate of the separate crystallites; \( J \) denotes the stationary nucleation rate; and \( K_1, K_2, A, \) and \( n \) are constants. Combining \( K_1 \) and \( K_2 \) to one constant \( K \), the rate of gas consumption [Eq. (1)] then becomes

\[ r = G^n J = K \left( e^{\frac{\Delta w}{RT}} - 1 \right) \left( e^{\frac{-A}{RT \Delta \mu^2}} \right) \]  

Driving Force

The difference between the chemical potential of a hydrate building unit in the aqueous solution and in the hydrate crystal [9] was used as the driving force in this work. The Chen-Guo two-step hydrate formation model [10] was used to calculate the difference of the chemical potential \( \Delta \mu \). The two-step hydrate formation mechanism can be interpreted as follows. The first step: The formation of a stoichiometric basic hydrate through a quasi-chemical reaction. The basic hydrate is defined as a complex compound formed by complete filling of the basic cavities (i.e., the large cavity) in the empty hydrate lattice with guest molecules. The second step: The adsorption of gas molecules into the empty small cavities, resulting in the nonstoichiometric property of hydrates. In the second step, only small size gas molecules (e.g., Ar, N₂, O₂, CH₄, etc.) dissolved in water may move into the empty small cavities. On the basis of this theory, \( \Delta \mu \) is calculated as follows

\[ \frac{\Delta \mu}{RT} = \lambda_1 \ln \left( 1 - \sum_j \theta_j \right) + \lambda_2 \sum_i x^*_i \ln \left( \frac{f_i^0}{f_i} \right) \]  

where \( \lambda_1 \) and \( \lambda_2 \) stand for the numbers of small and large cavities per water molecule, respectively. \( \lambda_1 = 2/46 \) and \( \lambda_2 = 6/46 \) for the structure I hydrate; \( \lambda_1 = 16/136 \) and \( \lambda_2 = 8/136 \) for the structure II hydrate. \( x^*_i \) denotes mole fraction of component \( i \) in large cavities, \( \Sigma x^*_i = 1 \). The symbol \( a_w \) is the activity of water. The vapor-phase fugacity (\( f \)) of component \( i \) can be calculated by the equation of state (EOS), \( \beta = 4.242 \text{ KMPa}^{-1} \) for structure I hydrates, and \( \beta = 10.224 \text{ KMPa}^{-1} \) for structure II hydrates. \( \theta_j \) represents the fraction of the small cavities occupied by the gas species \( j \). On the basis of the Langmuir adsorption theory, \( \theta_j \) is calculated as follows

\[ \theta_j = \frac{C_j f_j}{1 + \sum_k C_k f_k} \]  

The Langmuir constant \( C_j \) is formulated as

\[ C_j = X_j \exp \left( \frac{Y_j}{T - Z_j} \right) \]  

The constants \( A'_i, B'_i, \) and \( C_i \) in Eq. (8) and the constants \( X_i, Y_i, \) and \( Z_i \) in Eq. (10) are listed in Tables 1 and 2. The binary interaction coefficients, \( A'_i \), in Eq. (8) are listed in Table 3.

RESULTS AND DISCUSSION

Experimental Results

The gas hydrate formation rates for the synthetic pyrolysis gas in the water-in-oil emulsion were measured by recording the volume reduction at a given temperature and pressure in the batch reactor.
The composition of the gas mixture is listed in Table 4. The oil-water ratio of emulsion was 1.0. The normal volume ratio of gas to liquid (emulsion) was 90. To obtain the mole number of gas in the gas phase, the following equation was used

\[ n = \frac{PV}{zRT} \]  

(11)

where the compressibility factor \( z \) was calculated by the BWRS equation of state [16]. \( V \) is the volume of the gas phase in the reactor. The influences of temperature and pressure on the kinetics of hydrate formation were tested, respectively. The influences of pressure on gas consumption are plotted in Figures 1 and 2. The influence of temperature on gas consumption is plotted in Figure 3. From the figures, it can be seen that the hydrate formation rate increase with the temperature decrease and pressure increase. The reason for this is that the low temperature and high pressure are of benefit to the hydrate formation. The induction time of nucleation and growing time would be reduced under the low temperature and high pressure conditions. In addition, for the water-in-oil system, the solubility of gas in the liquid phase would be enhanced under this condition. Therefore, the gas molecules transferred into the hydrate slurry (composed of hydrate and emulsion) would be increased. To compare the gas hydrate formation rate of the pyrolysis gas in the water-in-oil emulsion and that in pure water, the experiment was carried out for the pyrolysis gas in pure water. The experimental results are plotted in Figure 4. Apparently, the gas hydrate formation rate was enhanced effectively in the water-in-oil emulsion. The absorption of gas molecules into the oil, which formed the transmicelle with water, could increase the contact of water with gas molecules. Therefore, more gas molecules could transfer into the hydrate phase. Furthermore, it was observed through the sapphire-windowed cell that the hydrate particles formed in the water-in-oil emulsion were dispersed in the emulsion phase without agglomeration, which indicated that water-in-oil emulsion could not only enhance the hydrate formation rate, but also avoid the hydrate agglomeration and growth.

<table>
<thead>
<tr>
<th>gas mixture</th>
<th>( \text{H}_2 )</th>
<th>( \text{CH}_4 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_3\text{H}_6 )</th>
<th>( \text{C}_4\text{H}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis gas</td>
<td>19.85</td>
<td>42.76</td>
<td>32.78</td>
<td>2.41</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Table 4. Composition of Pyrolysis Gas Mixture

![Figure 1. Rate of gas consumption for pyrolysis gas in the water-in-oil emulsion under different pressures at \( T = 270.15 \text{ K} \). ■, Experimental data (\( P = 5.0 \text{ MPa} \)); ▲, Experimental data (\( P = 4.5 \text{ MPa} \)); ▼, Experimental data (\( P = 4.0 \text{ MPa} \)).](image)
Calculating Results

In this work, we used Petal-Teja equation of state (PT EOS) [17] to calculate the fugacity of gas species. The parameters of hydrate formation kinetics in Eq. (4) were determined by using the experimental data in the literatures, which are listed in Table 5. On the basis of the Chen-Guo two-step hydrate formation mechanism, the second step (the adsorption of gas molecules into the empty small cavities) could progress much faster than the first step (the formation of a stoichiometric basic hydrate). That means that formation of basic hydrate is the control step during the procedure of whole hydrate formation.

The parameters in Eq. (4) for the mixture were determined by following mixing rules

$$ K = \sum_{i} x_i^* K_i $$

(12)

$$ A = \sum_{i} x_i^* A_i $$

(13)

where $x_i^*$ denotes the mole fraction of gas component $i$ in basic hydrate (large cavities). The value of constant $n$ is between 0.333 and 1 [8]. In this work, $n$ was taken to be 1 for pure gas and 0.5 for the gas mixture.

### Table 5. Parameters in Equation (4)

<table>
<thead>
<tr>
<th>System</th>
<th>$K$ / kmol·m$^{-3}$·min$^{-1}$</th>
<th>$A$·10$^7$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.0902</td>
<td>-0.02525</td>
<td>[4]</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.7425</td>
<td>27.4787</td>
<td>[15]</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.0275</td>
<td>-0.1922</td>
<td>[4]</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.0289</td>
<td>3.7135</td>
<td>this work</td>
</tr>
</tbody>
</table>

The parameters in Table 5 were obtained from the pure water system. In the water-in-oil emulsion, the gas solubility and diffusion coefficient in the liquid phase could be improved due to the absorption. The parameter $K$ in Eq. (4) contains...
the influence of the gas solubility and diffusion coefficient on the hydrate formation rate in pure water system [7,8]. For water-in-oil emulsion system, the parameter, \( K' \), was correlated as follows

\[
K' = 0.00042 \cdot K \cdot \left( \frac{P}{P_0} \right)^{1.53} \left( \frac{T_0}{T} \right)^{19.7}
\]  

(14)

Where \( P_0 = 1.01325 \times 10^5 \) Pa and \( T_0 = 273.15 \) K. The specific surface energy of the hydrate/liquid interface, \( \sigma \), would be reduced in the water-in-oil emulsion. The effective specific surface energy of the hydrate/liquid interface, \( \sigma_{eff} \), contained in the parameter \( A \) in Eq. (4) is defined [18] by

\[
\sigma_{eff} = \psi \sigma
\]

(15)

The factor \( \psi \) is a number between 0 and 1. In this work, \( \psi \) was correlated to be 0.118 from the experimental data. Therefore, Eq. (4) could be rewritten for the water-in-oil emulsion system as follows

\[
r = 0.00042 \cdot K \cdot \left( \frac{P}{P_0} \right)^{1.53} \left( \frac{T_0}{T} \right)^{19.7} \left( e^{\frac{\Delta \mu}{RT \cdot \psi}} - 1 \right)^n \times \left( \frac{1}{\Delta t} \right)
\]

(16)

The gas hydrate formation in the emulsion included two procedures: absorption and hydration, where vapor, liquid hydrocarbon, water and hydrate phase would coexist. The calculation procedure is summarized as:

(1) Input the gas composition in water-free basis \( y_i \), the ratio of oil to water and the ratio of gas to liquid. Input temperature \( T \), pressure \( P \) and the time intervals \( \Delta t \).

(2) Determine the composition of feed mixture \( z_{0i} \) from the ratio of oil to water and the ratio of gas to liquid.

(3) Based on \( T \), \( P \) and \( z_{0i} \), perform three-phase flash calculation, obtain the compositions of vapor, hydrocarbon-rich and water-rich phase, \( y_i \), \( x_i^A \), \( x_i^B \), mole fraction of various phases, \( V \), \( L_A \), \( L_B \), and vapor phase fugacity \( f_i \).

(4) From \( f_i \), calculate the occupied fraction of small cavity \( \theta_i \), and the mole fraction of basic hydrate \( i \), \( x_i^* \) by Eq. (6) – (10). Then, the hydrate formation driving force could be obtained from Eq. (5).

(5) Calculate the hydrate formation rate \( r \) from Eq. (16). Then, calculate the amount of hydrate phase \( H \) formed in the time interval \( \Delta t \).

(6) From \( \theta_i \), \( x_i^* \) and \( H \), calculate the composition of hydrate phase \( x_i^H \) and corrected feed composition \( z_i \) by Eq. (17) – (19).

\[
x_i' = \lambda_2 x_i^* + \lambda_3 \theta_i
\]

(17)

\[
x_i^H = \frac{x_i'}{\sum x_i'}
\]

(18)

\[
z_i = \frac{z_{0i} - H \cdot x_i^H}{1 - H}
\]

(19)

(7) Set \( z_0 = z_r \), repeat steps (3) – (6) to calculate the hydrate formation rate of every next time interval.

The tested calculations were implemented by using the foregoing procedure. The comparison of calculated and experimental hydrate formation rates under the different conditions are plotted in Figures 5 and 6. The calculation results of gas consumption in the water-in-oil emulsion are shown in Figure 7. It can be seen that the calculations are in good agreement with the experimental data. Figure 8 shows the curves of the mole fractions of hydrogen, methane and ethylene in the gas phase over time during the hydrate formation at temperature of 274.15 K and pressure of 5.0 MPa. It could be noticed that hydrogen and methane in the gas phase were enriched and most ethylene was transferred into the hydrate slurry, formed with hydrate and emulsion, which means the pyrolysis gas could be separated by forming hydrate to recover ethylene.

**CONCLUSION**

Experimental data on the kinetics of gas hydrate formation from a pyrolysis gas in the water-in-oil emulsion were presented. The experimental results
demonstrated that the rate of gas hydrate formation could be enhanced enormously in the water-in-oil emulsion than in pure water. Furthermore, it was observed that the hydrate particles would not agglomerate and grow to plug the equipment in the water-in-oil emulsion system. The obtained experimental data are valuable for designing industrial process of separating pyrolysis gas to recover ethylene by forming hydrates. The kinetic model by Firoozabadi et al. was extended to describe the kinetics of gas hydrate formation from mixtures in the water-in-oil emulsion. The difference between the chemical potential of a hydrate building unit in the aqueous solution and in the hydrate crystal was used as the driving force, which was calculated by Chen-Guo hydrate model. The algorithm was developed to calculate the hydrate formation rate for the emulsion system which involves vapor-liquid-liquid-hydrate four phase coexistence, and is found to describe the experimental data very well.

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