Simulation of Hydrate Dissociation Equilibrium for Carbon dioxide – methane Mixture

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The objective of the present study is to explore the potential of removing carbon dioxide from natural gas by forming gas hydrate. The parameters governing the dissociation of gas hydrate have been identified. An attempt has been made to select the favorable operating conditions for methane-carbon dioxide separation through the dissociation of gas hydrate. The *K*-factor method along with Peng-Robinson equation of state are employed in ICON simulator to obtain hydrate dissociation temperature and pressure, and phase equilibrium compositions.

Key words:
Gas hydrate, carbon dioxide, methane, natural gas

Introduction

Natural gas plays an important role in the world's supply of energy. It is one of the clean, safe, and most useful among all the available energy sources. Natural gas has been used for both residential, commercial, and industrial applications. Carbon dioxide which is an undesired component of natural gas is corrosive and non-combustible. This undesired gas must be removed from natural gas to a permissible level. Typical pipeline quality states that the composition of CO_2 in the treated gas stream must not exceed 2 % (Spillman, 1989). In Malaysia, Gas Malaysia has set an even more stringent limit where the level of CO_2 is further reduced to a maximum of 1.83 %.

A typical content of 0–8 % carbon dioxide can be removed by using commercially available absorption techniques. However, for the situations where the carbon dioxide fraction increases to 50–80 % in natural gas produced, the current equipment/techniques are not applicable for the efficient removal of carbon dioxide. Therefore, the available effective alternative is the gas hydrate method. Hydrates are ice-like solids that form when a sufficient amount of water and a hydrate former are present in proper combination of temperature and pressure (hydrate dissociation is favored by low temperature and high pressure) depending on the thermodynamics of the system. Methane and carbon dioxide clathrates occur naturally at temperature above freezing point of water (up to 30 °C) under pressure of p = 0.1 MPa (~1 bar) to p = 100 MPa (~1000 bar). Different types of gases form hydrate at different ranges of temperature and pressure. Gas hydrate can be converted back to gas and water easily by applying heat to the solid hydrate. This property can be exploited to separate carbon dioxide from natural gas by either capturing carbon dioxide or methane in hydrate form. A theoretical simulation technique is used to study the possibility of applying the property of gases to design a hydrator which can purify natural gas.

Background

Hydrates were first discovered by Davy and Faraday in the early 1820's. They reported the dissociation of an ice-like solid that formed above the freezing point of water in mixtures of chlorine and water. Since then, many researchers have attempted to identify the hydrate forming components as well as the pressure and temperature conditions for the hydrate dissociation. Hydrate dissociation in natural gas pipe lines leads to blockage in the pipes. Hence the researchers have started giving serious attention to these special types of compounds. The structure of hydrates was investigated by von Stackelberg (1949) using X-ray diffraction. Van der Waals and Platteeuw (1959) were the first to publish a rigorous thermodynamic model for calculating the conditions at which hydrates form. ICON is Petronas Steady State Simulator which was developed by Petronas Research and Virtual Materials Group (Malaysia). The ICON simulator used in this work is capable of predicting hydrate dissociation pressure (or dissociation temperature) at various temperatures (or pressures), gas composition and water/gas ratio. Hydrate simulation using ICON is based on the *K*-factor method and Peng-Robinson

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equation of state (1976). The Peng-Robinson equation of state was chosen for the calculation of hydrate dissociation temperature and pressure due to its compatibility with all fluid properties in natural gas. Hydrate dissociation pressure predicted by ICON is within the acceptable limits of the available literature. At the same time, ICON is not capable of predicting the equilibrium composition of each phase when gas hydrate forms.

The *K*-factor is defined as the distribution of the components between the hydrate and the gas phases i.e.,

$$K_i = \frac{y_i}{x_i} \qquad (1)$$

y_i and x_i are the mole fractions of component i in the vapor and hydrate, respectively. This factor is available in literature for each of the components of natural gas. The *K*-factor method is able to give the phase equilibrium composition of gas hydrate when temperature and pressure are specified.

Simulation

The *K*-factor method was devised by Carson and Katz (1942), although additional data and charts have been reported since then (Carroll, 2003). *K*-factor method normally has three applications: (1) given the temperature and pressure, calculate the compositions of the coexisting phases; (2) given the temperature, calculate the pressure at which the hydrate forms and the composition of the hydrate; and (3) given the pressure, calculate the temperature at which the hydrate forms and the composition of the hydrate. The *K*-factor method examined in this paper is that described by Carroll (2003). Furthermore, Carroll (2003) demonstrated that the *K*-factor method is accurate enough for predicting the hydrate conditions for the pure compounds. These mole fractions are on a water-free basis, and water is not included in the calculations. It is assumed that sufficient water is present to form hydrate. *K*-chart is available (Sloan, 1998) for hydrate forming components (methane, ethane, propane, *i*-butane, *n*-butane, hydrogen sulfide, and carbon dioxide) which are commonly encountered in natural gas. All non-formers are simply assigned a value of infinity. This is true by definition because $x_i = 0$ for non-former, so there is no non-former in the hydrate. For the purpose of simplifying the problem, carbon dioxide-methane is used for the calculations, instead of actual composition of natural gas. After establishing the procedure, it will be further extended using the combination of all other components present in natural gas.

The estimation of *K*-value for CH_4 and CO_2 is carried out by using a correlation of the following form suggested by Sloan, (1998):

$$
\begin{aligned}
\ln(K_{vsi}) = {} & A + B \cdot T + C \cdot \Pi + D \cdot T^{-1} + E \cdot \Pi^{-1} + \\
& + F \cdot \Pi \cdot T + G \cdot T^2 + H \cdot \Pi^2 + I \cdot \Pi \cdot T^{-1} + \\
& + J \cdot \ln(\Pi \cdot T^{-1}) + K \cdot (\Pi^{-2}) + L \cdot T \cdot \Pi^{-1} + \quad (2) \\
& + M \cdot T^2 \cdot \Pi^{-1} + N \cdot \Pi \cdot T^{-2} + O \cdot T \cdot \Pi^{-3} + \\
& + P \cdot T^3 + Q \cdot \Pi^3 \cdot T^{-3} + R \cdot T^4
\end{aligned}
$$

where Π = pressure, bar; T = temperature, °C; A, B...R are constants given in Table 1. The above equation was used to fit all the *K* values for methane and carbon dioxide, from the *K* chart for methane and carbon dioxide given in Figs. 1 and 2 respectively.

T a b l e 1 – *Values of the estimated constants and accuracy of prediction of eq. (2)*

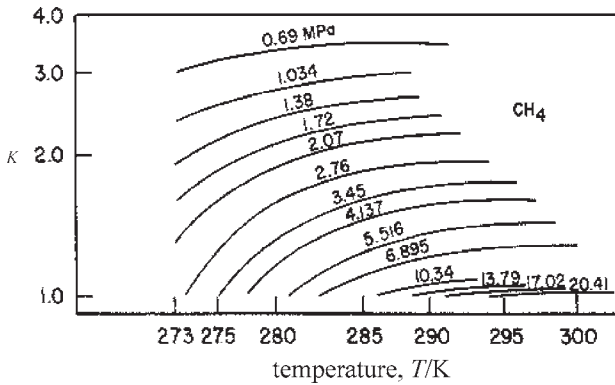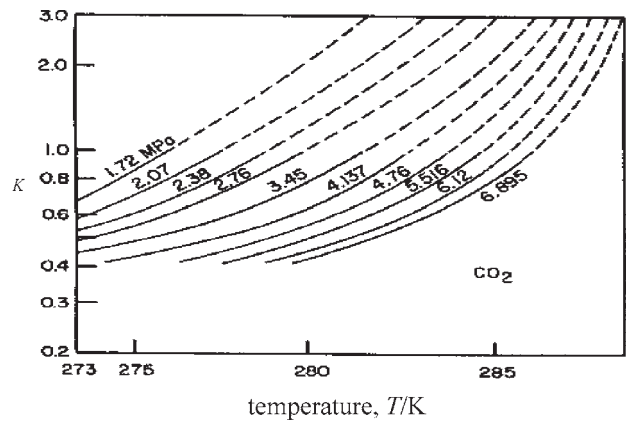| Coefficient	CO_2	CH_4
A	9.0242	1.63636
B	0	0
C	0	0
D	-207.033	31.6621
E	0	-49.3534
F	4.66E-5	-5.31E-6
G	-6.992E-3	0
H	-2.89E-6	0
I	-6.223E-3	0.128525
J	0	-0.78338
K	0	0
L	0	0
M	0.27089	0
N	0	-5.3569
O	0	0
P	8.82E-5	-2.3E-7
Q	2.55E-6	-2.0E-8
R	0	0
correlation coefficient, R^2	0.996	0.999

Fig. 1 – *Methane K_{vs} chart (Sloan, 1998)*

Fig. 2 – *Carbon dioxide K_{vs} chart (Sloan, 1998)*

Calculation algorithms

The present objective is to calculate the amount of the phases as well as the composition of the coexisting phases in the equilibrium mixture. The temperature, pressure, and compositions are the input variables.

The objective function to be solved, in the Rachford-Rice-form, is:

$$f(V) = \sum \frac{z_i(1-K_i)}{1+V(K_i-1)} = 0 \qquad (3)$$

where z_i is the composition of the feed on a water-free basis. An iterative procedure is used to solve for the vapor phase fraction, V, such that the function equals to zero. Once the phase fraction has been estimated, the vapor phase can be calculated as follows:

$$y_i = \frac{z_i K_i}{1+V(K_i-1)} \qquad (4)$$

Using the vapor phase fraction 'y_i', calculated from eq. (4), the composition of the solid phase (hydrate) is calculated using eq. (1):

$$x_i = \frac{y_i}{K_i} \qquad (5)$$

Sloan (1998) presented a phase diagram showing the critical temperature and pressure as well as hydrate dissociation quadruple points for methane and carbon dioxide. For any chosen pressure and composition, the temperature at which the hydrate forms or vice versa could be solved by using one of the following appropriate relations. The objective functions to be solved are:

$$f_1(T) = 1 - \sum \frac{y_i}{K_i} \qquad (6)$$
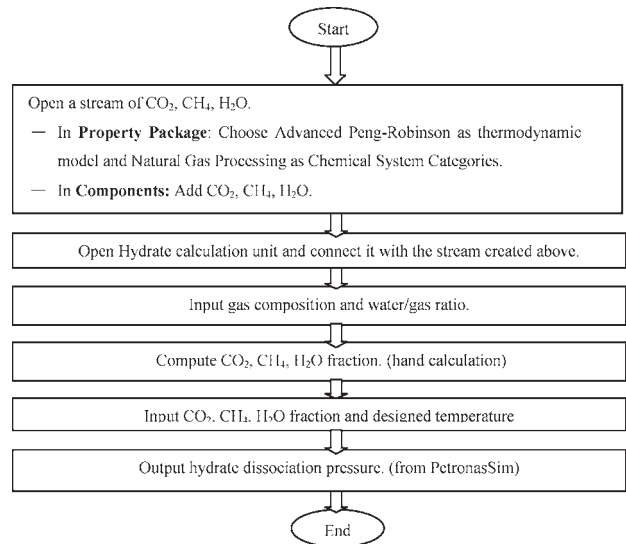
$$f_2(p) = 1 - \sum \frac{y_i}{K_i} \qquad (7)$$

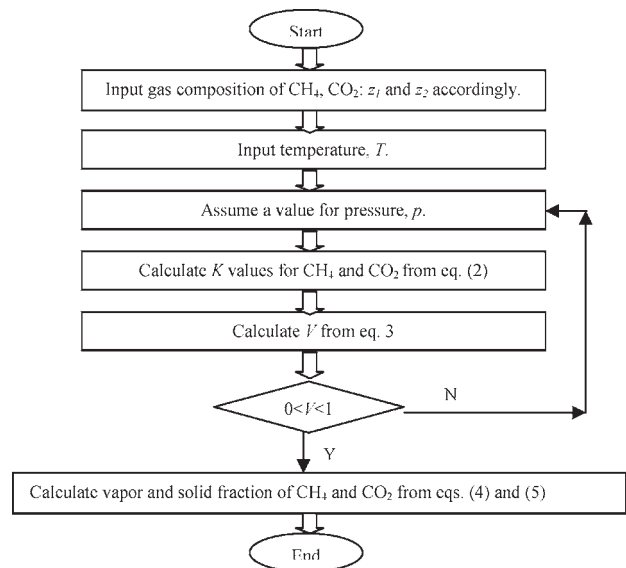Fig. 3 – *Simulation steps to obtain temperature and pressure dissociation in ICON*

Fig. 4 – *Calculation steps to obtain hydrate equilibrium composition using K-factor method*

Results and discussion

Effect of temperature, pressure, carbon dioxide fraction, and $r_{water/gas}$ ratio on hydrate dissociation

As the temperature increases the dissociation pressure of gas hydrate increases and vice versa (Fig. 5). In I-H-V (ice-hydrate-vapor) region, dissociation pressure increases as temperature increases, which is less than that required in L_w-H-V (liquid water-hydrate-vapor) region (Sloan, 1998).

At any desired temperature, for higher fraction of carbon dioxide in the gas, the lower is the pressure required to form gas hydrate (Fig. 5). Pure methane gas has highest dissociation pressures and pure carbon dioxide has the lowest dissociation pressure as compared to methane-carbon dioxide gas mixtures at the same temperature. Both methane and carbon dioxide affect each other in terms of hydrate dissociation.

For any fixed temperature and gas composition (carbon dioxide mole fraction), if the mole ratio of $r_{water/gas}$ is high, higher is the pressure required to form gas hydrate (Fig. 6). In the present study a water/gas mole ratio of 1 gives lowest dissociation pressure and a $r_{water/gas}$ ratio of 7.0 gives highest dissociation pressure. Theoretically, to convert 1 mole of gas to hydrate 5.75 mole of water is essentially required. But it is very difficult to convert all gases to hydrate and always some holes could not be occupied with the gas molecules. However, a minimum water/gas mole ratio of 5.75 is required to convert all gases into hydrate. For the purpose of comparison, the dissociation pressure at a minimum water/gas mole ratio of 5.75 is taken as the reference pressure. The increment in pressure required to form hydrate when water fraction increases depend on the composition of gas mixture. The effect
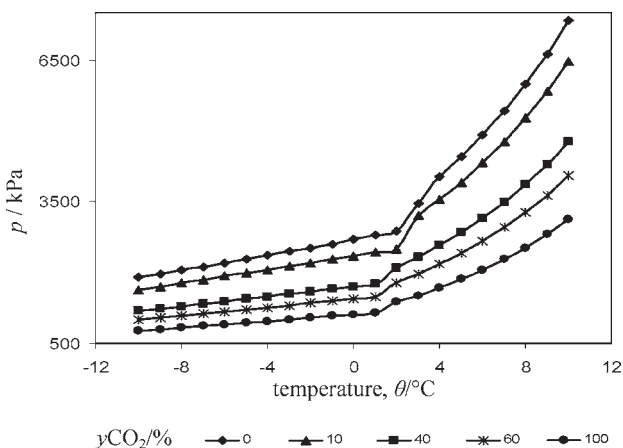
of water/gas mole ratio on hydrate dissociation is not as significant as that of temperature and pressure.

Effect of temperature and pressure on hydrate phase equilibrium composition

At low temperatures more carbon dioxide form hydrates as compared to methane as temperature increases, the concentration of methane in hydrate increases. However, the concentration of carbon dioxide in hydrate phase is always higher than that of vapor phase. The lower the temperature is, the larger the difference in concentration of carbon dioxide in hydrate phase and in vapor phase, indicating a better separation. At low pressure region (associated with low temperature), for higher pressure, the lower is the concentration of carbon dioxide in vapor phase or the more carbon dioxide form hydrates (Fig. 7). However, increase in pressure causes a reduction in vapor phase concentration, since gases are more incorporated in hydrate lattice.

F i g . 6 – *Delta p dissociation at various water/gas mole ratios (10 % CO_2, 90 % CH_4 gas stream) (ICON)*

F i g . 5 – *Pressure of dissociation versus temperature at different carbon dioxide fraction (water/gas ratio equals to 5.75) (ICON)*

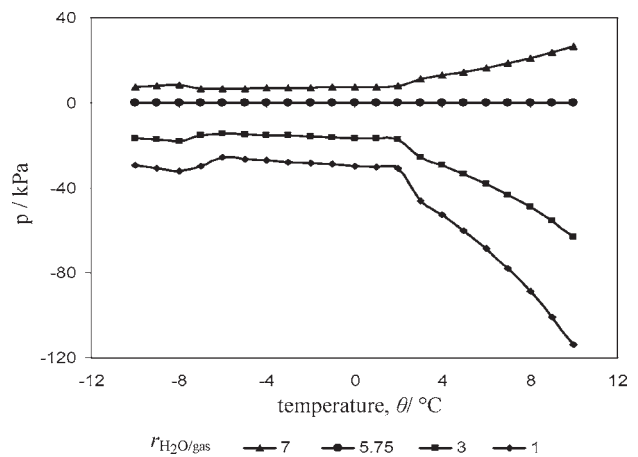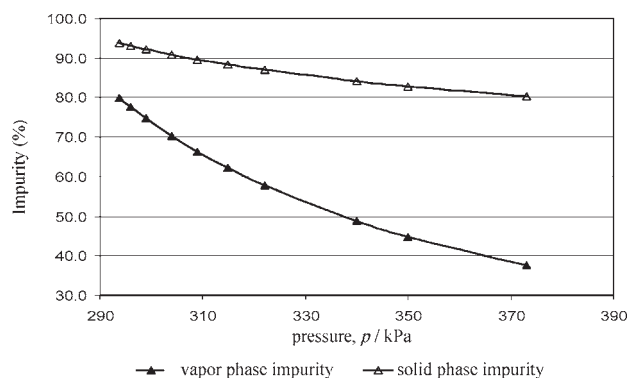F i g . 7 – *Phase impurity (% CO_2) versus pressure at 80 % feed impurity and –6 °C (K-chart method)*

T a b l e 2 – *Phase compositions of CH₄ and CO₂ at –6°C and various pressures (80 % feed impurity) (K-chart method)*

p/kPa	Vapor fraction y	Solid fraction x	CO_2 vapor y/%	CH_4 vapor y/%	CO_2 solid x/%	CH_4 solid x/%
293.7	0.99	0.01	79.9	20.1	93.8	6.2
296	0.84	0.16	77.6	22.4	93.0	7.0
299	0.70	0.30	74.7	25.3	92.1	7.9
304	0.53	0.47	70.3	29.7	90.8	9.2
309	0.41	0.59	66.3	33.7	89.6	10.4
315	0.32	0.68	62.1	37.9	88.3	11.7
322	0.24	0.76	57.7	42.3	86.9	13.1
340	0.12	0.88	48.7	51.3	84.1	15.9
350	0.07	0.93	44.7	55.3	82.8	17.2
373	0.01	0.99	37.5	62.5	80.4	19.6

Conclusions

Temperature, pressure and gas composition are the main variables governing the dissociation of gas hydrate. Based on the above, the following conclusions could be drawn:

1. Temperature increases, dissociation pressure increases;

2. Carbon dioxide content of gas mixture increases, dissociation pressure decreases;

3. At low temperature more carbon dioxide form hydrate as compared to methane;

4. At low pressure region (associated with low temperature) the higher the pressure is, the lower the mole fraction of carbon dioxide in vapor phase;

5. The lower the temperature is, the larger the difference in the concentration of carbon dioxide in hydrate phase and in vapor phase indicating a better separation.

The concentration of carbon dioxide in the hydrate phase is always higher than that of the vapor phase, indicating the possibility of capturing carbon dioxide in hydrate. However, there is a trade-off between high concentration of carbon dioxide and solid hydrate fraction (efficiency of separation).

The lowest temperature studied here was θ = –6 °C. In future it is proposed to investigate at still lower temperature, as well as adding more components of natural gas in the mixture. The ICON and *K*-factor methods are only considered as means for predicting hydrate dissociation temperature, pressure, phase equilibrium composition. They give the effects of temperature, pressure, gas composition, and water content, for the dissociation of gas hydrate. The exact temperature, pressure and equilibrium composition of the phases must be compared by experiments.

List of symbols

K　– phase equilibrium constant

p　– pressure, kPa

r　– water/gas mole ratio

R^2　– correlation coefficient

T　– thermodynamic temperature, K

V　– volume, dm³

x　– mole fraction, %

x_i　– hydrate mole fraction, %

y_i　– vapor mole fraction, %

z　– composition of feed gas mixture, %

θ　– temperature, °C

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