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Experimental Studies of the Separation of C2 Compounds from CH$_4$ + C$_2$H$_4$ + C$_2$H$_6$ + N$_2$ Gas Mixtures by an Absorption−Hydration Hybrid Method

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Ⓢ Supporting Information

ABSTRACT: An absorption−hydration hybrid method was employed for separating C2 components (C$_2$H$_4$ + C$_2$H$_6$) from low-boiling gas mixtures such as refinery dry gas using water-in-diesel emulsions under hydrate formation conditions. Span 20 was used to disperse the water or hydrate in diesel to form the emulsion or hydrate slurry. To simulate a three-stage separation process, three (CH$_4$ + C$_2$H$_4$ + C$_2$H$_6$ + N$_2$) feed gas mixture samples with different gas molar compositions were prepared. Separation experiments were performed under different conditions to investigate the influences of feed composition, temperature, pressure, initial water cut in the emulsion, and initial gas/liquid volume ratio on separation efficiency. The experimental results show that the absorption−hydration hybrid method is obviously superior to the single-absorption method. After three stages of separation at appropriate operating conditions, we found that C2 compounds can be enriched from ∼15 to more than 50 mol % in the (hydrate + diesel) slurry phase and that the content of C2 compounds in the residual gas phase can be reduced to lower than 2 mol %. Low temperature, low initial gas/liquid volume ratio, high pressure, and high water cut were found to be favorable for the recovery of C2 compounds. However, when the temperature was lower than 270.2 K and the water cut was higher than 30 vol %, the formation of flowable hydrate slurry became difficult.

1. INTRODUCTION

Low-carbon olefin/paraffin separations comprise a group of important separations in the petrochemical industry. To date, cryogenic distillation has been widely used in this area.[1] However, because of the very low dew points of the components, substantial energy is required to separate low-carbon olefin/paraffin mixtures by cryogenic distillation under high pressure and low temperature.[2] Other approaches used for this separation purpose include absorption using liquid solvents, adsorption using porous media, and membranes. However, these methods have their own limitations such as high corrosion, high cost, or low capacity. All of these limitations provide an incentive for ongoing research in olefin/paraffin separation technology. Recently, hydrate-based gas-mixture separation technology, namely, a separation method based on hydrate formation/dissociation, has attracted much attention.[3−10]

Hydrate-based gas separation relies on the fact that some components can form hydrates more easily than others and be enriched in the hydrate phase, thereby leading to differences in the relative concentrations of each component in the hydrate and residual gas phases.[11] In addition, separation of low-boiling gas mixtures by forming hydrates can be performed above the ice point and avoid deep cooling. To our knowledge, most separation research based on hydrate technology in the literature has focused on simple gas-mixture separation and has mainly been related to aqueous solutions. It has been reported that the hydrate formation rate and separation ability could be increased or the hydrate formation conditions could be moderated by adding suitable additives such as tetrahy-drofuran, sodium dodecyl sulfate, and others to water.[11−18] However, these additives can not guarantee the formation of a flowable hydrate, which is required for the continuous separation of gas mixtures in practical industrial processes.

Currently, hydrate formation from water-in-oil emulsions with or without antiagglomerants has attracted much attention because of its potential application in preventing the plugging of oil/gas pipelines.[19−23] The hydrate formation rate could be increased significantly by dispersing water in oil because of the large contact areas of water and oil containing hydrate formers. An antiagglomerant in the system could keep the hydrate particles suspended in oil rather than allowing them to aggregate and deposit from the oil phase, thus enabling the formation of a flowable hydrate slurry. In our previous works,[24,25] we proposed a new method, called the absorption−hydration hybrid method, for separating gas mixtures by using water-in-oil emulsions under hydrate formation conditions. In this method, the gas components are first selectively absorbed by the oil phase because of their different solubilities, and the dissolved gas molecules then further selectively form hydrates. That is, two separation processes occur in the equilibrium separation stage, so that high separation efficiency can be obtained. Another advantage of this method is that flowable hydrate slurries could be formed.

In this work, to find a new approach for the recovery of valuable C2 components (C_2H_4 and C_2H_6) from refinery dry gases with high efficiency, the absorption−hydration hybrid method was employed for the separation of CH_4 + C_2H_4 + C_2H_6 + N_2 quaternary gas mixtures using water-in-diesel emulsions formed by adding Span 20.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

2.1. Experimental Apparatus. A schematic outline of the experimental apparatus is shown in Figure S1 of the Supporting Information. The critical parts of the apparatus were a transparent sapphire cell and a steel-made blind cell, which were both installed in an air bath. The effective volume of the sapphire cell was 60 cm³, and that of the blind cell plus the tubes connected to it was 112 cm³. The designed maximum working pressure of these two cells was 20 MPa. To observe the experimental phenomena occurring in the cell clearly, an LG100H luminescence source was fixed to the outside of the cell. The temperature sensor used was a secondary platinum resistance thermometer (type Pt 100). A calibrated Heise pressure gauge and differential pressure transducers were used to measure the system pressure. The uncertainties of pressure and temperature measurements were ±0.01 MPa and ±0.1 K, respectively. The changes in the system temperature and pressure with elapsed time were recorded and displayed by a computer.

2.2. Materials and Preparation of Samples. Analytical-grade methane (99.99%), ethane (99.99%), ethylene (99.99%), and nitrogen (99.99%) were obtained from Beijing AP Beifen Gas Industry Company. Synthetic gas mixtures M1−M3 were prepared in our laboratory with the molar compositions listed in Table 1. A Hewlett-Packard gas chromatograph (HP 7890)

Table 1. Molar Compositions (mol %) of Feed Gas Mixtures M1−M3

component	M1	M2	M3
CH_4	58.65	61.14	56.05
C_2H_4	9.30	3.59	19.95
C_2H_6	6.16	2.12	11.82
N_2	25.89	33.15	12.18

was used to analyze the compositions of the feed gases and the experimental equilibrium gas mixtures. An electronic balance with a precision of ±0.1 mg was used in preparing aqueous solutions with the required contents of Span 20, which was supplied by Beijing Reagents Corporation. In all experimental runs, the mass content of Span 20 added to water was specified as 0.5 wt %.

2.3. Experimental Procedures and Data Processing. At first, the sapphire cell was dismounted from the apparatus, washed with distilled water, and dried, and then a suitable quantity of water-in-diesel emulsion was added to it. The system (sapphire cell + blind cell + tubes connecting the two cells) was then purged through vacuuming and replaced with feed gas to ensure the absence of air. Subsequently, the desired amount of feed gas was injected into the blind cell, and the air-bath temperature was adjusted to the desired value. Once both the temperature and pressure of the blind cell were constant, the pressure of the gas mixture in the blind cell was recorded as the initial pressure, P_1. Afterward, the desired amount of feed gas was injected into the sapphire cell from the blind cell, and the magnetic stirrer was started to accelerate hydrate formation.

The pressure of the residual gas mixture in the blind cell was recorded as P_2. With the absorption and hydration of the gas mixture in the emulsion system, the system pressure in the sapphire cell gradually decreased. After the system pressure had remained constant for a long time, the formation of hydrate was considered to be finished, and the pressure of the sapphire cell was recorded as P_E. It should be noted that the temperature was kept constant during the whole experimental process. The equilibrium gas mixture in the sapphire cell was sampled under constant pressure by pushing the piston in the sapphire cell using a hand pump, and the corresponding compositions were analyzed on the HP 7890 gas chromatograph. During each experimental run, the variation of pressure in the sapphire cell with time was recorded by a computer. The volume of the emulsion or slurry phase in the sapphire cell was obtained by measuring its height, as the inner radius of the sapphire cell was known to be 1.27 cm.

The gas composition in the slurry was determined by mass balance. The total number of moles of gas mixture (n_t) injected into the sapphire cell was calculated from the formula

$$n_t = \frac{P_1 V_t}{Z_1 RT} - \frac{P_2 V_t}{Z_2 RT} \tag{1}$$

where P_1 and P_2 are the initial pressure and the residual pressure of the blind cell after gas had been injected into the sapphire cell from it, respectively, as described before; V_t is the total volume of the blind cell plus tubes connected to it; T is the system temperature; R is the universal gas constant; and compressibility factors Z_1 and Z_2 were calculated with the Benedict−Webb−Rubin−Starling equation of state.

The total number of moles of the equilibrium gas phase in the sapphire cell (n_E) was determined as

$$n_E = \frac{P_E V_g}{Z_E RT} \tag{2}$$

where P_E is the equilibrium pressure in the sapphire cell and Z_E is the compressibility factor corresponding to T, P_E, and the gas-phase composition. V_g is the volume of equilibrium gas in the sapphire cell, which can be obtained by measuring the height of the equilibrium gas mixture.

The total numbers of moles of CH_4 (n_1), C_2H_4 (n_2), C_2H_6 (n_3), and N_2 (n_4) absorbed in the slurry phase were calculated as follows

$$n_1 = n_t z_1 - n_E y_1 \tag{3}$$

$$n_2 = n_t z_2 - n_E y_2 \tag{4}$$

$$n_3 = n_t z_3 - n_E y_3 \tag{5}$$

$$n_4 = n_t z_4 - n_E y_4 \tag{6}$$

where z_i and y_i are the molar fractions of component i (i = CH_4, C_2H_4, C_2H_6, and N_2) in the feed gas and in the equilibrium gas phase, respectively. The corresponding molar fractions of these four gases in the equilibrium slurry phase can then be obtained by the equations

$$x_1 = \frac{n_1}{n_1 + n_2 + n_3 + n_4} \tag{7}$$

$$x_2 = \frac{n_2}{n_1 + n_2 + n_3 + n_4} \tag{8}$$

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Table 2. Separation Results for Gas Mixtures M1–M3 Using a Water-in-Oil Emulsion with a Fixed Initial Pressure of 4.4 MPa and an Initial Water Cut of 20 vol % but Different Temperatures

T (K)	P_E (MPa)	equilibrium gas phase (mol %)				slurry phase (mol %)				S	R
		y_1	y_2	y_3	y_4	x_1	x_2	x_3	x_4		
Mixture M1											
274.15	3.06	59.91	3.96	2.25	33.88	56.38	18.87	13.19	11.55	5.17	74.23
272.15	2.80	58.90	3.57	2.04	35.49	58.27	17.95	12.39	11.40	5.41	78.19
270.15	2.69	57.66	2.64	1.53	38.17	59.87	17.58	11.93	10.62	7.08	85.08
268.15	2.61	57.49	3.10	1.22	38.19	60.06	16.85	12.19	10.91	6.73	84.68
Mixture M2											
272.15	3.37	56.81	1.55	0.69	41.25	74.80	9.80	6.42	8.98	7.25	70.68
270.15	3.22	56.17	1.43	0.56	41.83	73.49	9.00	5.98	11.53	7.51	75.12
268.15	3.23	56.65	1.20	0.60	41.55	72.44	9.66	5.94	11.96	8.68	77.48
Mixture M3											
274.15	2.53	67.26	8.74	4.43	19.57	44.85	31.15	19.20	4.81	3.82	79.29
272.15	2.54	66.59	8.46	4.13	20.62	45.58	31.35	19.45	3.61	4.04	80.28
270.15	2.59	65.81	8.04	3.78	22.37	45.81	32.44	20.25	1.50	4.46	80.96
268.15	2.94	65.11	10.79	5.16	18.93	42.95	33.18	21.43	2.44	3.42	70.33

$$x_3 = \frac{n_3}{n_1 + n_2 + n_3 + n_4} \tag{9}$$

$$x_4 = \frac{n_4}{n_1 + n_2 + n_3 + n_4} \tag{10}$$

The initial gas/liquid volume ratio is defined as

$$\Phi = \frac{22400 n_t}{V^L} \tag{11}$$

where V^L is the volume of the water-in-oil emulsion.

In this work, the partition coefficients S of C2 compounds ($C_2H_4 + C_2H_6$) between the equilibrium slurry phase and the gas phase and the recovery ratio R of C2 compounds in the slurry phase were used to characterize the separation ability of the absorption–hydration hybrid method employed in recovering C2 compounds from gas mixtures. S and R denote the selectivity and capacity of the separation process and are defined as

$$S = \frac{x_2 + x_3}{y_2 + y_3} \tag{12}$$

$$R = \frac{n_2 + n_3}{n_t(z_2 + z_3)} \times 100\% \tag{13}$$

3. RESULTS AND DISCUSSION

This study was aimed at the recovery of valuable C2 components (C_2H_4 and C_2H_6) from refinery dry gas. There are different kinds of dry gases corresponding to different petroleum processes, such as catalytic cracking dry gas and delayed coking gas. These dry gases usually have complicated compositions. Their main components include H_2, CH_4, C_2H_4, C_2H_6, and N_2. Compared with C_2H_4 and C_2H_6, H_2 and N_2 form hydrates at moderate pressure only with much greater difficulty, especially for H_2. The key components with respect to the recovery of C2 compounds through the formation of hydrates then should be CH_4, C_2H_4, and C_2H_6. With these considerations and for simplification, only four components, namely, CH_4, C_2H_4, C_2H_6, and N_2, were considered in this work. To simulate a three-stage separation of dry gas using the absorption–hydration hybrid separation method, we prepared three gas mixture samples, M1–M3, with different gas molar

compositions. Among them, mixture M1 was assumed to represent the feed gas of this three-stage separation process. Mixtures M2 and M3 were prepared for simulating the representative compositions of the gas phase and the hydrate slurry phase, respectively, produced in the first-stage separation of mixture M1 and were taken as the feed gas of the other two stages of separation. It should be noted that the gas composition in the slurry phase is reported on a water- and oil-free basis and that only gas components were considered in this work.

3.1. Blank Experiment. To provide a reference for showing the superiority of the absorption–hydration hybrid method employed in this work, we first performed a blank experiment, namely, separating gas mixture M1 using the single absorption method without hydrate formation. Pure diesel was used as the absorbent. The experimental temperature, initial pressure, and initial gas/liquid volume ratio in sapphire cell were set to 272.15 K, 4.1 MPa, and 110, respectively. The experimental results are listed in Table S1 of the Supporting Information, where y_1, y_2, y_3, and y_4 are the mole percentages of CH_4, C_2H_4, C_2H_6, and N_2, respectively, in the equilibrium gas phase; x_1, x_2, x_3, and x_4 are their counterparts in the liquid phase respectively; S is the partition coefficient of C2 compounds between the equilibrium liquid phase and the gas phase defined by eq 12; and R is the recovery ratio of C2 compounds in liquid phase and defined by eq 13. Table S1 (Supporting Information) shows that the partition coefficient S of C2 compounds is only 3.27 and the recovery ratio R of C2 compounds in the liquid is only 51.02%, indicating that large amounts of C2 compounds were still in the gas phase. From the results listed in Table S1 (Supporting Information), we believe that both the selectivity and capacity of the absorption separation are not high enough.

After the blank experiment, a series of equilibrium separation experiments were performed on mixtures M1–M3 using water-in-diesel emulsions under different hydrate formation conditions. The effects of temperature, feed gas composition, equilibrium pressure, initial water cut in the liquid (emulsion), and initial gas/liquid volume ratio on the separation efficiency were systematically investigated.

3.2. Effects of Temperature and Feed Gas Composition. First, the influence of temperature on the separation efficiency of the C2 compounds ($C_2H_4 + C_2H_6$) from synthetic

gas mixtures M1−M3 was studied. In this group of experiments, the system volume in the sapphire cell was kept constant during the absorption and hydrate formation process while system pressure decreased with the elapsed time. The initial pressure in the sapphire cell was set to 4.4 MPa, the initial volume ratio Φ between the gas and liquid phases (emulsion) was around 103, 101, and 113 for the separations of mixtures M1−M3, respectively, and the initial water cut Q_W in emulsion was specified as 20 vol %. Temperatures were specified at four different values. The experimental results are reported in Table 2, where y_1, y_2, y_3, and y_4 are the mole percentages of CH_4, C_2H_4, C_2H_6, and N_2, respectively, in the equilibrium gas phase; and x_1, x_2, x_3, and x_4 are the apparent mole percentages of CH_4, C_2H_4, C_2H_6, and N_2, respectively, in the slurry phase. Compared with the separation results listed in Table S1 (Supporting Information), one can clearly see that the absorption−hydration hybrid method gives a much higher separation efficiency than the absorption method in all cases. Both S and R are obviously higher than those for single absorption, and the content of C2 compounds in the gas phase fell from more than 15 to less than 5 mol %.

Generally, as shown in Table 2, the contents of both C_2H_4 and C_2H_6 in the gas phase decreased with decreasing temperature, which is reasonable because more gas was absorbed by the oil phase and converted into hydrate at lower temperature. Certainly, the recovery ratio R of C2 compounds in the slurry phase increased with decreasing temperature. What is interesting is that the partition coefficient S, denoting the separation selectivity, also increased with decreasing temperature. This indicates that lower temperature is favorable for the recovery of C2 compounds in a certain temperature range. However, when the temperature was lower than 270.2 K for mixtures M1 and M3, which had higher concentrations of C2 compounds, both S and R, in turn, decreased with decreasing temperature. This phenomenon was more obvious for mixture M3, which had the highest concentration of C2 compounds. This can be attributed to the fact that, under these temperature conditions, most water droplets in the emulsion system had been converted into ice particles before the gas mixture was injected into the sapphire cell, which substantially increased the viscosity of the bulk emulsion system, resulting in a lower dissolution rate and a lower hydrate formation rate. When the experiments were performed above 0 °C, we found that water was dispersed into the diesel oil as small droplets. In this case, hydrate formed first at the surface of the droplets and then grew along with their diameter.[23,26] In contrast, for the experiments carried out below 0 °C, we found that at least part or even all of the dispersed droplets had transformed into ice particles, resulting in hydrate being formed in both ice particles and liquid water droplets. Figure 1 shows the variation of pressure with elapsed time at different temperatures for mixture M3. It can be seen that, at 268.15 K, both the hydrate formation rate and the final quantity of gas consumed were much less than those at other temperatures, where the quantity of gas consumed is indicated by the pressure drop. In addition to the high viscosity of the bulk emulsion, another important factor leading to a low hydrate formation rate might be that both the average ice particle size and the porosity of the hydrate shells formed on the surface of ice particles might change with temperature and this change might be unfavorable for mass transfer through the hydrate shell at lower temperatures. The effect of this factor on mixture M2, which had the lowest C2 concentration, might not
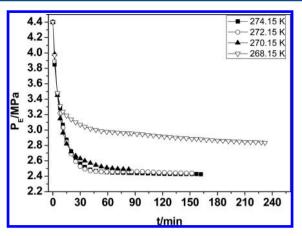

Figure 1. Kinetic curves for the separation of gas mixture M3 in water-in-oil emulsion at a fixed initial pressure of 4.4 MPa but different temperatures.

be as obvious because the quantity of hydrate formed after the establishment of equilibrium was the smallest. In this case, the hydrate shell might not be thick enough to result in a serious resistance on the mass transfer. When the initial pressures were the same, the initial thermodynamic driving force for hydrate formation at the same temperature was greatest for mixture M3 because this mixture contained the highest content of C2 compounds. Therefore, the quantity of hydrate formed to establish phase equilibrium was the greatest too. The hydrate shell covering the ice particles would also be the thickest. Thus, the influence of the hydrate shell on the mass transfer should be significant for mixture M3. In fact, as shown in Figure 1, at 268.15 K, equilibrium was not achieved in our experimental run for mixture M3 even after 4 h had elapsed.

In addition to temperature, the effect of feed gas composition on the separation efficiency was also investigated in this work. As shown in Table 2, with decreasing molar fraction of C2 compounds in the feed gases, a higher partition coefficient S for C2 compounds was obtained. As the composition of gas mixture M2 was close to that of the gas phase obtained in the separation of gas mixture M1 at 272.15 K and $P_0 \approx 4.4$ MPa, the separation of gas mixture M2 could be taken as the second-stage separation of gas mixture M1. One can see that, after two stages of separation, the content of C2 compounds in the gas phase could be reduced from more than 15 mol % to less than 2 mol %, indicating that more than 93% of the C2 compounds could be recovered in the hydrate slurry. Similarly, separation of gas mixture M3 could be taken as the second stage of enrichment of C2 components. After two stages of concentration, the C2 compounds could be enriched to more than 50 mol % in the hydrate slurry. Overall, the separations of gas mixtures M1−M3 together can be treated as a three-stage separation of gas mixture M1. Through this three-stage separation, nearly 90% of the C2 compounds could be removed from the gas phase and enriched from 15.5 mol % to more than 50 mol % in the (hydrate + diesel) slurry phase.

It should be pointed out that, although higher separation efficiency was achieved at relatively low temperature, as mentioned above, low operating temperature means higher refrigeration costs in practical industrial processes. The low hydrate formation rate and high viscosity of the hydrate slurry at lower temperatures are also unfavorable for practical applications. Given the combined considerations of factors including cost and separation efficiency, we consider 272.15 K

Table 3. Separation Results for Gas Mixture M1 Using an Water-in-Oil Emulsion at 272.15 K with a Fixed Initial Pressure of 4.4 MPa, an Initial Gas/Liquid Volume Ratio of 103, and an Initial Water Cut of 20 vol % but Different Equilibrium Pressures

P_E (MPa)	equilibrium gas phase (mol %)				slurry phase (mol %)				S	R
	y_1	y_2	y_3	y_4	x_1	x_2	x_3	x_4		
2.80	58.90	3.57	2.04	35.49	58.27	17.95	12.39	11.40	5.41	78.19
3.20	57.94	2.97	1.73	37.36	59.49	16.80	11.42	12.29	6.01	83.53
3.70	56.68	2.78	1.63	38.91	60.67	15.97	10.81	12.55	6.06	85.54

Table 4. Separation Results for Gas Mixture M1 Using Water-in-Oil Emulsions with Different Water Cuts at 272.15 K and an Initial Gas/Liquid Volume Ratio of around 103

Q_W (%)	P_E (MPa)	equilibrium gas phase (mol %)				slurry phase (mol %)				S	R
		y_1	y_2	y_3	y_4	x_1	x_2	x_3	x_4		
10	3.11	60.52	4.50	2.50	32.48	54.79	19.21	13.74	12.27	4.70	69.48
20	2.80	58.90	3.57	2.04	35.49	58.27	17.95	12.39	11.40	5.41	78.19
30	2.77	57.73	3.44	1.89	36.94	59.96	17.68	12.28	10.08	5.63	79.74

Table 5. Separation Results for Gas Mixture M1 Using a Water-in-Oil Emulsion at 272.15 K with a Fixed Initial Pressure of 4.4 MPa and a Water Cut of 20 vol % but Different Initial Gas/Liquid Volume Ratios

Φ	P_E (MPa)	equilibrium gas phase (mol %)				slurry phase (mol %)				S	R
		y_1	y_2	y_3	y_4	x_1	x_2	x_3	x_4		
103	2.80	58.90	3.57	2.04	35.49	58.27	17.95	12.39	11.40	5.41	78.19
89	2.78	59.29	3.42	1.95	35.34	57.77	17.38	11.95	12.90	5.46	79.89
69	2.73	59.40	3.23	1.88	35.54	57.60	17.35	11.92	13.08	5.78	81.33

to be appropriate for our separation purposes. Therefore, the subsequent experiments for separating gas mixture M1 were all carried out at 272.15 K.

3.3. Effect of Equilibrium Pressure. To investigate the influence of the equilibrium pressure (P_E) on the separation efficiency, we adjusted the final equilibrium pressures of the gas/slurry system to three different values by pushing the piston in the sapphire cell upward during hydrate formation. Temperature, initial pressure, initial gas-to-emulsion volume ratio, and water cut were specified as 272.15 K, 4.4 MPa, ~103, and 20 vol %, respectively. Mixture M1 was used as the feed gas mixture for this group of separation experiments. The experimental results are reported in Table 3. From Table 3, one can clearly see that both the partition coefficient S and the recovery ratio R of C2 compounds increased with increasing equilibrium pressure. This demonstrates that higher pressure is favorable for the recovery of C2 compounds from dry gas mixtures similar to mixture M1. The results for R were as expected, because more gas can be absorbed or converted into hydrate at higher pressure. On the other hand, the results for S deserve more attention. We believe that hydration separation contributes more to the overall separation process because more hydrate can be formed at higher pressure. The selectivity of hydration separation is much higher than that of absorption separation. As a result, S increases with increasing pressure. It should be noted that high operating pressure leads to high cost of the separation process. Table 3 shows that both S and R are not very sensitive to pressure at higher pressures. All of these factors should be taken into account when selecting operating pressures for practical separation processes.

3.4. Effect of Initial Water Cut. Three groups of water-in-oil emulsions with three different water cuts were prepared and used to perform separation experiments on gas mixture M1 to investigate the influence of the water cut on the separation results of the absorption−hydration hybrid method in terms of the recovery of C2 compounds from dry gas. The content of

Span 20 added in the water phase was still 0.5 wt %. The temperature, initial pressure, and initial gas-to-emulsion volume ratio were specified as 272.15 K, 4.4 MPa, and ~103, respectively. The system volume in the sapphire cell was kept constant in this group of experiments. The experimental results are reported in Table 4. As shown in Table 4, both the partition coefficient S and the recovery ratio R of C2 compounds increased with increasing water cut. This demonstrates that a higher water cut is favorable for the recovery of C2 compounds from dry gas using the absorption−hydration method. Similarly to high pressure, a high water cut leads to a greater contribution of hydration separation to the overall separation process. However, it was found that the hydrate slurry formed from the emulsions with higher water cuts had higher viscosities, so that more energy would be needed for the transportation of the hydrate slurry in practical separation processes. More seriously, for water cuts higher than 30 vol %, it might become impossible for the hydrate slurry to flow. This phenomenon was shown in Peng et al.'s work on the flow of hydrate slurries.[27] A reason for this behavior might be that, when the hydrate volume fraction is high, the viscosity of the hydrate slurry and the probability of agglomeration among hydrate particles are high. Therefore, we recommend that the water cut should be less than 30 vol % in practical use.

3.5. Effect of Initial Gas/Liquid Volume Ratio. The initial gas/liquid volume ratio is also an important factor that should be considered, as it directly affects the operating cost in practical separation processes. Lower gas/liquid volume ratios lead to higher costs in recycling the liquid between the absorption tower and the desorption tower. To evaluate the influence of the gas/liquid volume ratio on the separation performance of the absorption−hydration hybrid method, a series of separation experiments on gas mixture M1 was performed with three different initial gas/liquid volume ratios. The temperature, initial pressure, and water cut were specified as 272.15 K, 4.4 MPa, and 20 vol %, respectively. The

experimental results are listed in Table 5. As shown in Table 5, for initial gas/liquid volume ratios in the wide range of Φ = 69−103, both S and R increased with decreasing Φ, although this tendency was not significant. Both the equilibrium gas composition and the slurry composition were also not sensitive to Φ in our experimental range. Because operating cost is very sensitive to the initial gas/liquid ratio Φ, as already mentioned, we believe that a suitable initial volume ratio should be higher than 100.

CONCLUSIONS

A so-called absorption−hydration hybrid method involving the formation of hydrate from a water-in-oil emulsion was employed to separate gas mixtures similar to refinery dry gases. To simulate the recovery of valuable ethylene and ethane from different types of refinery dry gases through a three-stage equilibrium separation, three (CH_4 + C_2H_4 + C_2H_6 + N_2) quaternary gas mixtures were synthesized. Systematic experimental studies on the separation of C2 compounds (C_2H_4 + C_2H_6) from the (CH_4 + C_2H_4 + C_2H_6 + N_2) gas mixtures were performed using diesel oil + water emulsions under different hydrate formation conditions. The effects of temperature, feed composition, equilibrium pressure, initial water cut, and initial gas/liquid volume ratio on the separation efficiency were investigated. The experimental results showed that the separation efficiency of the absorption−hydration hybrid method is much higher than that of the absorption method. Through a three-stage separation, C2 compounds (C_2H_4 + C_2H_6) can be reduced from 15.5 mol % to less than 2 mol % in the residual gas phase and enriched to more than 50 mol % in the (hydrate + diesel) slurry phase. Nearly 90% of the C2 compounds could be recovered, with promising concentration in the C2-rich phase. In addition, our work shows that both the separation selectivity, which is indicated by the partition coefficient of C2 compounds between the hydrate slurry and gas phases, and the recovery ratio of C2 compounds can be increased effectively by decreasing the operating temperature ($\geq$270.15 K), increasing the equilibrium pressure, and increasing the water cut. However, temperatures that are too low (<270.15 K) and water cuts that are (>30 vol %) can be unfavorable for hydrate formation and the flow of hydrate slurry. Furthermore, we found that both the separation selectivity and recovery ratio of C2 compounds are relatively insensitive to the initial gas/liquid volume ratio and pressure in higher pressure range. Therefore, an appropriatelt high initial gas/liquid volume ratio and low operating pressure should be selected to decrease the operating costs. The knowledge obtained in this work could be useful for understanding and applying the absorption−hydrate hybrid method in separating gas mixtures such as refinery dry gases.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic diagram of the experimental apparatus (Figure S1) and absorption separation results on gas mixture M1 using pure diesel (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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