

The clathrate hydrate process for post and pre-combustion capture of carbon dioxide

Praveen Linga, Rajnish Kumar, Peter Englezos*

Department of Chemical and Biological Engineering, The University of British Columbia,
2360 East Mall, Vancouver, Canada V6T 1Z3

Available online 29 June 2007

Abstract

One of the new approaches for capturing carbon dioxide from treated flue gases (post-combustion capture) is based on gas hydrate crystallization. The basis for the separation or capture of the CO₂ is the fact that the carbon dioxide content of gas hydrate crystals is different than that of the flue gas. When a gas mixture of CO₂ and H₂ forms gas hydrates the CO₂ prefers to partition in the hydrate phase. This provides the basis for the separation of CO₂ (pre-combustion capture) from a fuel gas (CO₂/H₂) mixture. The present study illustrates the concept and provides basic thermodynamic and kinetic data for conceptual process design. In addition, hybrid conceptual processes for pre and post-combustion capture based on hydrate formation coupled with membrane separation are presented.

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Keywords: Gas hydrates; Gas separation; Post-combustion; Pre-combustion; CO₂ recovery

1. Introduction

There are two general approaches to CO₂ capture: either carbon can be removed before the fuel is burned (*pre-combustion capture*) or CO₂ can be removed from the flue gas (*post-combustion capture*) [1]. Post-combustion capture deals with CO₂ from conventional power plants. On the other hand, Integrated Coal Gasification Cycle (IGCC) plants offer one of the most promising routes to CO₂ capture by converting the gas from the gasifier into a stream of H₂ and CO₂ via a shift reaction [2]. CO₂ can then be removed for disposal and the resultant H₂ could be used in fuel cells or in gas turbines. Further work is needed to improve efficiency and reduce operation cost of an IGCC plant, particularly with CO₂ capture [3,4].

A variety of processes have been developed for removing or isolating a particular gaseous component from a multi-component gaseous stream. These processes include absorption, adsorption, membrane separation etc. [2,5]. It has been estimated that, the cost of separation and disposal of CO₂ from existing coal fired, air blown boilers would increase the cost of electricity by about 75% [6]. The cost of separation of CO₂ alone reduces the power generation efficiency from 38 to 26% [7]. A thorough

review on the processes for CO₂ separation is available in the literature [8]. Liquid absorption using amines was considered the most promising current method while some other methods are promising but too new for comparison. There is continued interest in the development of less energy intensive processes.

One of the new methods for separating CO₂ from flue gas or synthesis gas (mixture of CO₂–H₂) is through clathrate or gas hydrate formation. Clathrate or gas hydrates are crystals formed by water molecules and a number of substances such as CO₂, N₂, O₂, H₂, and natural gas components [9,10]. When gas hydrate crystals are formed from a mixture of gases the concentration of these gases in the hydrate crystals is different than that in the original gas mixture. This is the basis for the utilization of clathrate hydrate formation decomposition as a separation process.

Treated flue gas contains CO₂, N₂ and O₂. Since N₂ and O₂ form hydrate crystals at approximately the same conditions the treated flue gas is considered a CO₂/N₂ mixture. Thus, in post-combustion capture from power plants using hydrates, the task is to separate CO₂ from a CO₂/N₂ mixture in which the CO₂ molar content is approximately 15–20%. Pre-combustion capture involves separation of CO₂ from a mixture with H₂ in which the CO₂ molar concentration is approximately 40%. The present work provides fundamental key information required to develop the hydrate-based CO₂ separation processes from CO₂/H₂ and CO₂/N₂ gas mixtures.

* Corresponding author. Tel.: +1 604 822 6184; fax: +1 604 822 6003.
E-mail address: englezos@interchange.ubc.ca (P. Englezos).

2. The clathrate hydrate process

The first task towards process development is to determine the operating temperature and the minimum hydrate formation pressure at the operating temperature for both the post and pre-combustion capture cases. The equipment and the experimental procedure to obtain the equilibrium hydrate formation pressures at a given temperature for CO₂/N₂ and CO₂/H₂ mixtures are described in detail elsewhere [11,12]. A temperature of 0.6 °C was chosen as the operating temperature since it was decided to form hydrate crystals from liquid water and not from ice. Hydrate formation pressure increases with temperature and in order to minimize compression costs the smallest possible pressure is desired.

The second task is to establish the rate of hydrate formation and separation efficiency. For that purpose hydrate formation/decomposition experiments were carried out at 0.6 °C. The hydrate formation vessel has a volume equal to 323 cm³ [13]. The equipment as well as the procedure to carry out the experiments are described in detail elsewhere [13–15]. Briefly, the mode of operation was semi-batch i.e. gas was supplied at constant pressure into the vessel containing 140 cm³ of water. The equipment is properly instrumented to allow calculation of the mass of gas being consumed versus time. In addition, composition and temperature measurements allow determination of the amount of hydrate crystal formed. Following hydrate formation for about 120 min hydrate crystal/gas separation was carried out. The composition of the gas phase as well as the gas from the hydrate after it was decomposed was determined by gas chromatography [13].

2.1. Post-combustion capture

A conventional power plant emits flue gas of composition 15–20% CO₂, 5–9% O₂ and rest N₂. Pretreatment involves removal of acid gases (H₂S, SO₂) and particulates. The pretreated flue gas is to be used in the clathrate hydrate process for CO₂ separation. A CO₂/N₂ gas mixture containing 16.9% CO₂ was used in our experimental work [13]. The minimum pressure to form hydrate crystals from this flue gas mixture at 0.6 °C was found to be 7.7 MPa. The measured data compare well with those available in the literature [16]. It is noted that at 0.6 °C the minimum pressure required to form CO₂ and N₂ hydrates is 1.32 [17] and 17.13 MPa [18], respectively.

The rate of phase change from a water–gas mixture to hydrate is known to be dependent on the magnitude of the deviation of the experimental conditions from those at equilibrium [9,15]. Thus, experiments at 10.0 and 11.0 MPa were carried out. These conditions are significantly above the minimum pressure (7.7 MPa).

The following quantities are calculated based on kinetic and separation efficiency experiments described elsewhere [13,14]. The CO₂ recovery or split fraction (S.Fr.) of carbon dioxide in gaseous and hydrate phase is calculated as follows.

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{Feed}}} \quad (1)$$

where $n_{\text{CO}_2}^{\text{Feed}}$ is defined as number of moles of CO₂ in feed gas and $n_{\text{CO}_2}^{\text{H}}$ is the number of moles of CO₂ in hydrate phase at the end of the experiment. In addition, the separation factor (S.F.) is determined.

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} \times n_{\text{N}_2}^{\text{gas}}}{n_{\text{N}_2}^{\text{H}} \times n_{\text{CO}_2}^{\text{gas}}} \quad (2)$$

where $n_{\text{CO}_2}^{\text{gas}}$ is the number of moles of CO₂ in the gas phase at the end of the kinetic experiment, $n_{\text{N}_2}^{\text{gas}}$ is the number of moles of N₂ in the gas phase at the end of the kinetic experiment and $n_{\text{N}_2}^{\text{H}}$ is the number of moles of N₂ in the hydrate phase.

Fig. 1 shows the CO₂ content in the flue gas mixture (initial composition), the hydrate formed and the residual gas phase (final composition). As seen flue gas which consists of approximately 15–20% CO₂ can form hydrates which contain about 55–57% CO₂. The split fraction or CO₂ recovery was calculated and was found to be 36.7% for the experiment carried out at 11.0 MPa and 0.6 °C. The separation factor for the above experiment calculated from Eq. (2) is 5.3. For the experiment at 10.0 MPa and 0.6 °C, the values obtained for CO₂ recovery and separation factor are 42.1% and 13.2, respectively. As the pressure increases, the CO₂ recovery decreases. This is due to the fact that at higher pressure more number of N₂ gas will occupy its corresponding cages in the hydrate structure. This is also seen in the decrease in the separation factor.

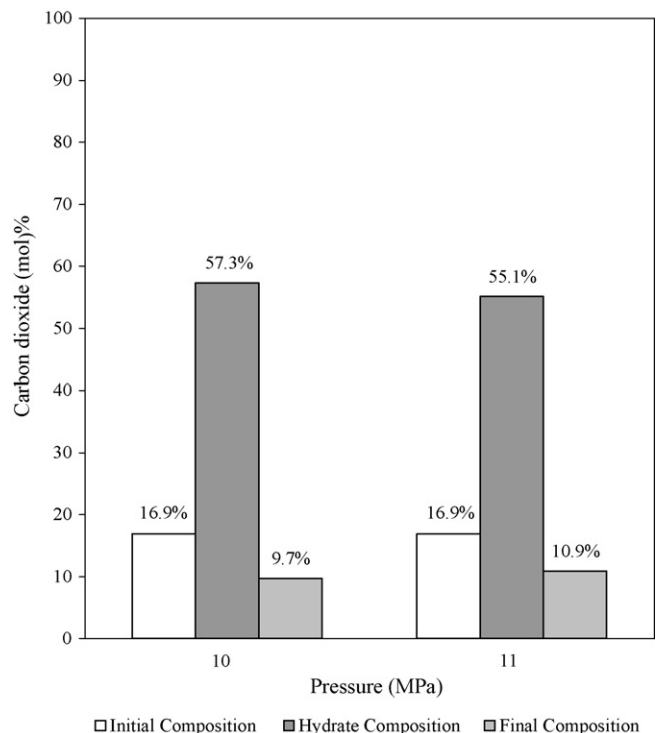


Fig. 1. Hydrate-based separation for CO₂ (16.9 mol.%)–N₂ (83.1 mol.%) gas mixture (temperature = 0.6 °C, 120 min growth).

2.2. Pre-combustion capture

The fuel gas from a gasifier comes out at 1000–2600 °F [19]. This gas is treated for removal of particulate matter and hydrogen sulfide. This gas clean up involves cooling (cold gas cleanup at 311 K) or no cooling (hot gas cleanup at 810 K) [19,20]. The gas cooler produces steam which is utilized by steam turbine to generate electricity. Treated synthesis gas coming out of an IGCC power station consists of approximately 40% CO₂ and 60% H₂ mixture at a total pressure of 2.5–5 MPa [1,17]. Thus, a mixture of 39.2% CO₂ and 60.8% H₂ was used as a model fuel gas (synthesis gas) in our experiment [12,13]. Again it was decided to employ liquid water instead of ice.

First, the equilibrium hydrate formation pressures at different temperatures were determined [12]. The results obtained indicate that the hydrate formation pressures from the H₂/CO₂ mixture are greater than those for pure CO₂. The minimum pressure to form hydrate crystals from this flue gas at 0.6 °C was found to be 5.1 MPa. Moreover, as the relative amount of H₂ to CO₂ increases the hydrate formation equilibrium of the mixture shifts to higher pressures at any given temperature. It is noted that at the same temperature the minimum pressures required to form CO₂ and H₂ hydrates are 1.32 MPa [17] and close to 300 MPa [21], respectively. The temperature of 0.6 °C was chosen as the operating temperature.

Subsequently, hydrate formation experiments were carried out in the 323 cm³ vessel in order to establish the separation efficiency. The experiments were carried out at 0.6 °C and 7.5 MPa and 8.5 MPa i.e. 2.4 MPa and 3.4 MPa above the hydrate equilibrium pressure of 5.1 MPa. The difference between the experimental pressure and hydrate equilibrium pressure is considered as the driving force [15]. Following hydrate formation for about 100 min hydrate crystal separation experiments are carried out [14].

In order to assess the process the following quantities were determined. First, the CO₂ recovery or split fraction (S.Fr.) of carbon dioxide in gaseous and hydrate phase is calculated as follows.

$$\text{S.Fr.} = \frac{n_{\text{CO}_2}^{\text{H}}}{n_{\text{CO}_2}^{\text{Feed}}} \quad (3)$$

where $n_{\text{CO}_2}^{\text{Feed}}$ is defined as number of moles of CO₂ in feed gas and $n_{\text{CO}_2}^{\text{H}}$ is the number of moles of CO₂ in hydrate phase at the end of the experiment. In addition, the separation factor (S.F.) is determined.

$$\text{S.F.} = \frac{n_{\text{CO}_2}^{\text{H}} \times n_{\text{H}_2}^{\text{gas}}}{n_{\text{H}_2}^{\text{H}} \times n_{\text{CO}_2}^{\text{gas}}} \quad (4)$$

where $n_{\text{CO}_2}^{\text{gas}}$ is the number of moles of CO₂ in the gas phase at the end of the kinetic experiment, $n_{\text{H}_2}^{\text{gas}}$ is the number of moles of H₂ in the gas phase at the end of the kinetic experiment and $n_{\text{H}_2}^{\text{H}}$ is the number of moles of H₂ in the hydrate phase.

Fig. 2 shows the CO₂ content in the CO₂/H₂ gas mixture (initial composition), the hydrate formed and the residual gas phase (final composition). As seen, the hydrate formed contains 85%

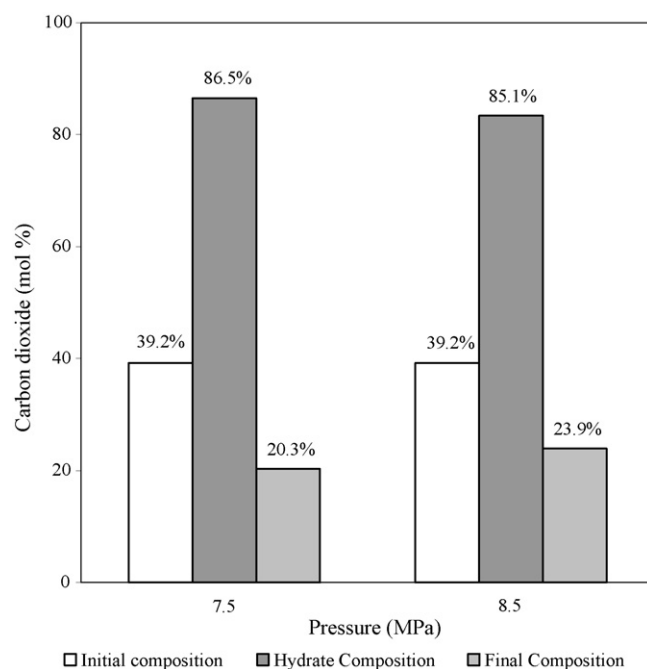


Fig. 2. Hydrate-based separation for CO₂ (39.2 mol.%)–H₂ (60.8 mol.%) gas mixture (temperature = 0.6 °C, 60 min growth).

CO₂. The split fraction or CO₂ recovery was calculated and was found to be 42.5% at 7.5 MPa and 0.6 °C. The separation factor for the above experiment calculated from Eq. (4) is 98.7. For a similar gas separation experiment at 8.5 MPa and 0.6 °C the values obtained for split fraction and separation factor are 36.1% and 32.4, respectively. The experiment performed at 8.5 MPa (higher driving force) shows decrease in the CO₂ recovery compared to a lower driving force of 7.5 MPa. The decrease of split fraction at higher driving force can be explained by the fact that at higher pressure H₂ gas competes with carbon dioxide for cage occupancy which results in lower occupancy of carbon dioxide in hydrate phase. A sharp decrease in separation factor from 7.5 to 8.5 MPa can also be explained similarly as at higher pressure more number of H₂ gas occupies hydrate cages and in turn reduces the relative composition of CO₂ in the hydrate phase.

3. Discussion

The above results indicate that following a one-stage hydrate formation/decomposition process for the CO₂/N₂ mixture, a CO₂-rich gas is obtained which contains 57.3% CO₂ at 10 MPa. Given that the equilibrium hydrate formation pressure of this gas is about 2.4 MPa, a second stage is advocated to obtain a more concentrated CO₂ mixture. The second hydrate formation vessel would operate at a lower pressure compared to the first one since the equilibrium pressure is lower by about 5.3 MPa. Preliminary results indicate that the new CO₂-rich mixture will contain about 83.2% CO₂. Moreover, we envision a hybrid process whereby hydrate formation in three stages is combined with a membrane process. This concept is illustrated in Fig. 3. Table 1, shows the split fraction and separation factors for the three stages for CO₂/N₂ separation [14,22]. This work is ongo-

Table 1
Split fraction and separation factors for the three stages for CO₂/N₂ separation

System	Experimental conditions	Split fraction or CO ₂ recovery	Separation factor
CO ₂ (16.9%)/N ₂	P _{exp} = 10.0 MPa, P _{eq} = 7.7 MPa	0.42	13.2
CO ₂ (57.0%)/N ₂	P _{exp} = 5.0 MPa, P _{eq} = 2.4 MPa	0.32	7.3
CO ₂ (83.0%)/N ₂	P _{exp} = 2.5 MPa, P _{eq} = 1.6 MPa	0.38	36.7

P_{exp}: Experimental pressure, P_{eq}: Equilibrium pressure at 273.7 K.

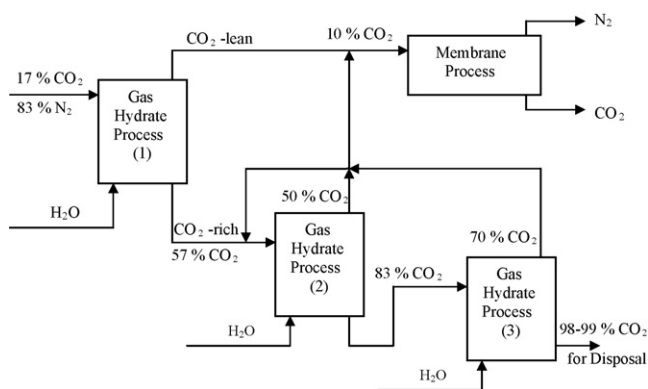


Fig. 3. A hybrid hydrate-membrane process for CO₂ recovery from flue gas.

ing and another objective is to identify additives to lower the hydrate formation pressures without compromising significantly the separation efficiency. Tetrahydrofuran is one such additive that has been suggested in the literature [23,24].

Regarding pre-combustion capture the hydrate contains more than 80% CO₂. Since, the hydrate forming conditions for this mixture are much more favorable than the original one containing 39.2% CO₂ it is proposed to add one more stage and obtain a further concentrated CO₂ stream. The equilibrium hydrate formation pressure of CO₂/H₂ gas mixture with 83.3% CO₂ and rest hydrogen is 1.4 MPa at 0.6 °C [12]. The second hydrate formation vessel would operate at a lower pressure compared to the first one since the equilibrium pressure is lower by about 3.7 MPa. Preliminary results indicate that the new CO₂-rich mixture contain more than 95% CO₂ in hydrate phase. In this case, it is also reasonable to envision a hybrid process to purify the H₂-rich streams. This concept is shown in Fig. 4. Table 2, shows the split fraction and separation factors for the two stages for CO₂/H₂ separation [14,25]. It is also possible that by recycling the CO₂ from the membrane process to the second gas hydrate process a 98–99 mol.% of CO₂ stream can be obtained. Finally, a suitable additive is also required to lower the hydrate forming conditions.

The major disadvantage of the above processes is the high pressure required specially in the first stage. As was mentioned above one way to alleviate this problem for the CO₂/N₂ case

Table 2
Split fraction and separation factors for the two stages for CO₂/H₂ separation

System	Experimental conditions	Split fraction or CO ₂ recovery	Separation factor
CO ₂ (39.2%)/H ₂	P _{exp} = 7.5 MPa, P _{eq} = 5.1 MPa	0.42	98.7
CO ₂ (85%)/H ₂	P _{exp} = 3.8 MPa, P _{eq} = 1.4 MPa	0.38	94.7

P_{exp}: Experimental pressure, P_{eq}: Equilibrium pressure at 273.7 K.

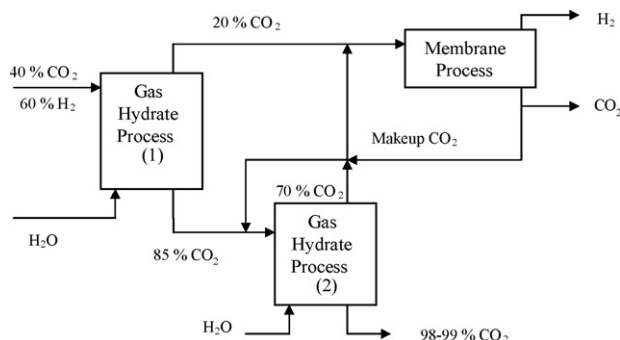


Fig. 4. A hybrid hydrate-membrane process for CO₂ recovery from fuel gas.

is to use THF [13,23,24] and propane for the CO₂/H₂ mixture [12,13]. The above-illustrated processes show the feasibility of the concept and not the economic viability. Clearly, from an economic viewpoint lower pressures are required which can be achieved by adding proper additives to reduce the hydrate formation pressure at any given temperature without compromising the CO₂ recovery and separation efficiency. Compression costs were calculated for a 500 MW conventional power plant, in order to pressurize the flue gas from 0.1 MPa and 70 °C to 10 MPa and 1 °C. It was found that four compression stages with inter-cooling are required [22,25]. The power penalty was found to be 385 MW which is approximately 75% of the power output. Clearly, this demonstrates the need for additives. The work on additives is ongoing and is the avenue to render the hydrate process economically attractive.

4. Conclusions

New data on a relatively novel method for separating carbon dioxide from flue gas (post-combustion capture) and fuel gas (pre-combustion capture) mixture, using gas hydrate formation is presented. Hydrate crystal formation from CO₂/N₂ mixtures showed that CO₂ prefers the hydrate phase. CO₂ recovery was found to be 36.7–42.1% in one stage at 11.0 and 10.0 MPa, respectively. Hydrate crystal formation from CO₂/H₂ mixtures demonstrated that CO₂ prefers the hydrate phase. In fact, very small amounts of H₂ were found in the

hydrate. The CO₂ recovery was found to be 42.5 and 36.1 at 7.5 and 8.5 MPa, respectively. Hybrid hydrate-membrane processes were proposed for pre and post-combustion capture. Compression calculations revealed that additives must be used in order to improve the economics of the process.

Acknowledgement

The financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is greatly appreciated.

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