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Purification of Natural Gas with High CO₂ Content by Formation of Gas Hydrates: Thermodynamic Verification

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Abstract: High carbon dioxide (CO₂) content in natural gas may constitute some environmental hazards when release to the atmosphere. A variety of conventional separation methods are presently being used to remove the undesired gas fraction from crude natural gas. One promising approach to capture CO₂ from natural gas is by formation of gas hydrate. Gas hydrates can be formed in a system containing water and small molecule gases such as CH₄ and CO₂ at appropriate pressure and temperature conditions. It is important to gain accurate data of the phase behavior of the gas hydrate forming systems to ensure that the process conditions are set in hydrate forming conditions. In this study, thermodynamics modeling approached is implemented to generate the phase equilibria data since the phase behavior measurements are often expensive, tedious and time consuming processes. The thermodynamic program, CSMGem is successfully used for prediction of equilibrium conditions for single and binary hydrate former systems with AAD% is less than 10%. The program is being further used to predict gas hydrate equilibrium for natural gas with different concentration of CO₂.

Key words: Natural gas, carbon dioxide, gas hydrate, phase equilibria, thermodynamic modelling

INTRODUCTION

Nowadays, natural gas has become an important source of energy and feedstock for chemical industries (Scholz *et al.*, 1981; Xiao *et al.*, 2009). Natural gas is a mixture of combustible gases formed underground by the decomposition of organic materials in plant and animal. Raw natural gas is composed of several gases. The main component is methane and it also contains varying amounts of heavier hydrocarbons, acid gases, water, mercury and inert gases (Mokhatab *et al.*, 2006).

Malaysia has the largest natural gas reserved among the Southeast Asian economies and is the third largest amongst the Asia Pacific economies. As per 1st January 2000, the recoverable reserves of Malaysian natural gas stand at 84.4 trillion standard cubic feet of which 48% is located at offshore Sarawak, 43% offshore east coast of Peninsular Malaysia and the remaining 9% at offshore Sabah. These large gas reserves are sufficient to last around 43 years with current production rate (Zulkifli *et al.*, 2002).

In natural gas, non-hydrocarbon gases (CO₂, N₂, H₂S) can account between 1 to 99% of overall composition (Thrasher and Fleet, 1995). High CO₂ concentrations are encountered in diverse areas including South China Sea, Gulf of Thailand, Central European Pannonian basin, Australian Cooper-Eromanga basin, Colombian Putumayo

basin, Ibleo platform, Sicily, Taranaki basin, New Zealand and North Sea South Viking Graben (Thrasher and Fleet, 1995). The composition of CO₂ can reach as high as 80% in certain natural gas wells such as wells at the LaBarge reservoir in western Wyoming and the Natuna production field in Indonesia (Holder *et al.*, 1988).

Due to stringent regulation on CO₂ content in commercial natural gas, high CO₂ content in natural gas has to be removed. Various methods for removing CO₂ have been suggested such as cryogenic fractionation, selective adsorption, gas absorption and membrane process. Although some of these processes have proved successful for the selective removal of CO₂ from multi-component gaseous streams, they still have some critical problems associated with large energy consumption, corrosion, foaming and low capacity (Kang and Lee, 2000). Moreover, the current technologies cannot purify CO₂ effectively when CO₂ increase to 50-80% in the natural gas stream. Hence, new separation technology which is environmental friendly and with low operational cost must be developed to cater for the separation of CO₂ from this high CO₂ content natural gas. One promising approach to capture CO₂ from natural gas is through gas hydrate formation. When gas hydrates are formed from natural gas, the concentrations of natural gas components in hydrate phase are different than that in the original gas mixtures.

Gas or clathrate hydrates are ice-like crystalline compounds which are formed through combination of water and small guest molecules like CH₄, CO₂, etc. under suitable conditions of low temperature and high pressure (Sloan and Koh, 2008). In a gas hydrate molecule, water forms special cavities and guest molecules are trapped inside the cavities. Depending on the type and size of guest molecule presents, different gas hydrate structures can be formed.

The three most common types of clathrate hydrate: structure I (sI), structure II (sII) and structure H (sH) have been well defined by Sloan and Koh, 2008. The type of hydrate that forms will highly depend on the composition of the gases in the feed as well as temperature and pressure of the system.

Over the last decade, the interest in using clathrate hydrates formation as separation method or storage and transportation medium has revived, especially for natural gas and CO₂. In literature, separation of CO₂ from gas streams and its sequestration in geological formation by gas hydrate formation have been widely studied by Sabil *et al.* (2010a,b). When gas hydrates are formed from natural gas, the concentrations of natural gas components in hydrate phase are different than that in the original gas mixtures. For example, in the case of methane-carbon dioxide (CO₂-CH₄) mixture, the hydrate phase will be richer in CO₂ than that CH₄ at certain condition (Kang and Lee, 2000). This selective information is the basis for utilization of gas hydrate formation as a separation process.

In order to successfully implement the hydrate formation as a method for separation of CO₂ from natural gas stream, the phase equilibria data need to be determined. The phase boundaries will limit the region in which this technology can be used for the separation process. In this study, thermodynamics modeling approached is implemented to generate the phase equilibria data since the phase behavior measurements are often expensive, tedious and time consuming processes. Since the modeling approached has been selected, a verification of the model is initially with some available literature data for single hydrate former system. The AAD% is calculated between the experimental and the modeling results. Once the model is proven suitable, the model is used to generate data for the binary and multi components systems.

THERMODYNAMIC APPROACH

The pressure and temperature conditions for the formation or dissociation of gas hydrate are governed by the thermodynamic equilibrium (Sloan and Koh, 2008). A system is in thermodynamic equilibrium when it is in

thermal, mechanical and chemical equilibrium. For a system at constant pressure and temperature, thermodynamic equilibrium can be characterized by the minimization of Gibbs energy. According to standard thermodynamic phase equilibrium criteria, the chemical potential of each component must be the same in every phase at equilibrium conditions.

$$\mu_A^1 = \mu_A^2 = \dots = \mu_A^k \quad (1)$$

where, μ_i^1 is the chemical potential of component A in phase 1 and k is the number of coexisting phases for multiphase multicomponent equilibria.

Based on the above equations, the equilibrium condition may be calculated either by direct minimization of the Gibbs' energy or by using the principle of equality of chemical potentials (Walas, 1985). The chemical potential can be expressed in terms of the fugacity of a component by the following Equation (2):

$$\mu = \mu^0 + RT \ln \frac{f(p)}{P^0} \quad (2)$$

where μ^0 is the chemical potential at reference state, T is the temperature, R is the universal gas constant, P⁰ is the pressure at the reference state and f (p) is the fugacity as a function of pressure. Combination of Eq. 1 and 2 results in the equality of fugacities for the thermodynamic equilibrium under consideration:

$$f_A^1 = f_A^2, f_B^1 = f_B^2 \quad (3)$$

where, f is the fugacity of component A or B in phase 1 or 2.

The fugacity approach as proposed by Kluda and Sandler (2000) has been used to model the hydrate in equilibrium. Their approach is basically based on solving the condition of equal fugacities of water in the hydrate phase and the fluid phases as shown in Eq. 4.

$$f_w^H(T, P) = f_w^F(T, P, x) \quad (4)$$

The thermodynamic modeled has been developed in commercial available hydrate software, CSMGem. Ballard and Sloan (2004) have reported the schematic of development procedure for the selected hydrate program. It has been proven that the hydrate formation temperatures and pressures for uninhibited systems are predicted quite well by CSMGem as compared with four other commercial hydrate programs; CSMHyd, DBRHydrate, Multiflash and PVTsim (Ballard and Sloan, 2002).

The present study shows the gas hydrate boundary conditions for natural gas components with different compositions, pressure:

$$AAD(\%) = (1/N) \sum_j^N \left| \frac{P_{cal} - P_{exp}}{P_{exp}} \right| \times 100 \quad (5)$$

and temperature conditions. To verify the accuracy of the model, absolute deviation (AAD%) has been calculated by comparing the predicted data with available literature data for single component systems such as methane, ethane, propane, carbon dioxide and nitrogen with water. Then, similar evaluations are carried out for binary gas systems with water.

RESULTS AND DISCUSSION

Equilibria of pure hydrate formers: A few single components in natural gas were selected to predict the hydrate phase equilibria when they are in contact with water. Hydrate equilibrium data for single gas hydrates such as methane, ethane and propane will become a basis for further understanding if phase equilibria of water with binary hydrate former systems. Figure 1 and 2 show the predicted three phase equilibria (hydrate-liquid water-vapor), H-L_w-V for pure component systems; CH₄ and CO₂ with available measurement data. As shown in the figures, pressure increases steeply with increasing temperature. Methane hydrate system yield a good agreement with available literature data but the hydrate equilibrium curves for CO₂ hydrate is slightly fluctuating with literature data. Technically, methane with small size of molecules forms sI hydrate whereas intermediate size of carbon dioxide allows its molecules to occupy the large cavity (5¹²6²) of sI hydrate.

Table 1 shows the absolute average deviation (AAD%) for five different pure components that have been studied in this work. All the hydrate formers have less than 5% of AAD and it can conclude that the pressure prediction for pure components using CSMGem gives good agreement with the available literature data. A maximum deviation of 4% is obtained by propane as a hydrate former and followed by carbon dioxide. Such a graphical comparison of data and deviation calculation for single-component hydrate formers gave reassurance that the prediction for hydrate equilibrium are acceptable in order to proceed to binary and multicomponent predictions.

Figure 3 shows the predicted hydrate equilibrium data for five different pure components in natural gas. The hydrate equilibrium lines of all components in natural gas have been compared since the work is on the separation

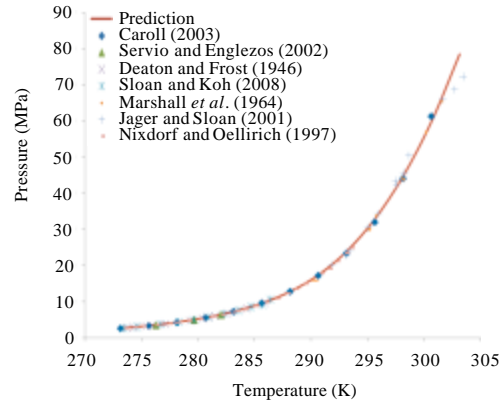


Fig. 1: Three phase (H-L_w-V) equilibrium line for methane hydrate system

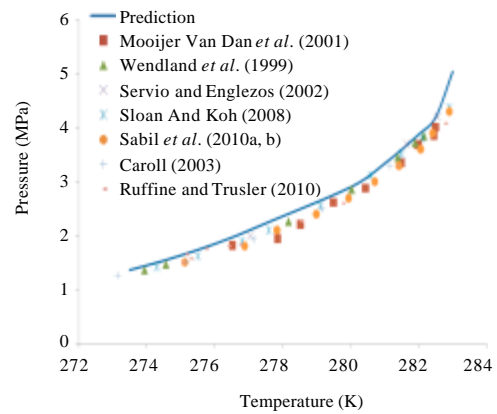


Fig. 2: Three phase (H-L_w-V) equilibrium line for carbon dioxide hydrate system

of CO₂ from natural gas. It been clearly observed that nitrogen tends to form a hydrate at higher pressure than the other four components at same temperature.

Due to differences in the volume and enthalpy of the vapour and liquid hydrocarbon, the three-phase hydrate formation line for ethane, propane and carbon dioxide change from H-L_w-V to H-L_w-L_{HC} (L_{HC} is liquid hydrocarbon). For each pure hydrate former, the predictions were bounded by the ice point (273 K) and the upper quadruple point (H-L_w-L_{HC}-V). Quadruple point is noted by the phases that are in equilibrium. Basically the lower quadruple point (Q₁) is approximately where the hydrate line intercepts the melting curve of pure water. Thus, all single hydrate formers have Q₁ approximately at 0°C (273 K). While the upper quadruple point (Q₂) is an interception within the hydrate line and the vapour pressure curve of the pure hydrate former. Neither

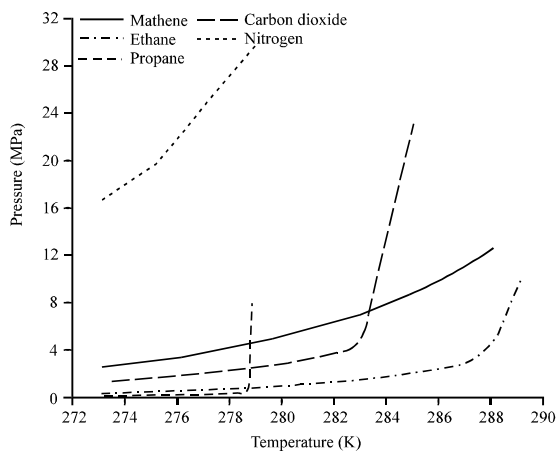


Fig. 3: Predicted hydrate equilibrium of single components in natural gas

Table 1: Absolute deviation (AAD%) results between the experimental data and predicted data for single hydrate systems

Hydrate former	No. of points	References	AAD (%)
Methane (CH ₄)	101	Servio and Englezos (2002)	1.5768
		Adisasmito <i>et al.</i> (1991)	
		Jager and Sloan (2001)	
		Carrol (2003)	
		Deaton and Frost (1946)	
Ethane (C ₂ H ₆)	62	Marshall <i>et al.</i> (1964)	2.6357
		Nixdorf and Oellrich (1997)	
		Deaton and Frost (1946)	
		Nixdorf and Oellrich (1997)	
		Holder and Hand (1982)	
		Galloway <i>et al.</i> (1970)	
		Holder and Grigoriou (1980)	
Propane (C ₃ H ₈)	39	Avlonitis (1988)	4.0267
		Reamer <i>et al.</i> (1952)	
		Deaton and Frost (1946)	
		Nixdorf and Oellrich (1997)	
		Miller and Strong (1946)	
Carbon Dioxide (CO ₂)	56	Robinson and Mehta (1971)	3.9056
		Kubota <i>et al.</i> (1984)	
		Adisasmito <i>et al.</i> (1991)	
		Carrol (2003)	
		Wendland <i>et al.</i> (1999)	
Nitrogen (N ₂)	73	Mooijer-van den Heuvel <i>et al.</i> (2001)	1.8734
		Servio and Englezos (2001)	
		Sabil <i>et al.</i> (2010b)	
		Ruffine and Trusler (2010)	
		Marshall <i>et al.</i> (1964)	
		Nixdorf and Oellrich (1997)	
Van Cleeff and Diepen (1960)			
Mohammadi <i>et al.</i> (2003)			
Jhaveri and Robinson (1965)			

nitrogen nor methane has an upper quadruple since they have lower critical points which are far below the Q₁. Such low critical temperatures prevent intersection of the vapour pressure line with H-L_w-V line above 273 K to produce an upper quadruple point. Methane and carbon dioxide hydrates have been compared in detail since

methane is the main component in the natural gas. It can clearly been observed that carbon dioxide favor to form hydrate than that methane in the region T = 273.2 to 283.3 K and P = 1.2 to 7.4 Mpa. But the hydrate phase will start richer with methane above this region due to the sudden changes of hydrate equilibrium line of carbon dioxide hydrate from the upper quadruple point.

Equilibria of binary guest mixtures: Similar evaluations have been carried out for binary gas systems with water. Table 2 shows the outcomes of absolute deviation (AAD%) for binary mixtures of methane with ethane, propane, carbon dioxide and nitrogen.

Table 2 has shown that all the predicted data are in accordance with previously published work. In general, according to the Gibbs phase rule, for a ternary system (included water) which consisting of two gases + water, the three-phase equilibrium has two degrees of freedom. Thus, a second intensive variable need to be defined as an addition of temperature for equilibrium pressure prediction. The overall composition of the feed stream has been well defined for this case. There are a decrease of hydrate pressure in the mixtures of methane with ethane and propane as compared with pure methane hydrate. These phenomena happen due to the changing of hydrate structure which is from sI to sII. In contrast, the hydrate equilibrium pressure increases as concentration of nitrogen in methane+nitrogen system increase. As been discussed before, nitrogen molecules itself will form hydrate at higher pressure as compared with the other components. Thus, the presence of nitrogen in the mixture will increase the hydrate pressure until it reaches the pure nitrogen hydrate equilibrium line as the concentration of nitrogen in the system increase.

Basically it is not easy to generalize which hydrate structure will be present when sI and sII hydrate formers are in a mixture. In pure water, methane forms sI hydrate with its molecules occupying the small cavities (5¹²). Since the molecular diameter of methane (4.4 Å) is smaller than the free diameters (~ 5.76 Å) of most cavities in the hydrate lattice, methane molecules can migrate in the hydrate lattice. Methane molecules will occupy the small cage in sII hydrate when there is the larger hydrate former present in the system. Thus, sII hydrate is formed for binary system of CH₄-C₃H₈ since propane molecules cannot enter any of the sI cavities. In this system, methane will occupy the small cavities while propane molecules occupy the larger cavities of structure II hydrate. Although methane and ethane form sI hydrates by themselves, the mixture of these components form sII hydrates at certain compositions. Subramanian *et al.* (2000) have reported that the structure of methane+ethane

Table 2: Absolute deviation (AAD%) results between the experimental data and predicted data for binary hydrate systems

Mixtures	No. of points	References	AAD (%)
CH ₄ -C ₂ H ₆	59	Deaton and Frost (1946) Nixdorf and Oelrich (1997) Holder and Grigoriou (1980)	4.2517
CH ₄ -C ₃ H ₈	59	Deaton and Frost (1946) Nixdorf and Oelrich (1997) Verma <i>et al.</i> (1975)	5.3372
CH ₄ -CO ₂	69	Adisasmito <i>et al.</i> (1991) Zhu <i>et al.</i> (2005) Fan and Guo (1999)	3.1032
CH ₄ -N ₂	50	Nixdorf and Oelrich (1997) Jhaveri and Robinson (1965) Mei <i>et al.</i> (1996)	8.4759

hydrates changes from sI to sII over a methane vapor composition range (y_{CH_4}) of 0.736–0.994 at 274.2 K.

The pressure versus temperature (P-T) diagram for CH₄-CO₂ mixtures have not been plotted due to inconsistency of CH₄ composition in the mixture from the literature data. But still the mixture has less AAD% as compared with the other three mixtures. Since the separation of CO₂ from natural gas mixture is the main objective of this work, P-T diagram for CH₄ - CO₂ system has been plotted using the predicted data (Fig. 4) at different concentration of CO₂. The purpose of doing this is to study the effect of CO₂ composition in the mixture. Hydrate equilibrium lines for pure CH₄ and CO₂ hydrates are plotted in the same graph for comparison purpose.

Phase equilibria of CH₄-CO₂ mixtures were investigated at temperature between 273.15 and 283.15 K. Mixture of CO₂ and CH₄ form sI hydrate only, like pure CO₂ and CH₄ with water (Uchida *et al.*, 2005). In the mixture of 50% CH₄-50% CO₂, the equilibrium line is predicted close to CO₂ hydrate line instead of in the middle of the both single hydrate formers. Gaudette *et al.* (1996) have determined that the distribution coefficient of methane between the gas and hydrate phase is approximately 2 for mixture of 50/50 CH₄- CO₂. Therefore, CO₂ hydrates do indeed form selectively over methane hydrates in the presence of 50/50 gas mixture. Seo *et al.* (2000) reported that the composition of CO₂ in the hydrate phase increase with increasing the CO₂ composition in vapor phase and decreasing the system pressure (Seo *et al.*, 2000). This selective information will be the basis for utilization of gas hydrate formation as an approach to separate carbon dioxide from methane.

Equilibria of natural gas with different concentration of carbon dioxide: Hydrate formation conditions were also been predicted for natural gas mixtures with and without CO₂. Several natural gases containing CO from three gas production fields have been reported by Adisasmito and Sloan (1992) are listed in Table 3 (Adisasmito and Sloan, 1992). The pure CO₂ was included to indicate the whole range of concentration.

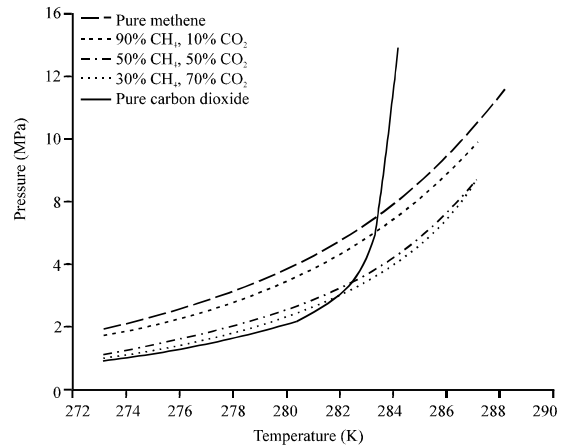


Fig. 4: Predicted hydrate equilibrium data for CO₂-CH₄ system

Table 3: Five different concentration of natural gas components

Component	Gas A	Gas B	Gas C	Gas D	Gas E	Gas F
CH ₄	76.62	52.55	24.42	12.38	7.86	-
C ₂ H ₆	11.99	8.12	3.99	1.96	1.13	-
C ₃ H ₈	6.91	4.74	3.07	1.66	0.86	-
i-C ₄ H ₁₀	1.82	1.31	0.75	0.37	0.20	-
n-C ₄ H ₁₀	2.66	1.88	0.92	0.48	0.33	-
CO ₂	-	31.40	66.85	83.15	89.62	100

The hydrate phase equilibria for natural gas system with overall carbon dioxide concentration of 31.4, 66.85, 83.15 and 89.62 mol% are depicted in Fig. 5. The temperatures have been further extended to predict the hydrate formation pressure since the temperature in literature is limited to 282 K. From the graph, it can be clearly observed that the equilibrium curve shift towards higher pressures as concentration of carbon dioxide in natural gas increase. The concentration of carbon dioxide in the system is obviously affecting the hydrate formation condition. The result obtained with the natural gases show the expected dependence of gas composition on the equilibrium conditions.

The hydrate equilibrium line rises vertically from the upper quadruple point (Q₂), with very large pressure changes for small temperature changes for each gas except gas A. Hydrate equilibrium line for gas A almost identical with that pure methane since the gas is mainly consist of methane. Structure II hydrates are formed in gas A, B and C which the small cavities are occupied by methane while the large cavities are mostly occupied by the other large components such as propane, isobutane and butane. In the mixtures have high concentration of CO₂ like gas D and E, structure I hydrates are formed where small cavities are occupied by methane. While the large cavities of structure I are being occupied by methane, ethane and carbon dioxide. In this condition, the

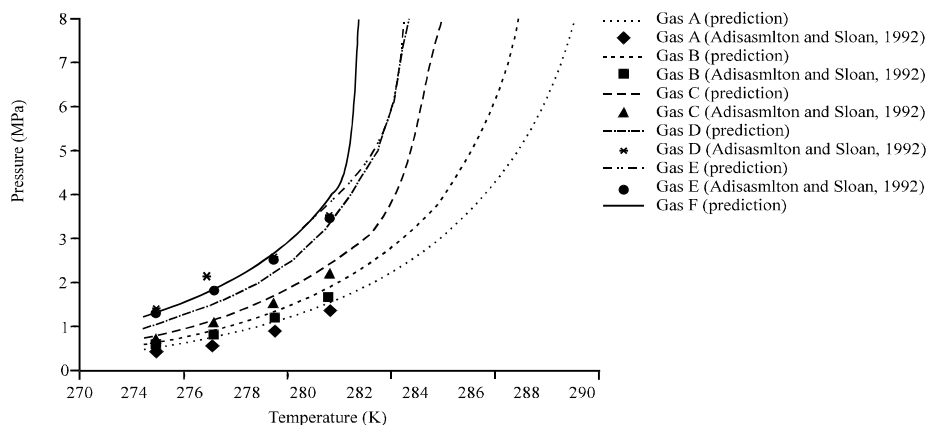


Fig. 5: Hydrate equilibrium data of natural gas with different concentration of carbon dioxide

very large molecules such as propane, butane and isobutane will act as gas diluents and do not participate in the structure I hydrate (Gaudette, *et al.*, 1996). Therefore, both gases required higher pressure for structure I formation.

CONCLUSION

In this study, the thermodynamics model has been successful used to predict the phase equilibrium data for single, binary and multi components hydrate former systems. The predicted data of the model has been compared with experimental data for single hydrate former systems including CH_4 , CO_2 systems and the calculated AAD% is less than 5% for three phase equilibrium condition namely H-L_w-V. The model is successful used to predict the mentioned equilibrium condition for binary and multi-component hydrate formers system. From this phase behavior data, the region where the hydrate formation can be used as separation process for CO_2 from natural gas can be identified.

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