

## Article

# Spectroscopic Identification on CO<sub>2</sub> Separation from CH<sub>4</sub> + CO<sub>2</sub> Gas Mixtures Using Hydroquinone Clathrate Formation

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**Abstract:** The formation of hydroquinone (HQ) clathrate and the guest behaviors of binary (CH<sub>4</sub> + CO<sub>2</sub>) gas mixtures were investigated by focusing on an application to separate CO<sub>2</sub> from landfill gases. Spectroscopic measurements show that at two experimental pressures of 20 and 40 bar, CO<sub>2</sub> molecules are preferentially captured in HQ clathrates regardless of the gas composition. In addition, preferential occupation by CO<sub>2</sub> is observed more significantly when the formation pressure and the CH<sub>4</sub> concentration are lower. Because the preferential occupation of CO<sub>2</sub> is found with binary (CH<sub>4</sub> + CO<sub>2</sub>) gas mixtures regardless of the composition of the feed gas, a clathrate-based process can be applied to CO<sub>2</sub> separation or concentration from landfill gases or (CH<sub>4</sub> + CO<sub>2</sub>) mixed gases.

**Keywords:** clathrate; hydroquinone; carbon dioxide; methane; landfill gas



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## 1. Introduction

Concern about global warming and subsequent climate change is growing steadily. The emission of carbon dioxide (CO<sub>2</sub>) due to excessive combustion of fossil fuels has been identified as the major contributor to global warming [1]. In particular, fossil fuel combustion is producing about 93% of CO<sub>2</sub> emissions, and CO<sub>2</sub> emission from energy generation is about 85% of total emissions in the U.S. [1]. Another major greenhouse gas is methane (CH<sub>4</sub>), and its global warming potential is 21 times greater than the same amount of CO<sub>2</sub> [2]. Some researchers recently reported that CH<sub>4</sub> is a greenhouse gas that is 25 times more potent (over a century) and 84 times more potent (over two decades) than CO<sub>2</sub> on a unit mass basis [3]. Mixtures of these two gas components are dealt with in many industrial processes such as natural gas sweetening, biogas upgrading, oil recovery enhancement, and landfill gas purification [4]. In these mixtures, CH<sub>4</sub> can be used as an energy source, while CO<sub>2</sub> cannot. Therefore, it is important to separate and sequester CO<sub>2</sub> from the source-gas mixtures thus that the greenhouse effect can be resolved and thus that additional energy can also be utilized. Currently, the separation of CO<sub>2</sub> from various gas mixtures, including flue gases, relies on the commercial process involving absorption using amine solutions. In addition, the potential for commercialization of adsorption and membrane technologies has also been investigated. However, high energy consumption and capital cost, along with difficulties maintaining membrane performance during long-term operation, remain barriers to their commercialization [4].

Another novel approach is to use clathrate compounds as a novel separation technology, which was suggested recently. Clathrate compounds are solid crystal compounds formed by the interaction between host and guest species. Hydrogen-bonded host molecules form a three-dimensional framework within which cages accommodate guest molecules. Many low molecular weight substances (including CH<sub>4</sub> and CO<sub>2</sub>) are known to act as guests to form clathrate compounds. Because formation conditions (e.g., temperature and pressure) are inherently dependent on the characteristics of the guest species, the clathrate

formation can be applied to separate a specific component from gas mixtures by controlling the temperature and pressure conditions. The most popular clathrate family are the gas hydrates, of which the host is water. Many researchers have reported that the formation of a gas hydrate can be used to separate a gas component from various gas mixtures, including flue gases [5,6]. Because only water is added to separate such gas mixtures, gas hydrate formation is environmentally benign. Some researchers reported CO<sub>2</sub> recovery through a hydrate-based gas separation (HBGS) process [7]. However, additional energy consumption for cooling to near the freezing point of water is required to form a gas hydrate. Such cooling load can be relieved when an additive such as tetrahydrofuran (THF) is added to a HBGS system [8]. Another disadvantage of a HBGS technology, however, is that vapor pressures due to water can contaminate the purity of the separated gas phase. To overcome such disadvantages, an organic material (hydroquinone, HQ) could be used as a host material. HQ is a solid crystal material at 298.0 K. It is converted into the clathrate compound under milder conditions (that is, 298.0 K or higher temperature with lower pressure) than for a gas hydrate without using an additive (approximately 0.08 MPa for CH<sub>4</sub>-loaded or CO<sub>2</sub>-loaded HQ clathrate). In addition, because HQ clathrates only have one type of cage, it can be used for selective separation of a specific gas component from the gas mixtures more easily than the gas hydrate. However, forming clathrate compounds with HQ is not simple when a solvent is used. Lee et al. [9] reported “dry synthesis” of CH<sub>4</sub>-loaded HQ clathrate by reacting solid HQ directly with the gas phase. Because dry synthesis can be used to form HQ clathrates with other guest molecules, including C<sub>2</sub>H<sub>4</sub> and CO, the HQ clathrate can be used to separate various guest molecules [10–12]. In particular, the HQ clathrate may be superior to gas hydrate in separation efficiency and selective separation because the former has only one type of cage, while the latter has two or three types.

In this study, we investigated cage occupation characteristics using CH<sub>4</sub> + CO<sub>2</sub> gas mixtures of various compositions for potential application to technology for the separation of landfill gases. Both CH<sub>4</sub> and CO<sub>2</sub> have been reported to form clathrate compounds as guest species with HQ [9,13]. In addition, it has been reported that their thermodynamic equilibria are similar [14]. Nonetheless, preferential occupation of CO<sub>2</sub> has been reported even though their thermodynamic equilibria are similar [15]. Therefore, we investigated such preference using CH<sub>4</sub> + CO<sub>2</sub> gas mixtures of various compositions, focusing on their potential application for separating landfill gases (almost equimolar gas mixtures of CH<sub>4</sub> and CO<sub>2</sub>). In this regard, we also performed a spectroscopic analysis of the HQ samples formed to obtain qualitative and quantitative information for gas-loaded HQ clathrates. These experimental and calculated results could provide fundamental information useful for designing a clathrate-based CO<sub>2</sub> gas separation (CBGS) technology for use with landfills or natural gases.

## 2. Materials and Methods

Pure HQ has a minimum purity of 99 mol%, which was purchased from Sigma-Aldrich Chemicals Co. in Korea (Seoul). Pure gases of CH<sub>4</sub> and CO<sub>2</sub> with nominal purities of 99.995% and 99.9%, respectively, were supplied by Daemyung Special Gas Co. (Cheonan-si, Korea). The gas mixtures of 20, 40, 50, 60, and 80 mol% CH<sub>4</sub> balanced with CO<sub>2</sub> were also manufactured and supplied by Daemyung Special Gas Co. Their analyzed compositions were found to be 20.04, 40.00, 49.91, 59.93, and 80.01 CH<sub>4</sub>, respectively. All these materials were used in the experiments without further treatment or purification.

The experimental methods used in this study were the same as those in our previous reports [16,17]. The experiments included 2 stages. The first stage was to prepare HQ samples after reactions with mixed gases. Then, the prepared samples were subjected to spectroscopic measurements. To prepare the HQ samples, about 5.0 g of pure HQ was placed in a high-pressure reactor with a volume of 200 cm<sup>3</sup> before purging and introducing reaction gases to reach the desired pressure. Then, the reactor was allowed to react at 298.0 K for 14 days. To prevent change in the composition and drop in pressure due to

guest enclathration into the solid phase, a reservoir vessel with a volume of 500 cm<sup>3</sup> was connected to the reactor. In this way, the experimental pressure of the gas phase was found to be constant after the reaction. Throughout the reaction, the pressure of the reactor was monitored with a digital pressure transducer (DXD model, Heise (Stratford, CT, USA)) connected to a data acquisition system (during the reaction, pressure changes were less than 1.0 bar). In addition, to promote reaction between the solid and the gas phases, HQ was ground into a fine powder and its particle size was (<100 μm) assured using a sieve. After 14 days, the pressure was slowly released from the reactor and samples were collected for spectroscopic measurements.

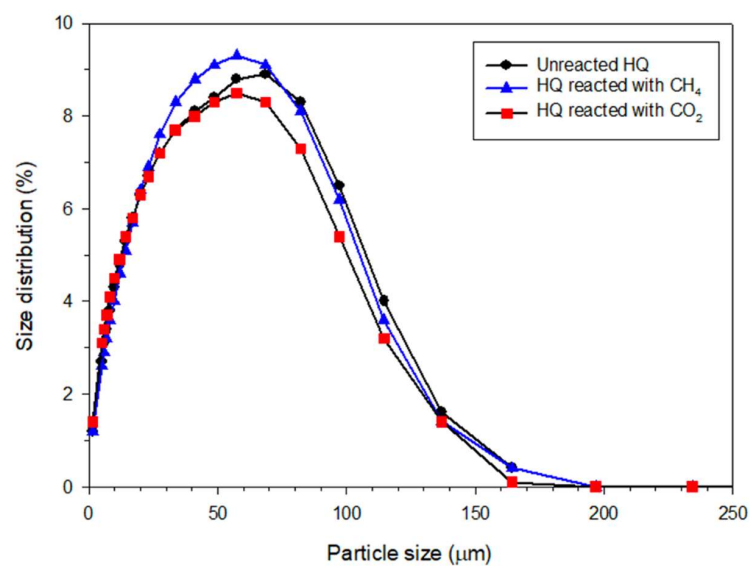
A laser scattering particle size analyzer (Helos/Rodos model) at Chungnam National University (Daejeon, Korea) was used to verify the size distribution of ground HQ powders before and after their reactions with pure CH<sub>4</sub> and CO<sub>2</sub>. X-ray diffractions for identifying the crystal structures of the prepared HQ samples were measured using a multi-purpose X-ray diffractometer (SMD 3000 model, Advanced Scientific Instrumentation Co.) at Kongju National University (Cheonan, Korea). The X-rays monochromatized to a wavelength of 1.5406 Å with a parabolic mirror and a channel-cut crystal were irradiated to the samples. Then, the reflection patterns were collected from 5.0 to 50.0° with a step size of 0.05° and a step time of 3 s. Guest enclathration and crystal structures of the prepared samples were also analyzed using a solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) device. The solid-state <sup>13</sup>C NMR was used with an Agilent DD2 400 MHz spectrometer in the Analysis Center for Research Advancement of the Korea Advanced Institute of Science and Technology (KAIST, Daejeon, Korea). The <sup>13</sup>C CP/MAS (cross-polarization/magic angle spinning) NMR spectra were collected at room temperature using a 1.6 mm HFX probe at a spinning rate of 20 kHz. The pulse of the proton was applied for 2 μs, and a phase-repetition delay with proton decoupling was 10 s. The X-ray diffractions and the NMR spectra were repeatedly collected (4 times) for each HQ sample. Because the HQ samples started to dissociate right after the release of the gas from the high-pressure reactor (i.e., right after shifting from the region of stability), we measured the samples as rapidly as possible after pressure release and sample collection [17].

### 3. Results and Discussion

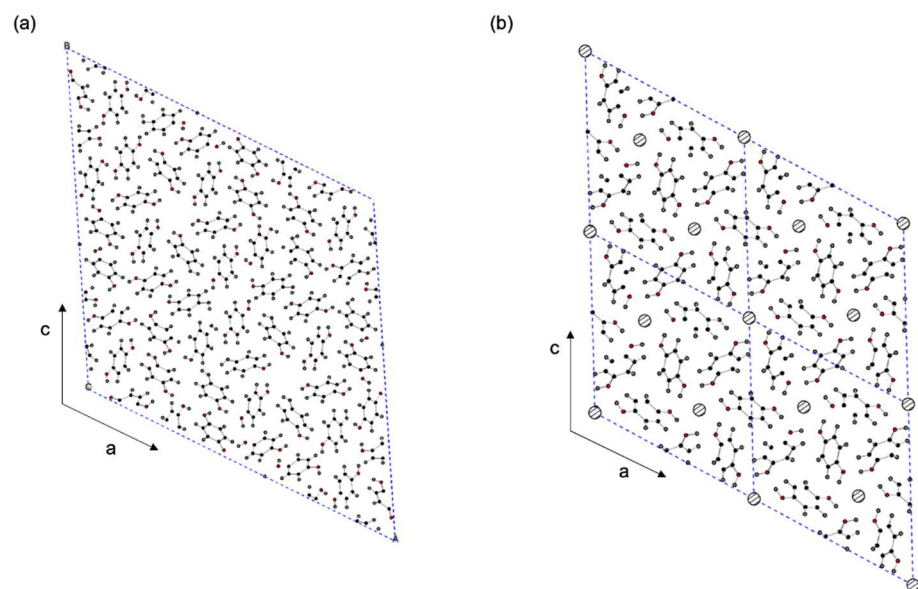
Because the reaction of HQ with gas mixtures occurs between solid and gas phases, HQ powder was used to promote the reaction, as mentioned earlier. To verify that the HQ was ground into powders with the desired particle size, and that the particle size distribution did not change before or after the reaction, the particle size distributions were checked using a laser scattering method. Figure 1 shows the accumulated size distribution of the ground HQ powders. As shown in the figure, the size of 95% of the HQ powder particles was 100 μm or smaller before the reaction. Furthermore, the size of the remaining 5% HQ powders was less than 150 μm. All of these indicate that the powder particles were as intended after sieving. After reaction with pure CO<sub>2</sub> and CH<sub>4</sub> at 40 bar, the size distribution does not change, as plotted in the figure. After the reaction, 95% of the HQ powder were also 100 μm or smaller, while the remaining HQ powder was less than 150 μm. Therefore, it can be said that the powders were properly controlled and prepared for the solid-gas reaction, as reported in our previous paper [9].

Unreacted pure HQ belongs to a rhombohedral R3 space group called the α-form. When it is converted into a clathrate compound, it shifts to its β-form (Figure 2) [18]. This occurs as guest molecules enter the HQ structure, where lattice parameters change while the same crystal structure (R3 space group) is maintained [18]. As mentioned earlier, HQ molecules maintain their three-dimensional framework by hydrogen bonding, and each cage is formed by three HQ molecules. One cage can hold only one guest molecule. Figure 3 shows the powder XRD patterns for the HQ samples after reaction with binary (CH<sub>4</sub> + CO<sub>2</sub>) gas mixtures of various compositions. Using the XRD patterns for pure CO<sub>2</sub> and CH<sub>4</sub> at 40 bar (not shown in the figure), the lattice parameters were calculated:  $a = 16.4488 \pm 0.0021$  Å and  $c = 5.7576 \pm 0.0014$  Å for CH<sub>4</sub>-loaded, and

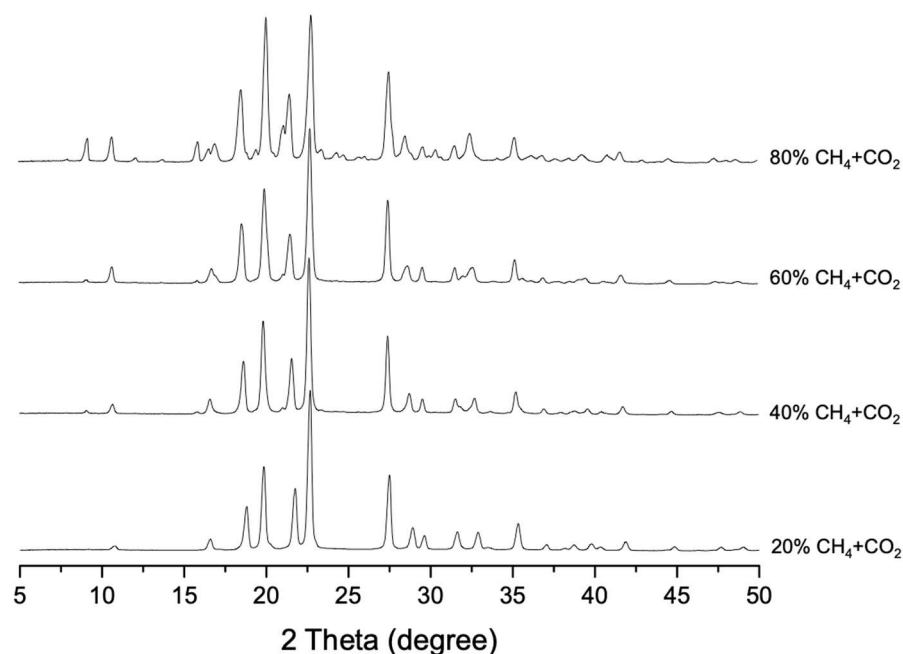
$a = 16.3231 \pm 0.0024 \text{ \AA}$  and  $c = 5.7594 \pm 0.0036 \text{ \AA}$  for  $\text{CO}_2$ -loaded HQ clathrates. The values were in good agreement with those in our previous report [13]. The HQ samples reacted with the gas mixtures, as shown in the figure, and were found to have converted into the  $\beta$ -form almost completely. In addition, lattice parameters were found to be in the ranges of  $a = 16.4677 \pm 0.0325 \text{ \AA}$  and  $c = 5.6926 \pm 0.0449 \text{ \AA}$  for 20 bar, and  $a = 16.4171 \pm 0.0332 \text{ \AA}$  and  $c = 5.7559 \pm 0.0406 \text{ \AA}$  for 40 bar, respectively. The lattice parameter of  $a$  was found to be increased, while that of  $c$  decreased as the  $\text{CH}_4$  composition in the gas mixtures increased at both experimental pressures. This trend agrees with the literature showing the continuous change of HQ samples reacted with  $(\text{CO}_2 + \text{CH}_4)$  gas mixtures at 30 bar [19]. Some additional diffracted signals were detected as the  $\text{CH}_4$  concentration increased due to enclathrated  $\text{CH}_4$  molecules and the existence of unreacted  $\alpha$ -form HQ. All the XRD patterns obtained at the formation pressure of 40 bar (not shown in the figure) showed complete conversion of HQ into the clathrate compound.



**Figure 1.** Accumulated size distribution of the ground HQ powders before and after the reactions with pure gases.

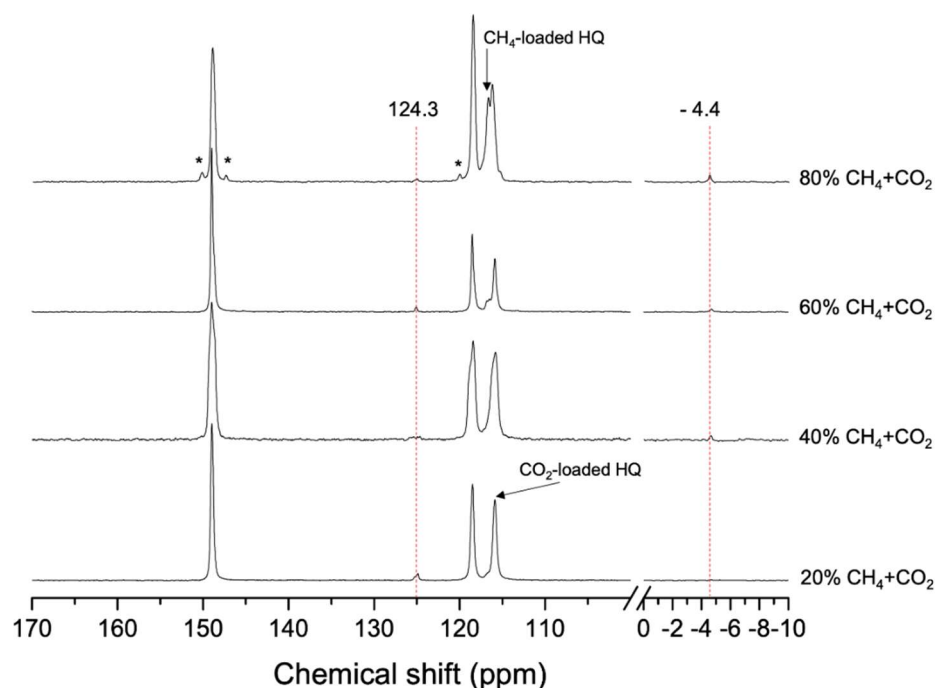


**Figure 2.** Crystal structures of (a)  $\alpha$ -form of pure HQ and (b) the  $\beta$ -form of HQ clathrate. Two axes indicate the direction of the lattice parameters of  $a$  and  $c$ .



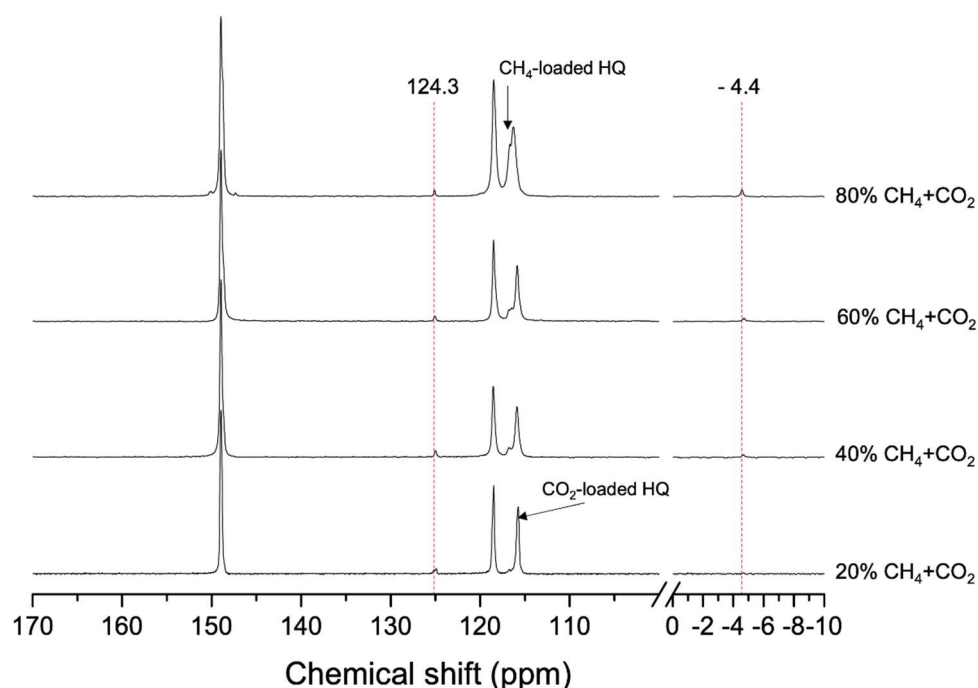
**Figure 3.** Powder XRD patterns for the HQ samples after reactions with binary ( $\text{CH}_4 + \text{CO}_2$ ) gas mixtures of various compositions at 20 bar.

To identify the crystal structures and enclathrated guest species, solid-state  $^{13}\text{C}$  NMR spectroscopy was performed using the same HQ samples used for the XRD measurements. Figure 4 shows the  $^{13}\text{C}$  NMR spectra for the HQ samples prepared at 20 bar. The results were similar to those with the XRD patterns. The samples were completely converted into clathrate compounds of the  $\beta$ -form (up to 60 mol%  $\text{CH}_4$ ) in the gas mixtures, while two small signals were detected on both sides of the hydroxyl-substituted carbon signals of HQ at 148.3 ppm when 80 mol%  $\text{CH}_4 + 20$  mol%  $\text{CO}_2$  was used. The red dotted lines at 124.3 and  $-4.4$  ppm are carbon signals from  $\text{CO}_2$  and  $\text{CH}_4$  molecules, respectively. This is considered direct evidence of guest enclathration. It shows that  $\text{CO}_2$  molecules can enter the HQ clathrate regardless of the composition of a gas mixture, while  $\text{CH}_4$  molecules are detected for all the NMR spectra except for one prepared at its lowest concentration (that is, 20 mol%). The difference between the two unsubstituted carbon signals at 115–120 ppm is known to depend on the nature of the guest molecule and whether a cavity is occupied [18]. As shown in the NMR spectra, the unsubstituted carbon signal on the right side becomes split at the 60 mol% and the 80 mol%  $\text{CH}_4$  concentrations. Such a split signal reflects overlapping of the  $\text{CH}_4$ -loaded and  $\text{CO}_2$ -loaded HQ clathrates. In other words,  $\text{CH}_4$ -loaded and  $\text{CO}_2$ -loaded HQ clathrates coexist in these samples. The difference in the unsubstituted carbon signals was found to be 2.62 ppm up to the 40 mol%  $\text{CH}_4$ , which agrees with the results from pure  $\text{CO}_2$ -loaded HQ clathrate [13]. As the  $\text{CH}_4$  concentration increases, the difference for  $\text{CO}_2$ -loaded clathrate drops to 2.29 ppm, while that for  $\text{CH}_4$ -loaded clathrate is 1.73 ppm, which is in good agreement with pure  $\text{CH}_4$ -loaded HQ clathrate [13]. It should be noted that all the HQ samples (except for the 80 mol%  $\text{CH}_4$  sample with 96% conversion) were found to react completely to form HQ clathrate compounds even at the low pressure of 20 bar.



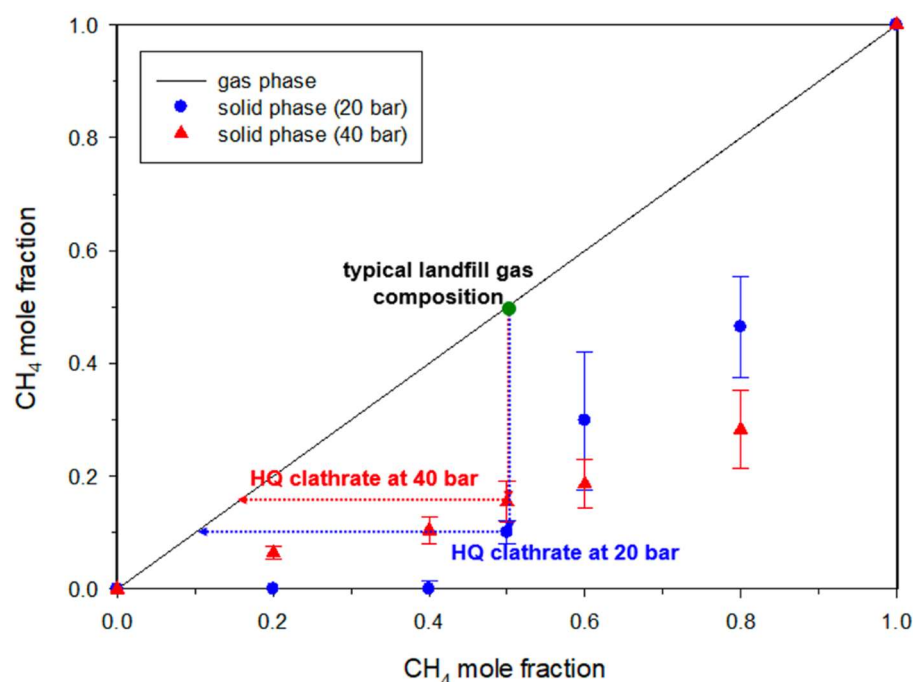
**Figure 4.** Solid-state  $^{13}\text{C}$  NMR spectra for the HQ samples after reaction with binary ( $\text{CH}_4 + \text{CO}_2$ ) gas mixtures of various compositions at 20 bar. Two dotted lines at 124.3 and  $-4.4$  ppm indicate the carbon signals from  $\text{CO}_2$  and  $\text{CH}_4$  in clathrate cages, respectively. Asterisk marks show the unreacted HQ in the  $\alpha$ -form.

If the formation pressure is increased, the conversion should be higher. Figure 5 shows the solid-state NMR spectra for the HQ samples prepared at 40 bar. As observed with the XRD patterns, all the HQ samples were converted to the  $\beta$ -form, and both  $\text{CH}_4$  and  $\text{CO}_2$  were enclathrated regardless of the feed gas composition. Therefore, two unsubstituted carbon signals indicated that  $\text{CO}_2$ -loaded and  $\text{CH}_4$ -loaded HQ clathrates overlapped. The difference between these signals shows a significant trend. For  $\text{CO}_2$ -loaded HQ signals, the difference was 2.72 ppm (larger than that for pure  $\text{CO}_2$ -loaded clathrate) at the  $\text{CH}_4$  concentration of 20 mol%. The difference for  $\text{CH}_4$ -loaded HQ signals was also 1.94 ppm larger than that for pure  $\text{CH}_4$ -loaded clathrate. However, as the  $\text{CH}_4$  concentration increases, the differences become smaller up to 2.20 and 1.70 ppm for  $\text{CO}_2$ -loaded and  $\text{CH}_4$ -loaded clathrates, respectively. In other words, the differences for the  $\text{CO}_2$ -loaded samples decrease from that of pure  $\text{CO}_2$ -loaded HQ clathrate to smaller values, while those for the  $\text{CH}_4$ -loaded samples also decrease from larger values to that of pure  $\text{CH}_4$ -loaded HQ clathrate. Therefore, guest occupation or mixture status can be inferred from the calculation of the differences and comparison of the calculated values with the values for pure gas-HQ clathrates.



**Figure 5.** Solid-state  $^{13}\text{C}$  NMR spectra for the HQ samples after reaction with binary ( $\text{CH}_4 + \text{CO}_2$ ) gas mixtures of various compositions at 40 bar. Two dotted lines at 124.3 and  $-4.4$  ppm indicate the carbon signals from  $\text{CO}_2$  and  $\text{CH}_4$  in clathrate cages, respectively.

Because the intensity of an NMR signal is proportional to the corresponding number of carbon atoms, the relative amounts of  $\text{CO}_2$ -loaded and  $\text{CH}_4$ -loaded HQ clathrate can be calculated by deconvolution and numerical integration of the unsubstituted HQ signals. Such relative amounts depend on the mole fraction of  $\text{CH}_4$  in the feed gas, which is plotted in Figure 6. There, in the solid phase, the  $\text{CH}_4$  composition is always lower than that in the feed gases, which indicates that more  $\text{CO}_2$  molecules are captured than  $\text{CH}_4$  molecules. Such preferential occupation by  $\text{CO}_2$  has been reported in previous literature [14,15], even though the thermodynamic equilibria of  $\text{CO}_2$ - and  $\text{CH}_4$ -loaded HQ clathrates are known to be similar [14]. For the highest  $\text{CH}_4$  concentration (80 mol%) in the gas mixture, the HQ clathrate samples show only 46.5 and 28.3 mol% at the formation pressure of 20 and 40 bar, respectively. That is, even when  $\text{CH}_4$ -dominant gas mixtures are used to form the clathrate compounds, concentrated  $\text{CO}_2$  can be obtained in the solid clathrate phase, which can be used again after release (or dissociation) from the HQ clathrates with only a 1-step reaction. In addition, because application to a CBGS technology is the focus of this study, the HQ samples prepared with equimolar gas mixtures (typical gas composition of landfill gases) were also analyzed (two dotted lines in Figure 5). Blue and red dotted lines indicate  $\text{CO}_2$  concentration from the equimolar  $\text{CO}_2 + \text{CH}_4$  gas mixture using HQ clathrate at 20 and 40 bar, respectively. As shown in the figure, less than 20 mol%  $\text{CH}_4$  can be achieved with only a 1-step reaction for both formation pressures. Moreover, almost pure  $\text{CO}_2$  can be separated and sequestered in the solid clathrates when such concentrated gases are used as feed gases in a second-stage reaction. Preferential enclathration of  $\text{CO}_2$  into the solid phase is substantial when the  $\text{CH}_4$  concentration and the formation pressure are lower. Because the preference for  $\text{CO}_2$  during enclathration is verified for all the gas compositions, such CBGS technology can be used for  $\text{CO}_2$  concentration or separation regardless of the composition of the feed gas.



**Figure 6.** Analyzed  $\text{CH}_4$  compositions in the solid clathrate phase after reactions with binary ( $\text{CH}_4 + \text{CO}_2$ ) gas mixtures of various compositions. Blue and red dotted lines illustrate  $\text{CO}_2$  concentration after reaction of HQ clathrate with an equimolar gas mixture (potential landfill gas) at 20 and 40 bar, respectively.

Because of the preference for  $\text{CO}_2$  during enclathration, and because the relative amounts of  $\text{CO}_2$ - and  $\text{CH}_4$ -loaded HQ clathrate have been identified, the CBGS technology is thought to be viable for application to  $\text{CO}_2$  separation from landfill gases. However, additional studies that include formation kinetics are needed to design a practical process.

#### 4. Conclusions

The formation of HQ clathrate and the behaviors of guest molecules from binary ( $\text{CH}_4 + \text{CO}_2$ ) gas mixtures were investigated for the purpose of application to  $\text{CO}_2$  separation from landfill gases. HQ was converted completely to the  $\beta$ -form clathrate at two experimental pressures of 20 and 40 bar regardless of the gas composition, except for the 20 mol%  $\text{CH}_4$  concentration at 20 bar. In addition, only  $\text{CO}_2$ -loaded HQ clathrates formed at lower pressure and lower  $\text{CH}_4$  concentrations, while the co-existence of  $\text{CO}_2$ - and  $\text{CH}_4$ -loaded HQ clathrates was observed under the remaining experimental conditions. Numerical integration of the solid-state  $^{13}\text{C}$  NMR spectra show that  $\text{CO}_2$  is more readily enclathrated than  $\text{CH}_4$  into the HQ clathrate regardless of the composition of the feed gas. Such preference is more substantial when the formation pressure and  $\text{CH}_4$  concentration are lower. When a simulated landfill gas (equimolar gas mixture of  $\text{CO}_2$  and  $\text{CH}_4$ ) was used as the feed gas, the  $\text{CH}_4$  concentration in the solid clathrate phase was found to be 20 mol% or lower. Therefore, preferential occupation by  $\text{CO}_2$  should allow viable application of this clathrate formation to separate or concentrate  $\text{CO}_2$  from various landfill gases.

**Author Contributions:** Conceptualization, J.-H.Y. and J.-W.L.; methodology, J.-W.L.; validation, J.-H.Y. and J.-W.L.; investigation, D.L.; resources, D.L.; data curation, J.-W.L.; writing—original draft preparation, J.-H.Y. and J.-W.L.; writing—review and editing, J.-H.Y. and J.-W.L.; supervision, J.-W.L. All authors have read and agreed to the published version of the manuscript.

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