

Gas hydrate formation process for pre-combustion capture of carbon dioxide

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ABSTRACT: A new process is proposed for the CO₂ separation/recovery of gas mixture. It is based on gas hydrate crystallization. In this study, gas hydrate from CO₂/H₂ gas mixtures was formed in a semi-batch stirred vessel at constant pressure and temperature. This mixture is of interest to CO₂ separation and recovery from Integrated Coal Gasification (IGCC) plants. During hydrate formation the gas uptake was determined and composition changes in the gas phase were obtained by gas chromatography. The impact of Tetrahydrofuran (THF) and Sulfur hexafluoride (SF₆) on hydrate formation from the CO₂/H₂ were observed. The addition of THF or SF₆ not only reduced significantly the equilibrium formation conditions but also helped to form hydrates easier. The present study illustrates the concept and provides basic for the separation/recovery of CO₂ (pre-combustion capture) from a fuel gas (CO₂/H₂) mixture.

Keywords: Gas hydrate, Gas separation, pre-combustion, IGCC, CO₂ recovery

1. INTRODUCTION

The emission of carbon dioxide from the burning of fossil fuels has been identified as the major contributor to the green house emission and subsequent global warming and climate change. Particularly, fossil fuel electric power plants are producing about one third of CO₂ emission worldwide [1]. There are three pathways for CO₂ separation: pre-combustion de-carbonization, oxyfuel combustion and post combustion CO₂ separation from flue gases. Carbon

dioxide can be captured in power station, the flue gas stream (post-combustion capture) or an integrated gasification combined cycle process (pre-combustion capture). At present, the capture of CO₂ from flue gases is done using amine solvents [2]. Pre-combustion carbon capture, involves the removal of all or part of the carbon content of fuel before burning it. The basic idea with pre-combustion de-carbonization is to convert a fossil fuel to a synthesis gas that contains mostly hydrogen and carbon dioxide. In pre-combustion process, the fuel

gas produced contains a high concentration of CO₂ (25-40%), and comes out at a total pressure of 2.5-5 MPa. And, the separated hydrogen can be used in a gas turbine or a fuel cell [3]. Chemical-physical absorption and solid physical adsorption are processes employed for the separation of CO₂ mixtures [4]. Since the energy cost is a major factor, new processes are being considered. One such process is based on gas hydrate [5].

Gas hydrates are non-stoichiometric crystalline compounds formed when “guest” molecules of suitable size and shape are incorporated in the well-defined cages in the “host” lattice made up of hydrogen-bonded water molecules. These compounds exist in three distinct structures I (sI), structure II (sII), and structure H (sH), which contain differently sized and shaped cages. The sI and sII hydrates consist of two types of cages, whereas the sH hydrate consists of three types of cages [6].

The purpose of the present study is to obtain CO₂/H₂ hydrate kinetic and CO₂ recovery from gas hydrate process.

2. EXPERIMENTAL

2.1 Materials

The gas composition was chosen so that they represent industrial composition. In pre-combustion, treated synthesis gas coming out of an IGCC power station consist of approximately 40% CO₂ and 60% H₂ mixture at a total pressure of 2.5-5 MPa [7]. Thus, the gas compositions were determined by gas chromatography and are as follow: 39.2%CO₂ and 60.8% H₂.

2.2 Apparatus and procedure

The apparatus is shown in Fig.1. It consists of Reactor (R), which is a high pressure-cell or vessel equipped with temperature and pressure control systems. Vessel SV acts as a reservoir that supplies gas into the Reactor (R). All vessels are immersed in an insulated bath. An Omega copper-constantan thermocouple is inserted

into the cell to measure the liquid temperatures during the kinetic experiments.

The high pressure-cell is shown in Fig. 2. It has two circular viewing windows on the front and back. Mixing of the cell contents is accomplished using a magnetic stir bar that is magnetically coupled to a set of rotating magnets placed directly underneath the cell. A typical mixing arrangement creates a vortex that is undesirable when kinetic experiments are carried out.

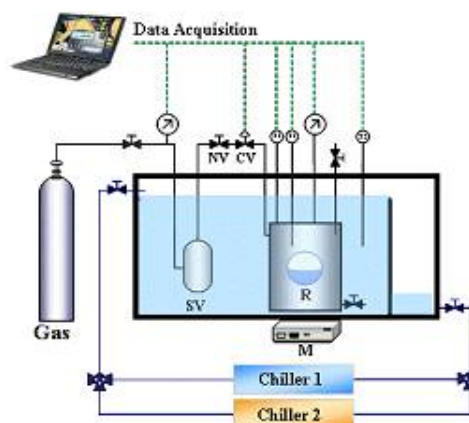


Figure 1: Experimental apparatus

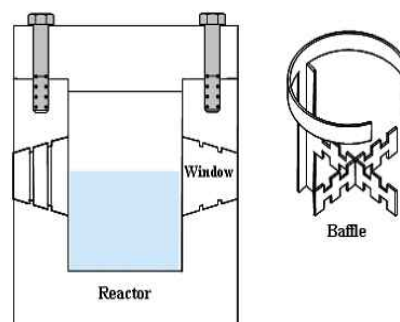


Figure 2: Reactor with Baffle.

This vortex creates a ring consisting of hydrates and occluded water that leaves a small hole at the center of the gas/liquid interface that gradually may disappear. In order to prevent this vortex and to enhance mixing of the cell contents a baffle arrangement is used. For every hydrate formation experiment, 140cc of liquid sample is charged in the high pressure-cell. This volume coincides with the top of the horizontal bar of the baffle, which is also the

gas-liquid water interface. Air in the cell is flushed out by repeating pressurizations with hydrate forming-gas up to 3.0 MPa and depressurizations to atmospheric pressure three times. Subsequently, vessels SV and R are filled with the hydrate forming gas until the desired pressure is obtained. At any given time, the number of moles of the gas that have been consumed is the difference between the number of moles of the gas at time $t = 0$ (start of stirring) present in the vessel SV and the number of moles of the gas at time t . Equation (1) is used to calculate the moles of the gas consumed.

$$\Delta n = V_{sv} \left(\frac{P}{zRT} \right)_0 - V_{sv} \left(\frac{P}{zRT} \right)_t \quad (1)$$

Where the compressibility factor, z , is calculated by Pitzer's correlations [8]. In order to measure the composition of the gas phase in the reactor, a Varian CX 3400 gas chromatograph (GC) (Varian Korea Inc.) is connected on-line with the reactor and automated with a PC.

3. RESULTS AND DISCUSSION

3.1 CO₂/H₂/THF hydrate formation

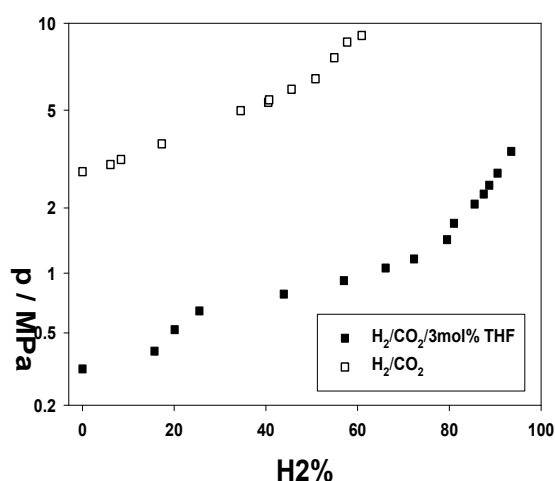


Figure 3: Isothermal phase equilibrium (pressure-composition) relations for the H₂+CO₂+THF at 280.1K. ■ 3mol%THF

(Hashimoto et al.)[9], □ no addition THF (Sugahara et al.)[10]

The pressure required for hydrate formation from CO₂/H₂ mixtures is high for a commercial industrial process. This implies significant compression would be required. Therefore, the use of THF has been proposed. Hashimoto (2006) Presented thermodynamic data showing that addition of 3 mol% of THF in the water lowers the hydrate formation pressure from 9 to 0.97 MPa for a 40%CO₂/60%H₂ mixture at 280.1K. [9,10,11]. While equilibrium data for the above mixtures are available. Unfortunately, studies on the kinetics of hydrate growth coupled with compositional analysis of the gas phase are very limited. Thus, the purpose of the present study is to obtain kinetic information.

Table I: List of experimental conditions along with measured induction time (T = 280.1K)

System	P _{exp} [MPa]	P _{eq} [MPa]	Driving force [P _{exp} -P _{eq}]	Induction Time [min]
CO ₂ -H ₂ - 1mol%THF	4.5	2.47	2.03	3
CO ₂ -H ₂ - 3mol%THF	3.0	0.97	2.03	0.3

Gas uptake measurements for hydrate formation in the presence of 1mol% and 3mol% THF were studied at 280.1K. Table I show the experimental conditions and measured induction time. As seen in the Table, the gas uptake experiments were obtained under the same driving force and the kinetic result was presented in Fig. 4. The difference between the experimental pressure and hydrate equilibrium pressure is considered as the driving force.

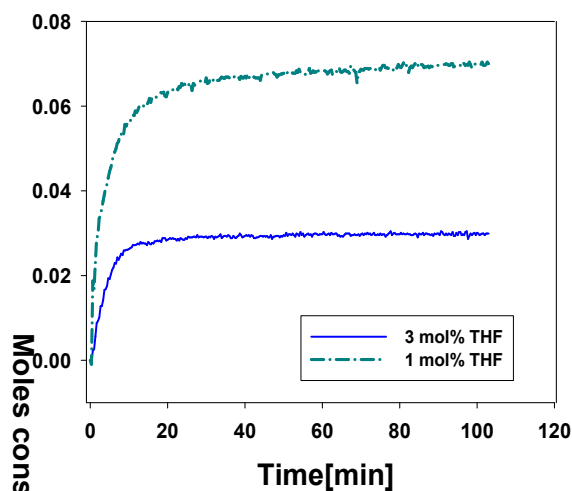


Figure 4: Comparison of hydrate formation data from CO₂(39.2mol%)-H₂(60.8mol%) at 280.1 K and same driving condition. More detailed experimental conditions presented in Table I.

As seen in the Fig. 4, more gas was consumed when lower concentration of THF was used. This is probably related to the differences in the rate of filling of the cavities.

It is possible that high concentration of THF might occupy more cavities in the hydrate structure, thus the other guest (gas) has less chance to enter the cavities. Therefore the addition with high concentration of THF showed less gas consumption rate in our experimental run. It was also found that very fast gas consumption rate was obtained at early stage of hydrate formation, and then the rate was rapidly decreased.

Further studies would be required to determine the optimum THF concentration for better CO₂ separation and recovery efficiency.

3.2 CO₂/H₂/SF₆ hydrate formation

Kumar (2006) have studied hydrate formation conditions for CO₂/H₂ gas mixture with C₃H₈. The results presented that the hydrate formation pressure are substantially lower than CO₂/H₂ [12].

In the present study, The impact of Sulfur hexafluoride (SF₆) on hydrate formation from the CO₂/H₂ were tested.

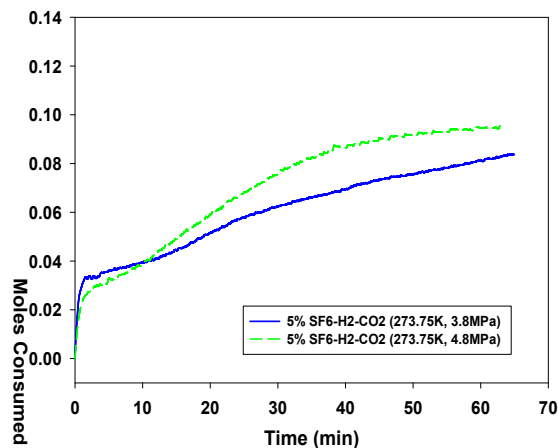


Figure 5: CO₂/H₂ Hydrate formation rate with 5mol% SF₆ at 273.75K

Fig. 5 shows the gas uptake measurement for CO₂/H₂ mixture with addition of SF₆. It can be seen that the rate of hydrate formation was dependent on the magnitude of the driving force. It was also noticed that the rate of gas consumption was continuously increased whereas the system with THF showed different pattern.

Although the experimental conditions in Fig.4 and 5 are different, one should note that the total consumed gas in the system with SF₆ was much higher than that in the system with THF addition.

Compatible experiments should be required and it will be tested soon in our laboratory.

3.3 CO₂ recovery

The composition of the gas phase as well as the gas from the hydrate after it was decomposed was determined by gas chromatography. Fig. 6 shows the CO₂ content in the initial feed gas, the hydrate and the residual gas phase (final composition).

Hydrate-based CO₂ separation from CO₂(39.2mol%)-H₂(60.8 mol%) mixtures showed that CO₂ prefers the hydrate phase.

The CO₂ content in the hydrate phase was found to be 79.5–84.7%. Better separation efficiency was obtained at the system with SF₆

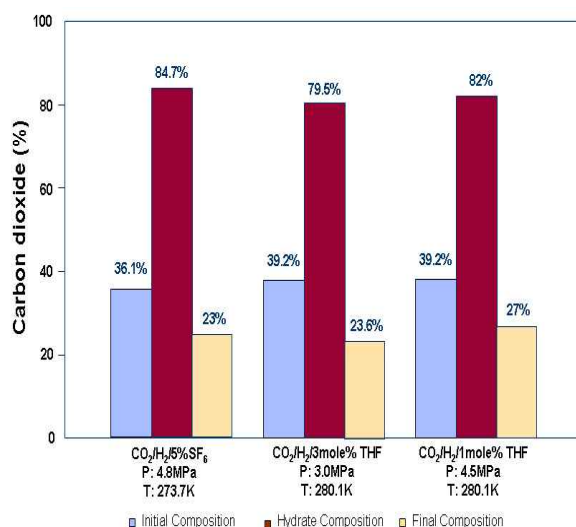


Figure 6: CO₂ recovery from CO₂/H₂ gas mixture

5. CONCLUSION

The impact of Tetrahydrofuran (THF) and Sulfur hexafluoride (SF₆) on hydrate formation from the CO₂/H₂ were observed. The addition of THF or SF₆ reduced the hydrate formation pressure for a CO₂/H₂ separation process. Our experimental data showed that CO₂ prefers the hydrate phase. In particular better CO₂ separation efficiency was obtained in the system with SF₆.

Our results support that SF₆ can be used for excellent additive for the hydrate-based CO₂ separation

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