

Separation of CO₂ from flue gases using hydroquinone clathrate compounds

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Abstract—Hydroquinone (HQ) samples reacting with (CO₂+N₂) gas mixtures with various compositions at pressures ranging from 10 to 50 bar are analyzed using spectroscopic methods and an elemental analyzer. The results indicate that while both CO₂ and N₂ can react with HQ to form clathrate compounds, CO₂ has higher selectivity than N₂. In particular, at an operating pressure of 20 bar or greater, the CO₂ content in the clathrate compound is 85 mol% or higher regardless of the feed gas composition. Moreover, if a two-step clathrate-based process is adapted, CO₂ at a rate of 93 mol% or higher can be recovered from flue gases. Thus, the clathrate compound described here can be used as a CO₂ separation/recovery medium for CO₂ in flue gases.

Keywords: Clathrate, Flue Gas, Carbon Dioxide, Nitrogen, Separation

INTRODUCTION

Clathrate compounds are non-stoichiometric crystalline compounds formed by the enclosure of low-molecular-weight gaseous or volatile liquid 'guest' species into three-dimensional lattice structures of hydrogen-bonded 'host' molecules [1]. A variety of host species are known to react with numerous guest molecules. One of the best-known clathrate compounds is a gas hydrate whose host molecule is water. Gas hydrate has attracted specific attention since the water content in oil and natural gas pipelines was found to form hydrate particles with low-molecular-weight hydrocarbons, which grow further to block or cause plugging problems in the pipelines [2]. Although the material was thought initially to be hazardous, gas hydrates could have useful applications owing to two features. Above all, a considerable amount of gas (as much as 170 volumes of the same gas at STP) can be stored in a unit volume of solid gas hydrate [1]. In addition, because the formation of the gas hydrate depends on the molecular size and chemical properties of the guest species, the formation conditions (temperature and pressure) of specific gas hydrates differ depending on the guest species used. Therefore, when a mixture of two or more guest species is used, the process of enclosure of the guest into the hydrate structure would be different (a guest species with a milder formation condition would be enclosed in gas hydrate more readily) [1,3]. This is useful for the separation or concentration of a specific gas from a gas mixture. Many investigations of the separation of a variety of mixed gases through the formation of gas hydrate have been reported thus

far. One of the most significant applications is the separation or recovery of carbon dioxide (CO₂) from flue gas [4,5].

Concerns over the levels of atmospheric CO₂ emissions and the resulting environmental impacts have been growing as industrialization based on fossil fuels progresses [6]. At present, over 85% of world energy demand is supplied by fossil fuels, and fossil-fueled power plants are responsible for roughly 40% of total CO₂ emissions [7]. Therefore, intense research has been performed on the separation and sequestration of CO₂ from emission sources so as to mitigate total CO₂ emission to the atmosphere. One method involves the use of a post-combustion chemical absorber such as monoethanolamine (MEA) [7,8]. MEA reacts with CO₂ in the flue gas to form MEA carbamate, which is currently used in a commercial separation process. However, the MEA process has a low CO₂ loading capacity, a high equipment corrosion rate, and high energy-consumption during regeneration of the absorbent [7,8]. To mitigate such disadvantages, other separation processes using physical adsorbents or membranes have also been studied. In the case of membrane separation, CO₂ molecules in flue gas pass through an inorganic or polymeric membrane by a solution-diffusion mechanism. Meanwhile, activated carbon, carbon molecular sieves, or zeolite particles, are commonly used as physical adsorbents, where the adsorption selectivity for CO₂ over N₂ and O₂ is the key principle [6,7,9,10]. However, the cost of the compressor for the membrane system may be greater than the MEA system, and the CO₂ stream recovered through the membrane is generally not pure CO₂ but rather a stream of mixed gases enriched with CO₂ [6,7]. In addition, the CO₂ stream is a stream of mixed gases when recovered from the physical adsorption system. When the selectivity of CO₂ on an adsorbent is too strong, it makes desorption difficult after the separation process [7,11-14]. To overcome such disadvantages

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of conventional separation processes, Kang and Lee suggested a novel technology to separate CO₂ from the flue gas [4]. Because high pressure is required to form gas hydrate, they reported that using tetrahydrofuran (THF) as a promoter can decrease the forming pressure significantly. In addition, gas hydrate formation kinetics was also investigated for hydrate-based CO₂ capture and sequestration processes [15]. However, the recovered gas stream can be contaminated when the promoter is vaporized, and the energy cost for cooling the entire system to nearly the freezing point of ice can be regarded as a disadvantage.

Using a host material other than water can overcome such disadvantages. If a host material that is a solid at room temperature and that can react with CO₂ to form a clathrate compound is used for separation, the energy cost for cooling and that due to product contamination can be alleviated. One of the most promising candidates meeting the above criteria is hydroquinone (HQ). Recently, Lee et al. reported the gas-phase synthesis and spectroscopic characterization of CH₄-loaded HQ clathrates [16]. In addition, Lee et al. investigated the formation of HQ clathrates with various gases, reporting that conversion rates into gas-loaded HQ clathrates differed depending on the guest species used under the given conditions [17]. In this report, CO₂ molecules were found to convert completely, even at pressures lower than those used with N₂ and CH₄. It has also been reported that the selective separation of a specific gas from a mixture can be achieved because there is only one type of cavity in the HQ clathrate.

In this study, guest enclathration of mixed (CO₂+N₂) gases with various compositions into the HQ clathrate was observed via a series of spectroscopic methods in an effort to apply HQ to the separation of CO₂ from flue gas. In addition, the gas-storage capacity of HQ samples under various pressure conditions was analyzed using an elemental analyzer while also cross-checking of the calculated results using the solid-state ¹³C nuclear magnetic resonance (NMR) method. The experimental and calculated results obtained in this study can provide useful and fundamental data for those who design clathrate-based processes for the separation of CO₂ from flue gas, or for evaluating the viability of the process.

EXPERIMENTAL SECTION

HQ powder with a purity of 99 mol% was supplied by Sigma-Aldrich Chemicals Co. CO₂ and N₂ gases with a purity of 99.9 and 99.5 mol%, respectively, were purchased from Daemyoung Special Gas Co. The CO₂+N₂ gas mixtures were also supplied from Daemyoung Special Gas Co. The nominal compositions of the gas mixtures were 19.69, 39.93, 59.92, and 80.08 mol% CO₂, all balanced with N₂. Hereafter, these will be referred to as 20, 40, 60, and 80 mol% CO₂, respectively, all of which balanced with N₂, as noted above. These materials were used without further purification or treatment. The HQ clathrate compounds were prepared by charging HQ powders in a high-pressure cell and allowing it to react with the gases for seven days. The cell was made of 316 stainless steel with an internal volume of approximately 200 cm³. A reservoir cell (~500 cm³) was attached to the reactor to supply the gases during the reaction and thus minimize any changes in composition. Approximately 5.0 g of HQ powder was finely ground to give a powder

with a particle size of less than 45 μm so as to promote the gas-phase reaction. After the HQ powders were loaded, the equilibrium cell was evacuated to remove residual air and was subsequently pressurized to a desired pressure with pure or mixed gases. To monitor the pressure in the equilibrium cell, a digital pressure indicator (Heise, ST-2H) was used. When the formation reaction of HQ clathrates reached a steady-state after a time lapse, the product was collected for analysis by slowly releasing the gas from the cell.

The NMR spectra were measured with a Bruker DSX400 NMR spectrometer in the National Instrumentation Center for Environmental Management (NICEM) of Seoul National University (SNU). Solid-state ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR was used to confirm the occupancy of guest molecules. The ¹³C NMR spectra were collected at ambient temperature by placing samples within a 4 mm o.d. zirconia rotor and recording at a Larmor frequency of 100.6 MHz with a spinning rate of 9 kHz. The pulse length of the proton was 2 μs and a pulse repetition delay of 10 s under proton decoupling was employed when the radio-frequency field strengths of 50 kHz corresponding to a 90° pulse of 5 μs duration were used. The downfield carbon resonance peak of adamantane, which was assigned as a chemical shift of 38.3 ppm at 300 K, was used as an external chemical-shift reference. A dispersive Raman spectrometer (Horiba Jobin Yvon, Lab-RAM HR model) equipped with a multichannel thermal-electric-cooled CCD detector in a laser diode back-illumination system was also used for sample analysis purposes in this study. The excitation source was an Ar-ion laser emitting a 514 nm line with power of 40 W and a spectral resolution of 1 cm⁻¹. The Raman spectroscopic measurements were conducted at ambient temperature. The compositional contents of C, H, N, and O in the HQ clathrates were determined using an automatic elemental analyzer (CE Instrument, Flash EA1112) at the National Center for Inter-University Research Facility of SNU. Approximately 3.0 mg of each sample was analyzed using the dynamic flash combustion method with a TCD detector. From these measurements, the experimental results were found to be in good agreement with the theoretical values with deviations of less than ±2%.

RESULTS AND DISCUSSION

Fig. 1 shows the ¹³C NMR spectra of the HQ samples before and after a reaction with 20 mol% CO₂+balanced N₂ and 80 mol% CO₂+balanced N₂ gas mixtures at various pressures at room temperature. HQ is a molecule with a benzene ring connected to two hydroxyl (-OH) groups. Because it has two equivalent carbon atoms with a 1 : 2 ratio, two groups of atomic signals are observed for unreacted pure HQ, as shown in Fig. 1. When HQ is converted into the clathrate compound by a reaction with guest molecules, the split signals are transformed into three distinct signals for the arranged carbon atoms in a centro-symmetric structure [16-18]. The chemical shift of the carbon atoms attached to the hydroxyl group is observed at 148.8 ppm, whereas the signals from the non-substituted carbon atoms are obtained at 118.3 and 116.7 ppm. This is in good agreement with the findings in previous reports [18,19]. In addition, as HQ was converted into the clathrate compound after reacting with the mixed gases, an additional signal was observed at 124.8

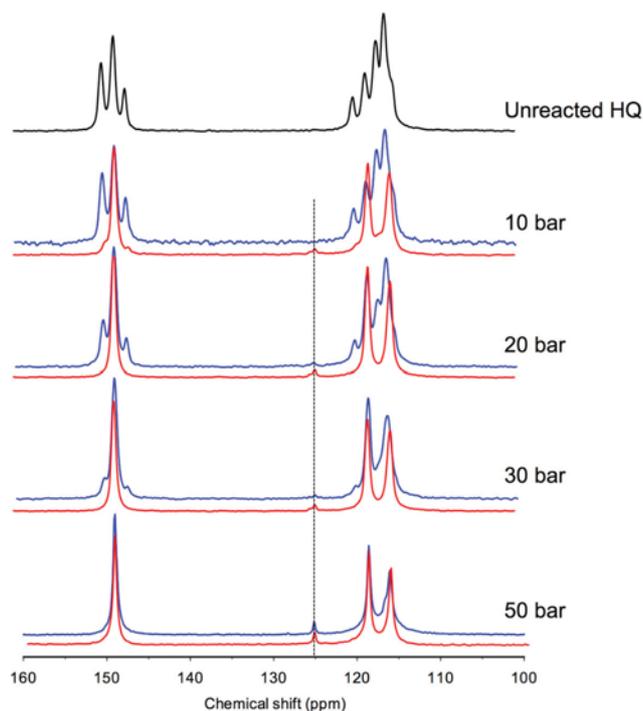


Fig. 1. Solid-state ¹³C CP/MAS NMR spectra of HQ samples after reacting with 20 mol% CO₂+balanced N₂ (blue line) and 80 mol% CO₂+balanced N₂ (red line) gas mixtures at 298 K under various pressures. The ¹³C NMR spectrum for an unreacted pure HQ sample (black line) is also plotted as a reference. The dotted line at 124.8 ppm indicates the atomic signal from CO₂ molecules captured in clathrate cages.

ppm. This signal is attributed to the CO₂ molecules in the clathrate cages [17]. When the HQ powders react with gases at a low pressure of ~10 bar, only a slight transformation of HQ to the clathrate compound is observed. Based on atomic signals from pure HQ (shoulders around 148.8 ppm), it was confirmed that full conversion into the clathrate compound was not achieved. However, HQ was fully converted into the clathrate compound with the 20 mol% CO₂+balanced N₂ gas mixture at 50 bar. When the reaction occurs at higher CO₂ concentration (80 mol% CO₂+balanced N₂), we can expect a conversion rate of HQ which is higher than 80%, even under a low pressure of ~10 bar. The conversion was found to be fully achieved at 20 bar or greater pressures for this gas mixture. Therefore, it can be concluded that the conversion into the clathrate compound is enhanced when the CO₂ concentration in the gas mixture as well as the formation pressure both increase.

The Raman spectra of the HQ clathrate samples are shown in Fig. 2. The strongest signal for pure HQ is a triplet at around 1,600 cm⁻¹, which is attributed to the C-C stretching vibrational mode of HQ molecules [17]. When HQ molecules are well arranged to form the clathrate compound, the peak positions of the triplet do not change, whereas the relative intensities change due to the structural transformation of the HQ molecules in the clathrate compound. Kubinyi et al. reported the weakening of a vibrational Raman band of pure HQ in CH₃CN upon the formation of the solid HQ clathrate [20]. When the clathrate compound is formed, an additional band corresponding to the C-O vibrational mode appears at

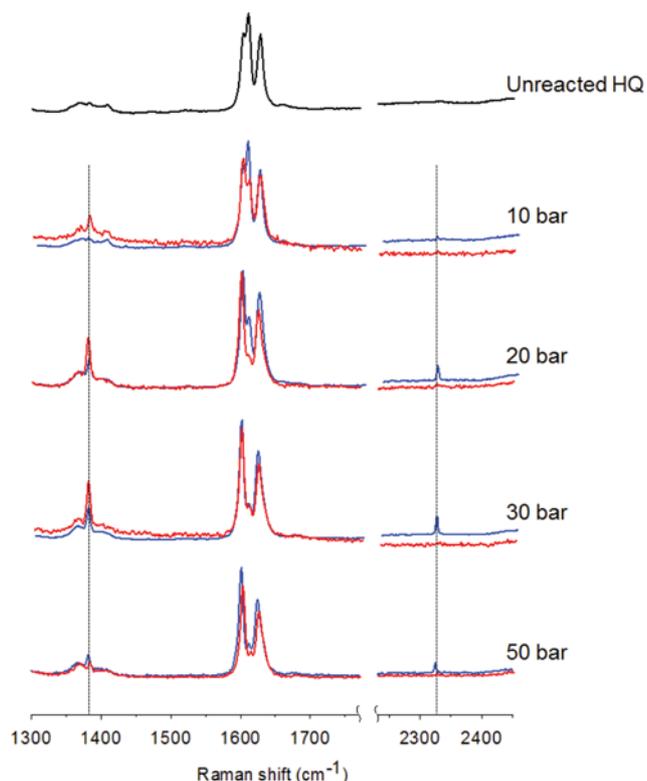


Fig. 2. Raman spectra of HQ samples after reacting with 20 mol% CO₂+balanced N₂ (blue line) and 80 mol% CO₂+balanced N₂ (red line) gas mixtures at 298 K under various pressures. The Raman spectrum for unreacted pure HQ sample (black line) is also plotted as a reference. Dotted lines at 1,382 and 2,326 cm⁻¹ represent the C-O vibrational band of CO₂ molecules and the N-N vibrational band of N₂ molecules engaged in clathrate cages, respectively.

1,382 cm⁻¹, providing direct evidence of CO₂ enclathration [17]. As observed in the ¹³C NMR spectra, CO₂ enclathration increased in accordance with an increase in the formation pressure or an increase in the CO₂ concentration in the mixed gas. In addition, an additional Raman band at around 2,326 cm⁻¹ was observed, which is attributable to the N-N stretching vibrational mode of N₂ molecules [17]. Nearly all of the samples showed the C-O band of CO₂ molecules, whereas a few samples formed with the 20 mol% CO₂+80 mol% N₂ mixtures showed an N-N band. This implies that CO₂ molecules have stronger enclathration preference over N₂.

The same HQ samples used for the spectroscopic methods were also analyzed with the elemental analyzer to identify quantitatively the enclathration preference and CO₂ storage capacity levels. Fig. 3 shows the results pertaining to stored gas amounts for HQ samples formed at room temperature and at pressures of 10, 20, 30, and 50 bar. As shown, the captured CO₂ concentrations in the clathrate samples were greater than those of N₂ under all experimental conditions considered in this work, indicating a higher enclathration preference of CO₂ for HQ clathrates. The total amounts of captured gases in the HQ samples were found to be 0.101-3.365 mole per 1 kg of HQ clathrate solid depending on the experimental gas compositions and formation pressures. On the basis of the ideal

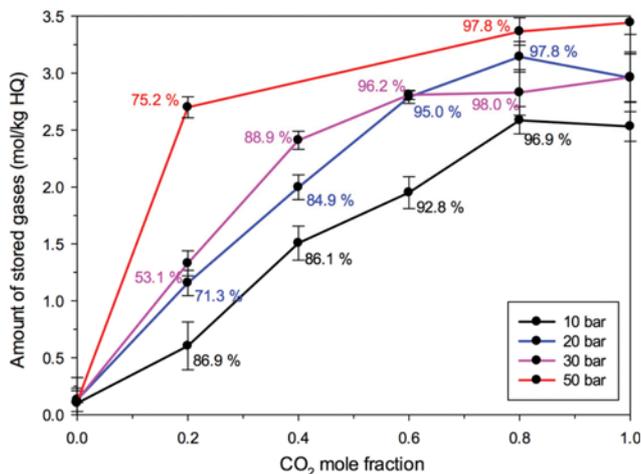


Fig. 3. Amount of gases stored in HQ clathrates prepared with $\text{CO}_2 + \text{N}_2$ gas mixtures of various compositions at 298 K under various pressures. Solid lines with symbols indicate the total number of moles of CO_2 and N_2 molecules stored per 1 kg of HQ clathrates, while the percentages below the symbols represent the CO_2 concentrations in solid clathrates.

full occupation of guests in the clathrate framework, the stoichiometry of the HQ clathrate is known to be $1\text{Gas} \cdot 3\text{HQ}$. Therefore, the experimental results indicate that approximately 20-93% of the cages in the HQ clathrate are filled with gas molecules. The enclathration preference of CO_2 was observed to increase as its concentration in the feed gas became higher. When the CO_2 concentration in the feed gas exceeded 60 mol%, the CO_2 composition in the clathrate compound was 92-98 mol%. These values correspond to 1.61-3.30 mol $\text{CO}_2/\text{kg HQ}$ (or 36.1-73.9 L (STP) $\text{CO}_2/\text{kg HQ}$), which is comparable to the CO_2 sorption capacity of 0.65 and 2.5 mol/kg reported in previous studies [21,22].

Experimental results obtained from spectroscopic and elemental analyses suggest that the storage capacity in the HQ clathrate is enhanced as the formation pressure increases, or as the CO_2 concentration in the feed gas increases. Therefore, quantitative analyses with a ^{13}C solid-state NMR spectrometer and an elemental analyzer were conducted for HQ samples formed with various gas compositions under various pressures (10-50 bar). Because CO_2 molecules are expected to show some non-ideality under increased pressures, the fugacity of CO_2 in the gas mixtures, instead of the partial pressure, was calculated and used. Fugacity coefficients of CO_2 in the gas mixtures were obtained with the following equation [23]:

$$\ln \hat{\phi}_k = \frac{P}{RT} \left[B_{kk} + \frac{1}{2} \sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij}) \right], \quad (1)$$

where i , j , and k represent the components in the mixture; B is the second virial coefficient; $\hat{\phi}$ is the fugacity coefficient in the mixture, and y denotes the mole fraction in the gas phase. Virial coefficients for pure materials are calculated from an equation with a reduced pressure and temperature [23], while critical values and other variables for the mixture are obtained using the associative law suggested by Prausnitz et al. [24]. Fig. 4 shows the cage occupancy and storage capacity of CO_2 in the HQ clathrate according to the fugacity of CO_2 in the feed gas. Except for the low fugacities

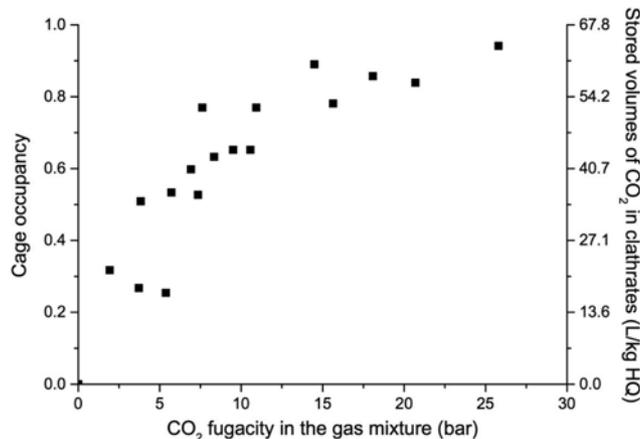


Fig. 4. Cage occupancies and stored volumes of CO_2 in HQ clathrates as a function of CO_2 fugacity in the feed gases.

of CO_2 , where significant errors are expected due to the large signal-to-noise ratio (due to a small amount of captured gas), the cage occupancy was found to increase in proportion to the fugacity of CO_2 . At CO_2 fugacities of less than 5 bar, the cage occupancy of CO_2 was less than 50%, corresponding to 1.51 mol $\text{CO}_2/\text{kg HQ}$ or 33.9 L (STP) $\text{CO}_2/\text{kg HQ}$. However, at larger CO_2 fugacities, the cage occupancy of CO_2 increases to 90%, corresponding to 2.72 mol $\text{CO}_2/\text{kg HQ}$ or 61.0 L (STP) $\text{CO}_2/\text{kg HQ}$. These results indicate that large amounts of CO_2 can be removed from $\text{CO}_2 + \text{N}_2$ gas mixtures with high selectivity, even at low operating pressures. Typical flue gases contain around 10-20 mol% CO_2 and balanced $\text{N}_2 + \text{O}_2$ (O_2 being less than 4 mol%) [4,11]. Fig. 5 shows a conceptual diagram of CO_2 separation/recovery process by the formation of the HQ clathrates. The symbols in the figure indicate the experimental results for the HQ samples at 20 and 30 bar, while the dotted and solid lines indicate the CO_2 concentration

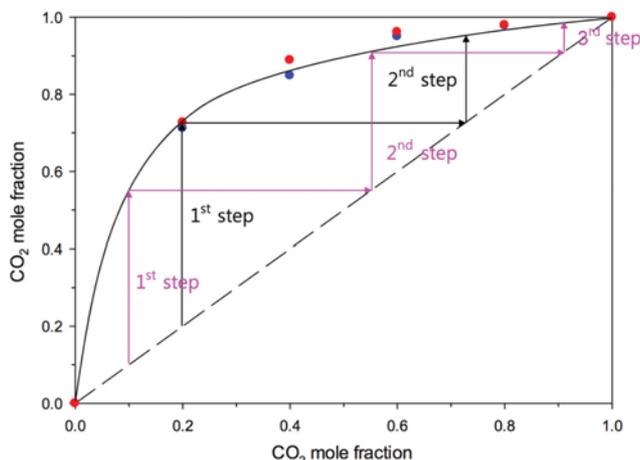


Fig. 5. Conceptual diagram of the CO_2 separation/recovery process by the formation of the HQ clathrates. Symbols indicate the experimental results for HQ samples at 20 bar (blue) and 30 bar (red), while the dotted and solid lines indicate the mole fraction of CO_2 in the feed gas and in the solid clathrate, respectively.

tions in the feed gas and in the clathrate compound, respectively. As shown, the HQ samples at 20 and 30 bar show little difference in terms of the CO₂ concentration, which indicates that CO₂ fugacity reaches a level sufficient for full conversion to the clathrate compound when the total pressure is 20 bar or greater, regardless of the mixed gas composition. In addition, the diagram indicates that the CO₂ can be concentrated to 70 mol% through a one-step clathrate-based process from the 20 mol% CO₂+balanced N₂ flue gas. If the recovered gas mixture is used as the feed gas to a second stage of clathrate-based separation, the recovered CO₂ concentration reaches 93 mol%. This concept may be applied to other flue gases having lower CO₂ concentrations. For the 10 mol% CO₂+balanced N₂ flue gas, the recovered CO₂ concentration with the two-step process can be concentrated to about 90 mol%. This recovery concentration can be further enriched to 98 mol% with a three-step process, as shown in Fig. 5. Although additional modifications may be required to recover a pure CO₂ gas stream, the experimental results obtained here suggest that the HQ clathrate compound can be used for CO₂ separation from flue gases. Considering the storage capacity and milder operating conditions, the clathrate-based process could be viable or cost-efficient compared with conventional and hydrate-based separation processes.

CONCLUSION

HQ samples reacting with CO₂+N₂ gas mixtures with various compositions at various pressures (from 10 to 50 bar) were analyzed by spectroscopic methods to evaluate the efficiency of HQ clathrate compounds for the separation of CO₂ from flue gases. An elemental analyzer was used to obtain quantitative results regarding the separation efficiency and storage capacity of CO₂. Spectroscopic analyses indicate that both CO₂ and N₂ can react with HQ to form clathrate compounds, while CO₂ has higher enclathration preference over N₂ such that the CO₂ concentrations in the solid clathrate are higher than those in the feed gas. When the operating pressure is 20 bar or greater, the CO₂ concentration in the clathrate compound is 85 mol% or higher, regardless of the feed gas composition. In summary, CO₂ is concentrated from typical flue gas (10-20 mol% CO₂+balanced N₂) through a multi-step clathrate-based process at room temperature and under moderate pressure levels. If a two-step or three-step clathrate-based process is devised, 90 mol% or higher CO₂ concentrations can be recovered from CO₂-containing flue gas streams. The qualitative and quantitative results obtained in this investigation will provide useful and fundamental data for designing and evaluating a clathrate-based process for separating CO₂ from flue gases.

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