Gas-Hydrate Phase Equilibria for the High-Pressure Recycled-Hydrogen Gas Mixtures[†]

Qing-Lan Ma,* Xiu-Lin Wang, Guang-Jin Chen, Chang-Yu Sun, and Lan-Ying Yang

High Pressure Fluid Phase Behavior & Property Research Laboratory, China University of Petroleum, Fuxue Road, Changping District, Beijing 102249, P. R. China

A novel technique for hydrogen recovery from the high-pressure recycled-hydrogen gas mixtures through forming hydrate was proposed. The systematic experimental studies were performed on the gas-hydrate equilibrium for two gas mixtures in pure water and the oxacyclopentane aqueous solution. The effect of temperature, pressure, and initial gas−liquid ratio on the separation was studied. The gas-hydrate equilibrium data were obtained at pressures ranging from (10 to 12) MPa and at temperatures from (274.15 to 281.15) K. The experiments provided the fundamental data for designing the industrial process and determining the suitable operational conditions. The measured data were compared with the predictions by using the Chen−Guo hydrate thermodynamic model.

Introduction

Enhancing the partial pressure and hydrogen content in the hydrogen cracking is of high benefit to enhancing the rate of desulfating, denitrogenating, and saturating the unsaturated hydrocarbons to improve the quality of oil.[1] In the practical operation, some light hydrocarbons, such as methane and ethane, would remain in the recycled hydrogen, which would reduce the hydrogen content in the reactor and therefore reduce the reaction rate and the recovery efficiency of product.[1] Generally, some amount of recycled hydrogen is discharged from the process, and some fresh hydrogen is added to maintain the partial pressure and hydrogen content. The discharge of recycled hydrogen will increase the hydrogen consumption and bring about a great economic loss. If the light hydrocarbons in the recycled hydrogen mixture could be removed effectively, the hydrogen would be enriched, which would decrease the amount of recycled hydrogen discharged and could keep the hydrotreating facilities running safely and economically for a long time. Currently, the hydrotreating is performed at a pressure higher than 10 MPa, and the mole fraction of hydrogen in the recycled hydrogen mixture is required to be more than 0.85. The conventional approaches for hydrogen recovery include cryogenic separation, adsorption, and membrane separation.[2,3] However, the cryogenic separation consumes a large amount of refrigeration energy. The separation efficiency of adsorption and membrane separation is relatively low, and the hydrogen pressure after separation will be lowered greatly. In recent years, it has been accepted that separating gas mixture by forming hydrate is advantageous for the low-boiling gas mixtures such as (H_2 + CH_4). There have been many studies reported related to applying hydrate technique to the separation of gas mixture.[4−13] Gas hydrate is such an inclusion compound in which the cage-like structure of hydrogen-bonded water molecules could include a variety of guest molecules.[14] The basic mechanism of separating gas

mixture by forming gas hydrates is that, after hydrate formation from a gas mixture, the compositions of gas components are different in the equilibrious vapor and hydrate phases because of the differences in hydrate formation conditions of the gas components. Hydrogen can hardly form hydrate at relative low pressures because its molecular diameter is too small to stabilize the cavities. Hydrogen can form structure II (sII) clathrate hydrates only at very high pressures (∼200 MPa at T/K ≈ 273) without a promoter.[15,16] Therefore, recovering hydrogen from recycled hydrogen by forming hydrate is regarded as a perfect approach. Almost all hydrogen could be separated from light hydrocarbons through forming hydrate at a temperature slightly above 273.15 K and a pressure below 5.0 MPa.

In this work, a systematic gas-hydrate phase equilibrium study was performed on the recovery of hydrogen from two synthetic high-pressure recycled-hydrogen gas mixtures. The influence of temperature, pressure, and initial gas−liquid ratio on the separation was surveyed. Considering that the hydrogen hydrate formation pressure can be lowered by adding the thermodynamic promoter oxacyclopentane,[17,18] the experimental observation was carried out on the system containing oxacyclopentane to explore the influence of oxacyclopentane on the separation efficiency. The experimental study has provided the basic data for the industrial process design of recovering hydrogen from a high-pressure recycled-hydrogen gas mixture via the hydrate technique.

Experimental Apparatus and Procedures

Materials. Analytical grade hydrogen and hydrocarbon gases supplied by Beifeng Gas Industry Corporation, Ltd., China, were used in preparing the synthetic gas mixtures. A Hewlett-Packard gas chromatograph (HP 6890 with a thermal conductivity detector) was used to analyze the composition of the gas mixture. The deviation of the mole composition (three parallel analyses) was less than 0.01 %. The oxacyclopentane used for preparing the aqueous solution was supplied by Beijing Reagents Corporation (BRC). Water used in the experiments was deionized and distilled. Referring to the typical recycled-hydrogen

---

* Corresponding author. Phone: +86 10 89732126. E-mail: maql@cup.edu.cn.

Table 1. Composition of the Gas Mixtures

gas mixture	H_2	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$
M_1	0.8734	0.0570	0.0122	0.0218	0.0230	0.0043	0.0070	0.0013
M_2	0.8995	0.0583	0.0124	0.0088	0.0092	0.0040	0.0066	0.0012

Table 2. Gas-Hydrate Equilibrium Data of M_1 in Pure Water at the Different Temperature Conditions ($P = 12.0$ MPa, $R = 160$ v/v)

		$T/\text{K} = 274.15$		$T/\text{K} = 275.15$		$T/\text{K} = 276.15$		$T/\text{K} = 277.15$		$T/\text{K} = 278.15$	
	z_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8734	0.9500	0.0592	0.9457	0.0581	0.9405	0.0554	0.9386	0.0536	0.9369	0.0524
CH_4	0.0570	0.0313	0.3301	0.0318	0.3410	0.0333	0.3460	0.0338	0.3486	0.0345	0.3479
C_2H_6	0.0122	0.0077	0.0600	0.0080	0.0595	0.0092	0.0488	0.0095	0.0461	0.0097	0.0445
C_3H_8	0.0218	0.0031	0.2205	0.0039	0.2235	0.0055	0.2205	0.0057	0.2242	0.0054	0.2338
$i\text{-}C_4H_{10}$	0.0230	0.0022	0.2441	0.0039	0.2383	0.0040	0.2547	0.0044	0.2568	0.0048	0.2583
$n\text{-}C_4H_{10}$	0.0043	0.0017	0.0319	0.0021	0.0291	0.0024	0.0275	0.0027	0.0244	0.0031	0.0198
$i\text{-}C_5H_{12}$	0.0070	0.0034	0.0453	0.0038	0.0431	0.0043	0.0399	0.0044	0.0397	0.0046	0.0380
$n\text{-}C_5H_{12}$	0.0013	0.0006	0.0087	0.0008	0.0069	0.0008	0.0074	0.0009	0.0063	0.0010	0.0052
$100 \cdot \alpha$		99.42		99.45		99.52		99.54		99.57	

Table 3. Gas-Hydrate Equilibrium Data of M_1 in Pure Water at the Different Pressure Conditions ($T = 274.15$ K, $R = 160$ v/v)

		$P/\text{MPa} = 10.0$		$P/\text{MPa} = 10.5$		$P/\text{MPa} = 11.0$		$P/\text{MPa} = 11.5$		$P/\text{MPa} = 12.0$	
	z_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8734	0.9429	0.0373	0.9454	0.0416	0.9480	0.0475	0.9490	0.0548	0.9500	0.0592
CH_4	0.0570	0.0371	0.2966	0.0350	0.3110	0.0322	0.3317	0.0316	0.3322	0.0313	0.3301
C_2H_6	0.0122	0.0078	0.0652	0.0075	0.0665	0.0078	0.0609	0.0077	0.0610	0.0077	0.0600
C_3H_8	0.0218	0.0036	0.2409	0.0036	0.2320	0.0035	0.2245	0.0035	0.2201	0.0031	0.2205
$i\text{-}C_4H_{10}$	0.0230	0.0025	0.2698	0.0024	0.2609	0.0024	0.2512	0.0023	0.2473	0.0022	0.2441
$n\text{-}C_4H_{10}$	0.0043	0.0019	0.0332	0.0019	0.0320	0.0019	0.0309	0.0018	0.0314	0.0017	0.0319
$i\text{-}C_5H_{12}$	0.0070	0.0035	0.0491	0.0035	0.0474	0.0035	0.0458	0.0034	0.0460	0.0034	0.0453
$n\text{-}C_5H_{12}$	0.0013	0.0007	0.0085	0.0007	0.0082	0.0007	0.0079	0.0007	0.0078	0.0006	0.0087
$100 \cdot \alpha$		99.68		99.62		99.55		99.47		99.42	

mixtures, two gas mixtures were prepared. The mole compositions of the mixtures are listed in Table 1.

Apparatus. The experimental apparatus used in this study has been described in detail in previous papers by this laboratory.[19−23] The apparatus consisted of a cylindrical transparent sapphire cell (2.54 cm in diameter, effective volume of 60 cm³) installed in an air bath and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation of the hydrate crystals in the solution can be observed directly through the transparent cell wall. The accuracy of temperature and pressure measurements was ± 0.2 K and ± 0.025 MPa, respectively.

Procedure. First, the sapphire cell was cleaned with deionized water and then rinsed three times with the prepared experimental liquid. After the cell was thoroughly cleaned, 20 cm³ of liquid sample was added into the cell, which was then installed in the air bath. The air-bath temperature was adjusted to the given value. After being equilibrated with the bath temperature, the cell was then charged with the gas mixture to 1.0 MPa and vented three times to ensure the absence of air before being charged to the given pressure and starting the motor and the data acquisition system. Subsequently, hydrate nucleation was then started with the agitation of the magnetic stirrer. The system pressure was kept stable for 2 h. When the gas-hydrate equilibrium was established, the gas phase was sampled and analyzed at least three times using the gas chromatograph. The average values were then taken as the compositions of gas phase. The compositions of components in the hydrate phase were obtained by analyzing the compositions of gas released from dissociated hydrate with the gas chromatograph.

Results and Discussion

In this study, the compositions of gas mixtures in the gas and hydrate phases were water- and oxacyclopentane-free. z_i,

x_i, and y_i represent the mole fraction of component i in the feed gas (the prepared gaseous mixture sample), the hydrate phase, and the gas phase, respectively. R is the initial gas−liquid ratio. The hydrogen recovery efficiency in the gas phase, α, was defined as

$$\alpha = \frac{ey_{H_2}}{z_{H_2}} \qquad (1)$$

where the mole fraction of the gas phase at equilibrium, e, is determined with the following mass balance equation

$$e = \frac{z_i - x_i}{y_i - x_i} \qquad (2)$$

First, the gas-hydrate equilibria of two synthetic gas mixtures in the pure water were surveyed. The experimental data obtained are listed in Tables 2 to 5. Tables 2 to 4 give the effects of temperature, pressure, and initial gas−liquid ratio on the gas-hydrate equilibrium for the gas mixture M_1. The data indicate that the low temperature and high pressure benefit the hydrate formation. As a result, we could obtain the gas mixture with a high content of hydrogen under this condition. The mole fraction of hydrogen in the gas phase was enriched from 0.8734 to 0.9500 at 274.15 K and 12 MPa. However, the occupancy capacity of hydrogen in the hydrate cavities would increase with the increase of pressure; therefore, high pressure would reduce the hydrogen recovery efficiency. The hydrogen content in the gas phase was even affected by the initial gas−liquid ratio. The smaller the initial gas−liquid ratio, the higher the hydrogen content in the gas phase. The reason for this is that the small gas−liquid ratio means there was more water in the system and

Table 4. Gas-Hydrate Equilibrium Data of M_1 in Pure Water at the Different Initial Gas−Liquid Ratio Conditions ($P = 12.0$ MPa, $T = 274.15$ K)

|	z_i	$v/(v/v) = 140$		$v/(v/v) = 160$		$v/(v/v) = 180$		$v/(v/v) = 200$	
		y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8734	0.9513	0.0630	0.9500	0.0592	0.9471	0.0552	0.9428	0.0510
CH_4	0.0570	0.0309	0.3285	0.0313	0.3301	0.0319	0.3358	0.0331	0.3403
C_2H_6	0.0122	0.0073	0.0632	0.0077	0.0600	0.0081	0.0577	0.0083	0.0584
C_3H_8	0.0218	0.0031	0.2163	0.0031	0.2205	0.0039	0.2206	0.0047	0.2245
$i\text{-}C_4H_{10}$	0.0230	0.0020	0.2415	0.0022	0.2441	0.0027	0.2485	0.0042	0.2458
$n\text{-}C_4H_{10}$	0.0043	0.0016	0.0324	0.0017	0.0319	0.0020	0.0298	0.0023	0.0280
$i\text{-}C_5H_{12}$	0.0070	0.0032	0.0465	0.0034	0.0453	0.0036	0.0448	0.0037	0.0461
$n\text{-}C_5H_{12}$	0.0013	0.0006	0.0086	0.0006	0.0087	0.0007	0.0080	0.0009	0.0060
$100 \cdot \alpha$		99.37		99.42		99.48		99.55	

Table 5. Gas-Hydrate Equilibrium Data of M_2 in Pure Water at the Different Temperature Conditions ($P = 12.0$ MPa, $R = 160$ v/v)

|	z_i	$T/K = 274.15$		$T/K = 275.15$		$T/K = 276.15$		$T/K = 277.15$		$T/K = 278.15$	
		y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8995	0.9359	0.0533	0.9334	0.0497	0.9313	0.0477	0.9288	0.0459	0.9253	0.0431
CH_4	0.0583	0.0426	0.4237	0.0428	0.4464	0.0435	0.4546	0.0448	0.4514	0.0471	0.4307
C_2H_6	0.0124	0.0090	0.0915	0.0095	0.0850	0.0097	0.0847	0.0100	0.0823	0.0102	0.0855
C_3H_8	0.0088	0.0028	0.1484	0.0034	0.1440	0.0037	0.1454	0.0041	0.1457	0.0043	0.1584
$i\text{-}C_4H_{10}$	0.0092	0.0018	0.1814	0.0025	0.1770	0.0034	0.1645	0.0039	0.1635	0.0042	0.1754
$n\text{-}C_4H_{10}$	0.0040	0.0024	0.0412	0.0028	0.0341	0.0029	0.0335	0.0029	0.0360	0.0031	0.0339
$i\text{-}C_5H_{12}$	0.0066	0.0047	0.0508	0.0048	0.0517	0.0047	0.0575	0.0047	0.0619	0.0049	0.0631
$n\text{-}C_5H_{12}$	0.0012	0.0008	0.0105	0.0008	0.0112	0.0008	0.0119	0.0008	0.0128	0.0009	0.0112
$100 \cdot \alpha$		99.76		99.78		99.81		99.85		99.86	

therefore the amount of hydrate formation was increased. The hydrocarbon molecules transferred into the hydrate phase were more than that of hydrogen. Consequently, the separation efficiency was enhanced. However, when the amount of water increased to some extent, the enrichment of hydrogen in the gas phase became less sensitive. In addition, too much water would increase the energy consumption of the recycled liquid pump in the practical process. According to the foregoing analysis, an optimization should be made when designing a separation process. The gas mixture M_2 contained more hydrogen and less C3+ fractions compared with the gas mixture M_1. The experimental data of M_2 are listed in Table 5. It could be seen that the hydrogen recovery efficiency was lower compared with the gas mixture M_1. The hydrate formation pressures of propane and butane are lower than methane and ethane at the same temperature.[24] Therefore, the hydrate

formation pressure of the gas M_2 would be higher than that of the gas M_1 under the same temperature because it contained few C3+ fractions, which means the hydrate formation driving force of the gas M_2 was less than that of the gas M_1 under the same condition. Hence, for the gas M_2, the amount of hydrate formation was less, and the separation efficiency was lowered.

Second, to enhance the separation efficiency, the experiments were performed for the gas M_2 with oxacyclopentane added into water. Oxacyclopentane can form sII hydrate very easily, especially when methane exists as a help gas. The hydrate formation pressure will increase with increasing hydrogen content in the gas mixture, which can be seen in Figure 1. Figure 2 shows the calculated hydrate formation conditions of the gas mixture M_2 in the absence and presence of oxacyclopentane by the Chen−Guo hydrate model.[25] It can be seen that the hydrate formation curve is shifted to the right with added oxacyclopentane, which means that the hydrate formation driving force is increased at the same operating pressure, and therefore the
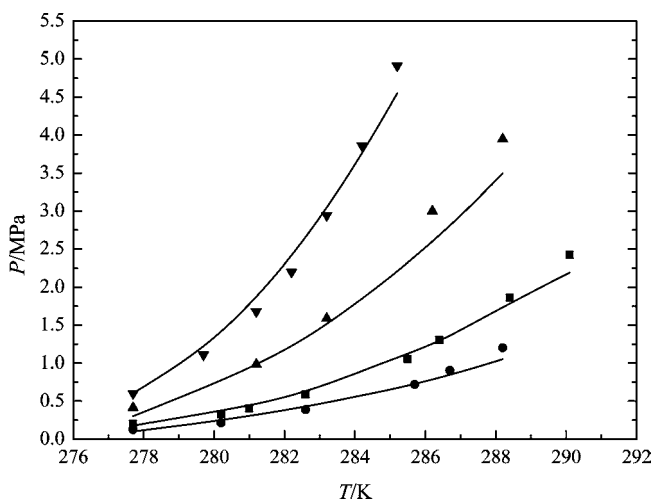
Figure 1. Hydrate formation conditions of hydrogen (1) + methane (2) gas mixtures in the presence of 0.06 oxacyclopentane in aqueous solution. ●, experimental data ($x_1 = 0.000$);[22] ■, experimental data ($x_1 = 0.3474$);[22] ▲, experimental data ($x_1 = 0.6971$);[22] ▼, experimental data ($x_1 = 0.8913$);[22] −, calculation results by the Chen−Guo hydrate model.[25]
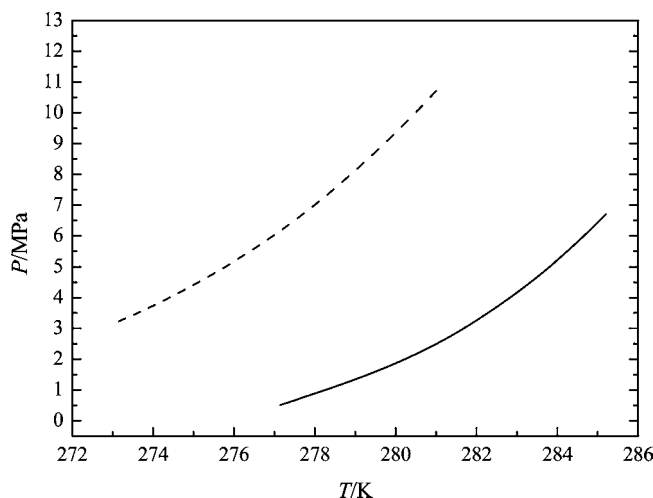
Figure 2. Structure-II hydrate formation conditions of the gas mixture M_2. - - -, without oxacyclopentane; —, with 0.01 oxacyclopentane.

Table 6. Gas-Hydrate Equilibrium Data of M_2 in the 0.01 Oxacyclopentane Aqueous Solution at the Different Temperature Conditions (P = 12.0 MPa, R = 160 v/v)

	z_i	T/K = 278.15		T/K = 279.15		T/K = 280.15		T/K = 281.15	
		y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8995	0.9496	0.0640	0.9482	0.0617	0.9474	0.0597	0.9461	0.0573
CH_4	0.0583	0.0246	0.6200	0.0248	0.6350	0.0251	0.6399	0.0255	0.6515
C_2H_6	0.0124	0.0097	0.0574	0.0102	0.0503	0.0103	0.0492	0.0105	0.0468
C_3H_8	0.0088	0.0032	0.1021	0.0034	0.1018	0.0035	0.1016	0.0037	0.1010
$i\text{-}C_4H_{10}$	0.0092	0.0030	0.1125	0.0031	0.1142	0.0034	0.1108	0.0036	0.1105
$n\text{-}C_4H_{10}$	0.0040	0.0031	0.0190	0.0033	0.0161	0.0033	0.0163	0.0034	0.0149
$i\text{-}C_5H_{12}$	0.0066	0.0058	0.0199	0.0059	0.0187	0.0059	0.0189	0.0061	0.0156
$n\text{-}C_5H_{12}$	0.0012	0.0010	0.0045	0.0011	0.0029	0.0011	0.0030	0.0011	0.0030
$100 \cdot \alpha$		99.59		99.63		99.64		99.67	

Table 7. Gas-Hydrate Equilibrium Data of M_2 in the Different Concentrations of Oxacyclopentane Aqueous Solutions (P = 12.0 MPa, T = 278.15 K, R = 160 v/v)

	z_i	C = 0.000		C = 0.005		C = 0.008		C = 0.010		C = 0.020	
		y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i	y_i	x_i
H_2	0.8995	0.9253	0.0431	0.9378	0.0597	0.9420	0.0636	0.9496	0.0640	0.9546	0.0664
CH_4	0.0583	0.0471	0.4307	0.0329	0.6155	0.0294	0.6265	0.0246	0.6200	0.0213	0.6181
C_2H_6	0.0124	0.0102	0.0855	0.0105	0.0541	0.0103	0.0537	0.0097	0.0574	0.0087	0.0684
C_3H_8	0.0088	0.0043	0.1584	0.0050	0.0922	0.0045	0.0933	0.0032	0.1021	0.0026	0.1026
$i\text{-}C_4H_{10}$	0.0092	0.0042	0.1754	0.0045	0.1123	0.0040	0.1114	0.0030	0.1125	0.0025	0.1106
$n\text{-}C_4H_{10}$	0.0040	0.0031	0.0339	0.0032	0.0215	0.0032	0.0197	0.0031	0.0190	0.0032	0.0161
$i\text{-}C_5H_{12}$	0.0066	0.0049	0.0631	0.0052	0.0373	0.0056	0.0263	0.0058	0.0199	0.0060	0.0157
$n\text{-}C_5H_{12}$	0.0012	0.0009	0.0112	0.0009	0.0078	0.0010	0.0051	0.0010	0.0045	0.0011	0.0027
$100 \cdot \alpha$		99.86		99.71		99.66		99.59		99.55	

operating temperature could be raised. The experimental data of M_2 on the gas-hydrate equilibrium versus temperature are listed in Tables 6 and 7. The mole concentration of oxacyclopentane in the aqueous solution was 0.01. Compared with the data of pure water system listed in Table 5, the operation temperature was raised at the same pressure with oxacyclopentane added, which could reduce the refrigeration energy consumption, and the separation efficiency was enhanced at the same time. Under the same conditions, for example, T = 278.15 K and P = 12.0 MPa, the mole fraction of hydrogen in the gas phase was enriched from 0.9253 to 0.9496 with oxacyclopentane added. The ratio of small to large cavities is 2:1 in sII hydrate. Oxacyclopentane and C3+ fractions will occupy most of the large cavities and cannot occupy the small cavities. Although hydrogen could occupy the small cavities stably at this condition, methane will be more stable than hydrogen in the small cavities,

which means methane will occupy the small cavities prior to hydrogen and will dominate the occupancy of small cavities. When oxacyclopentane is added, it is well-known that the converting rate will be much faster; therefore, more water and methane were converted into hydrate in 2 h. The mole fraction of methane in the hydrate phase was enriched from 0.4307 to 0.6200, and the separation efficiency could be enhanced. The effect of oxacyclopentane concentration on the gas-hydrate equilibrium was shown in Table 7. The hydrogen content in the gas phase increased with the oxacyclopentane concentration increasing. However, with the increasing hydrogen content and decreasing hydrocarbon fractions in the gas phase, the effect of oxacyclopentane concentration on the separation efficiency would be unnoticeable. Furthermore, increasing the oxacyclopentane concentration would bring about more hydrogen
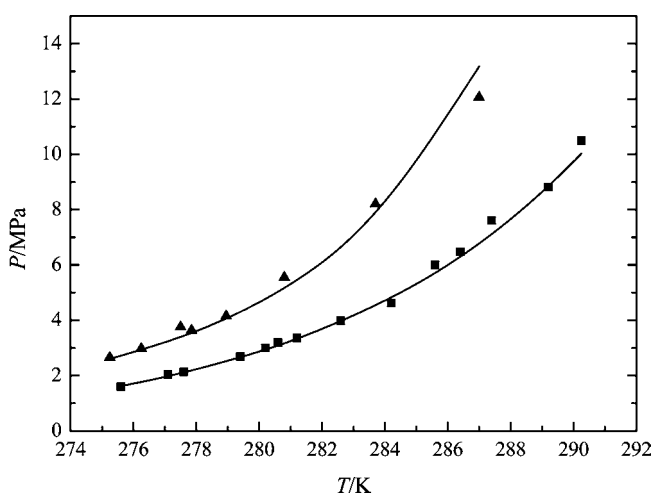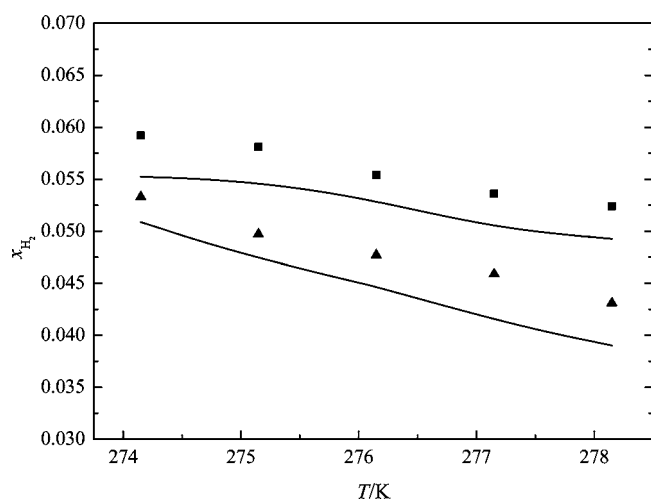

Figure 3. Hydrate formation conditions for (single sH hydrate former + methane) systems. ▲, experimental data for (i-pentane + CH_4);[26,27] ■, experimental data for (MCH + CH_4);[28−31] —, calculation results by the Chen−Guo hydrate model.[32]
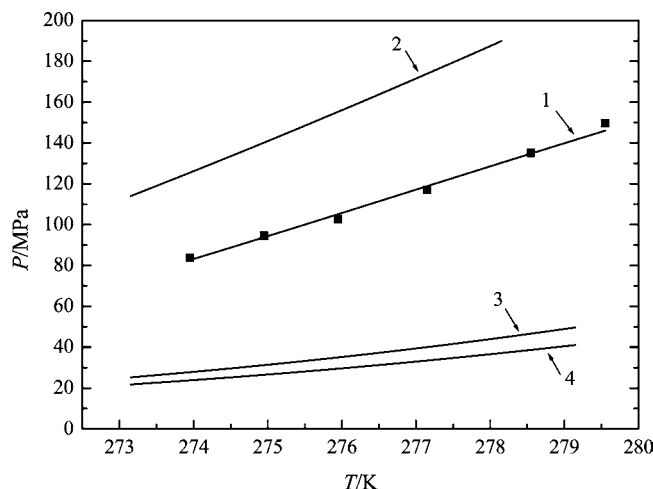
Figure 4. Structure-H hydrate formation conditions for systems containing hydrogen. ■, experimental data for (MCH + H_2);[33] line 1, calculation result for (MCH + H_2); line 2, calculation result for (i-pentane + H_2); line 3, calculation result for gas mixture M_1; line 4, calculation result for gas mixture M_2.
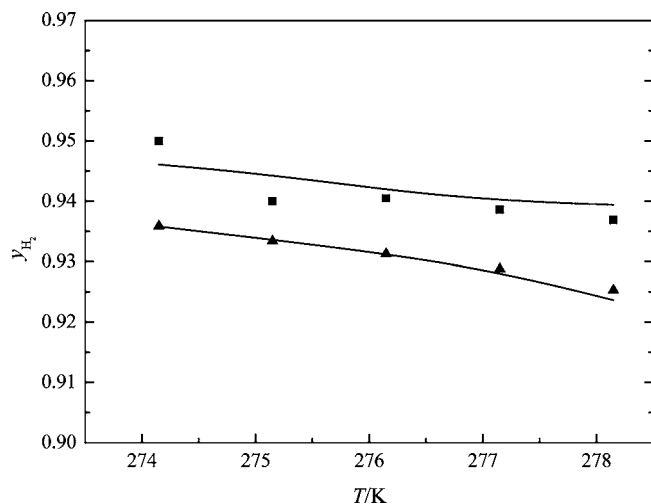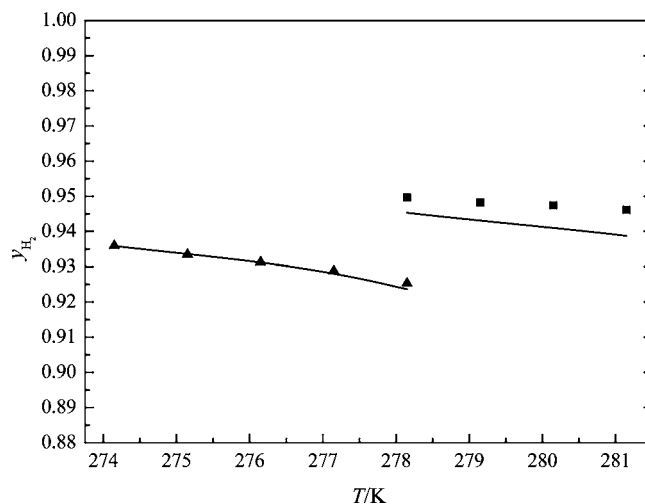
Figure 5. Comparison of calculated and experimental mole fractions of hydrogen in the gas phase ($P = 12.0$ MPa). ■, experimental data of gas M_1; ▲, experimental data of gas M_2; —, calculation results.

Figure 7. Comparison of the hydrogen content in the gas phase in pure water and in the oxacyclopentane aqueous solution for gas M_2 ($P = 12.0$ MPa). ■, experimental data (0.01 oxacyclopentane aqueous solution); ▲, experimental data (pure water); —, calculation results.
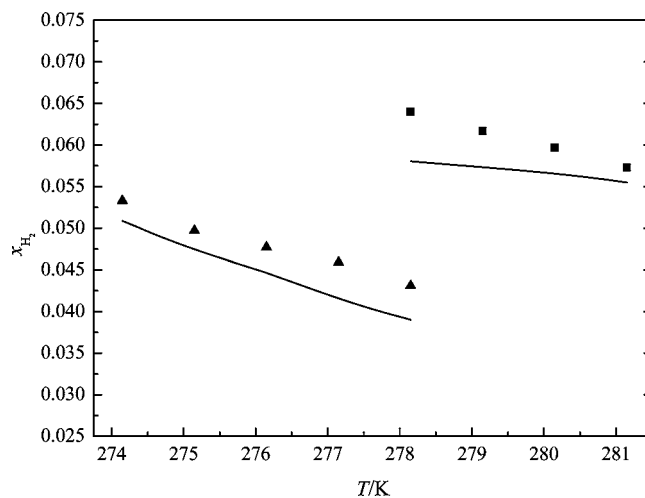

Figure 6. Comparison of calculated and experimental mole fractions of hydrogen in the hydrate phase ($P = 12.0$ MPa). ■, experimental data of gas M_1; ▲, experimental data of gas M_2; —, calculation results.

Figure 8. Comparison of the hydrogen content in the hydrate phase in pure water and in the oxacyclopentane aqueous solution for gas M_2 ($P = 12.0$ MPa). ■, experimental data (0.01 oxacyclopentane aqueous solution); ▲, experimental data (pure water); —, calculation results.

molecules being adsorbed into the small cavities of hydrate, which would reduce the hydrogen recovery efficiency.

From the experimental data, it is noticed that there are some *n*- and *i*-pentanes in the hydrate phase. It is well-known that pentane cannot form structure I and II hydrates, and it can only form structure-H (sH) hydrate. Methane and hydrogen are the help gases for the sH hydrate formation. Figures 3 and 4 show the sH hydrate formation conditions of methylcyclohexane (MCH) and *i*-pentane in the presence of methane and hydrogen as the help gas, respectively, and also give the comparison of experimental data with the calculated results by the Chen−Guo hydrate model.[32] It could be seen from the figures that the sH hydrate formation pressures are enhanced enormously for the (sH hydrate former + hydrogen) systems. The mixtures M_1 and M_2 contain sH hydrate former pentane and help-gases methane and hydrogen. To confirm whether sH hydrate was formed during the experiment, we calculated the sH hydrate formation conditions of the mixtures by the Chen−Guo hydrate model.[32] The calculated results plotted in Figure 4 indicate that the mixtures seem to be able to form sH hydrate only at the pressures higher than 20 MPa. Hence, there should not be sH hydrate formed at the experimental conditions in this work. The gas mixture M_1 and M_2 could be partially condensed at the

experimental conditions according to the $P-T$ flash calculations. Pentane in the hydrate phase might result from some amounts of pentane which were carried by the melting hydrate because the gas and condensed hydrocarbons were not discharged completely. The further investigation should be carried out on the hydrate structure in the future research.

The experimental data were compared with the predictions using the Chen−Guo hydrate model.[34] The algorithm of the vapor−liquid−liquid-hydrate four-phase equilibrium calculation[35] was used to make the predictions in this study. The results plotted in Figures 5 and 7 indicate that the predictions of hydrogen content in the gas phase are in good agreement with the experimental data, and the average deviation is 0.216 %. Nevertheless, Figures 6 and 8 show that the predictions of hydrogen content in hydrate phase are all smaller than the experimental data. The reason for this might be that the extra gaseous hydrogen was carried by the melting hydrate. Furthermore, Figures 7 and 8 clearly demonstrate that oxacyclopentane could promote the hydrate formation at the elevated temperature conditions and enhance the hydrogen recovery efficiency.

Conclusion

The gas-hydrate equilibrium data of two synthetic recycled-hydrogen gas mixtures were measured. The effect of temperature, pressure, and initial gas−liquid ratio on the separation efficiency was studied. The experimental data show that the enrichment of hydrogen in the gas phase is favorable by having a lower temperature, high pressure, and small gas−liquid ratio. The promoter oxacyclopentane could enhance the separation efficiency effectively, especially for the gas mixture containing less C3+ fractions. The experimental data are of value for constructing the gas-hydrate equilibrium model for the system containing hydrogen.

Literature Cited

(1) Hou, X. L. *Advances of refining technology in China*; China Petrochemical Press: Beijing, 1997.

(2) Perry, E. Process for the Recovery of Hydrogen from Ammonia Purge Gases. U.S. Patent 4172885, 1979.

(3) Sircar, S.; Golden, T. C. Purification of Hydrogen by Pressure Swing Adsorption. *Sep. Sci. Technol.* **2000**, *35*, 667–687.

(4) Glew, D. N. Liquid Fraction Process Using Gas Hydrates. U.S. Patent 3231630, 1966.

(5) Spencer, D. F. Methods of Selectively Separating CO_2 from a Multicomponent Gaseous Stream. U.S. Patent 6106595, 2000.

(6) Ballard, A. L.; Sloan, E. D., Jr. In *Hydrate Separation Process for Close-Boiling Compounds*, Proceeding of the 4th International Conference on Gas Hydrates, Yokohama, Japan, May 2002; pp 1007−1011.

(7) Yoshitaka, Y.; Takeshi, K. In *Studies on Separation and Purification of Guest Component*, Proceeding of the 4th International Conference on Gas Hydrates, Yokohama, Japan, May 2002; pp 428−432.

(8) Zhang, L. W.; Chen, G. J.; Guo, X. Q.; Sun, C. Y.; Yang, L. Y. The Partition Coefficients of Ethane Between Vapor and Hydrate Phase for Methane + Ethane + Water and Methane + Ethane + THF + Water Systems. *Fluid Phase Equilib.* **2004**, *225*, 141–144.

(9) Zhang, L. W.; Chen, G. J.; Sun, C. Y.; Fan, S. S.; Ding, Y. M.; Wang, X. L.; Yang, L. Y. The Partition Coefficient of Ethylene between Hydrate and Vapor for Methane + Ethylene + Water and Methane + Ethylene + SDS + Water System. *Chem. Eng. Sci.* **2005**, *60*, 5356–5362.

(10) Kang, S. P.; Lee, H. Recovery of CO_2 from Flue Gas Using Gas Hydrate: Thermodynamic Verification through Phase Equilibrium Measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397–4400.

(11) Ma, C. F.; Chen, G. J.; Wang, F.; Sun, C. Y.; Guo, T. M. Hydrate Formation of ($CH_4 + C_2H_4$) and ($CH_4 + C_3H_6$) Gas Mixtures. *Fluid Phase Equilib.* **2001**, *191*, 41–47.

(12) Klauda, J. B.; Sandler, S. I. Phase Behavior of Clathrate Hydrates: a Model for Single and Multiple Gas Component Hydrates. *Chem. Eng. Sci.* **2003**, *58*, 27–41.

(13) Ma, Q. L.; Chen, G. J.; Ma, C. F.; Zhang, L. W. Study of Vapor-Hydrate Two-Phase Equilibria. *Fluid Phase Equilib.* **2008**, *265*, 84–93.

(14) Sloan, E. D. *Clathrate hydrates of natural gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(15) Mao, W. L.; Mao, H. K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q. Z.; Hu, J. Z.; Shu, J. F.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. S. Hydrogen Clusters in Clathrate Hydrate. *Science* **2002**, *297*, 2247–2249.

(16) Lokshin, K. A.; Zhao, Y. Fast Synthesis Method and Phase Diagram of Hydrogen Clathrate Hydrate. *Appl. Phys. Lett.* **2006**, *88*, 131909–131909-3.

(17) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. Stable Low-Pressure Hydrogen Clusters Stored in a Binary Clathrate Hydrate. *Science* **2004**, *306*, 469–471.

(18) Lee, H.; Lee, J. W.; Kim, D. Y.; Park, J.; Seo, Y. T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. Tuning Clathrate Hydrates for Hydrogen Storage. *Nature* **2005**, *434*, 743–746.

(19) Fan, S. S.; Guo, T. M. Hydrate Formation of CO_2-Rich Binary and Quaternary Gas Mixtures in Aqueous Sodium Chloride Solutions. *J. Chem. Eng. Data* **1999**, *44*, 829–832.

(20) Mei, D. H.; Liao, J.; Yang, J. T.; Guo, T. M. Hydrate Formation of a Synthetic Natural Gas Mixture in Aqueous Solutions Containing Electrolyte, Methanol, and (Electrolyte + Methanol). *J. Chem. Eng. Data* **1998**, *43*, 178–182.

(21) Zhang, S. X.; Chen, G. J.; Ma, C. F.; Yang, L. Y.; Guo, T. M. Hydrate Formation of Hydrogen + Hydrocarbon Gas Mixtures. *J. Chem. Eng. Data* **2000**, *45*, 908–911.

(22) Zhang, Q.; Chen, G. J.; Huang, Q.; Sun, C. Y.; Guo, X. Q.; Ma, Q. L. Hydrate Formation Conditions of a Hydrogen + Methane Gas Mixture in Tetrahydrofuran + Water. *J. Chem. Eng. Data* **2005**, *50*, 234–236.

(23) Wang, X. L.; Sun, C. Y.; Yang, L. Y.; Ma, Q. L.; Tang, X. L.; Zhao, H. W.; Chen, G. J. Vapor-Hydrate Equilibria for the Methane + Hydrogen + Tetrahydrofuran + Water System. *J. Chem. Eng. Data* **2009**, *54*, 310–313.

(24) Katz, D. L.; Cornell, D.; Kobayashi, R.; Poettmann, F. H.; Vary, J. A.; Elenbaas, J. R.; Weinaug, C. F. *Handbook of natural gas engineering*; McGraw-Hill: New York, 1959.

(25) Ma, Q. L.; Chen, G. J.; Zhang, L. W. In *Study on Hydrate Formation Conditions in Presence of Thermodynamic Promoter Tetrahydrofuran*, Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, Canada, July 2008.

(26) Mehta, A. P.; Sloan, E. D., Jr. Structure H Hydrate Phase Equilibria of Methane + Liquid Hydrocarbon Mixtures. *J. Chem. Eng. Data* **1993**, *38*, 580–582.

(27) Østergaard, K. K.; Tohidi, B.; Danesh, A.; Burgass, R. W.; Todd, A. C. Equilibrium Data and Thermodynamic Modelling of Isopentane and 2,2-dimethylpentane Hydrates. *Fluid Phase Equilib.* **2000**, *169*, 101–115.

(28) Mehta, A. P.; Sloan, E. D., Jr. Structure H Hydrate Phase Equilibria of Paraffins, Naphthenes, and Olefins with Methane. *J. Chem. Eng. Data* **1994**, *39*, 887–890.

(29) Mehta, A. P.; Sloan, E. D., Jr. A Thermodynamic Model for Structure-H Hydrates. *AIChE J.* **1994**, *40*, 312–320.

(30) Becke, P.; Kessel, D.; Rahimian, I. In *Influence of Liquid Hydrocarbons on Gas Hydrate Equilibrium. SPE 25032*, Proceedings of European Petroleum Conference, Cannes, France, Nov 1992.

(31) Tohidi, B.; Danesh, A.; Burgess, R.; Todd, A. In *Hydrate Equilibrium Data and Thermodynamic Modeling of Methylcyclopentane and Methylcyclohexane*, Proceedings of the 2nd International Conference on Natural Gas Hydrates, Toulouse, France, June 1996.

(32) Chen, G. J.; Sun, C. Y.; Guo, T. M. Modelling of The Formation Conditions of Structure-H Hydrates. *Fluid Phase Equilib.* **2003**, *204*, 107–117.

(33) Chapoy, A.; Anderson, R.; Tohidi, B. In *Effect of Clathrate Structure and Promoter on the Phase Behavior of Hydrogen Clathrates*, Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, Canada, July 2008.

(34) Chen, G. J.; Guo, T. M. A New Approach to Gas Hydrates Modeling. *Chem. Eng. J.* **1998**, *71*, 145–151.

(35) Ma, Q. L.; Chen, G. J.; Sun, C. Y.; Guo, T. M. A New Algorithm of Vapor-Liquid-Liquid-Hydrate Multi-Phase Equilibrium Flash Calculation. *J. Chem. Ind. Eng. (China)* **2005**, *56* (9), 1599–1605.