

HYDRATE PROCESSES FOR CO₂ CAPTURE AND SCALE UP USING A NEW APPARATUS

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ABSTRACT

One of the new approaches for capturing carbon dioxide from treated flue gas (post-combustion capture) and fuel gas (pre-combustion capture) is based on gas hydrate crystallization. The presence of small amount of tetrahydrofuran (THF) substantially reduces the hydrate formation pressure from a flue (CO₂/N₂) gas mixture and offers the possibility to capture CO₂ at medium pressures [1]. A conceptual flow sheet for a medium pressure hydrate process for pre-combustion capture from a fuel gas (CO₂/H₂) was also developed and presented. In order to test the hydrate-based separation processes for pre and post combustion capture of CO₂ at a larger scale a new apparatus that can operate with different gas/water contact modes is set up and presented.

Keywords. Hydrogen; carbon dioxide; gas hydrates; gas separation; IGCC; flue gas

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*) [2]. "Post combustion capture" of CO₂ refers to separating carbon dioxide from the flue gas emitted from conventional power plants utilizing fossil fuels. 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 [3]. 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 [4, 5]. Due to the emission of carbon dioxide the production and use of energy from fossil fuels is linked to the global environmental problem known as the greenhouse effect [6]. Aaron and Tsouris [7] reviewed in detail

all processes available for recovery of CO₂ from a flue gas mixture including some which are still at the laboratory stage and concluded the absorption with monoethanolamine (MEA) is the best method. However the regeneration of the solvent makes the absorption process energy intensive. Separation of CO₂ from a flue gas mixture and its compression are the largest contributors to the cost [8-10].

The need to reduce costs motivates further research into the subject. Among the new concepts for CO₂ capture is gas hydrate crystallization [7, 11]. Clathrate or gas hydrates are ice-like inclusion crystals formed by small molecules like methane, ethane, carbon dioxide and water at suitable temperature, pressure and material availability conditions [12-14]. The small molecules are enclosed in cages formed by hydrogen-bonded water molecules.

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 and decomposition as a separation process [15, 16]. The input to the proposed process is a flue gas after the removal of particulates and SO_x .

Figure 1 illustrates the basic idea behind the gas separation using gas hydrate technology. A CO_2/N_2 mixture is fed in to the process where it comes into contact with a THF solution at suitable temperature and pressure conditions and forms hydrate crystals. The crystals are separated and subsequently decomposed to create the CO_2 -rich stream while the rest constitute the CO_2 -lean one.

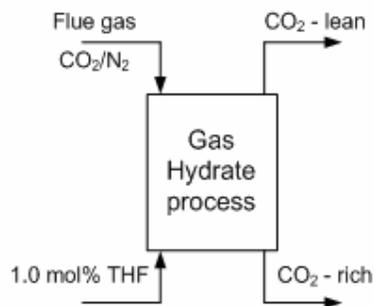


Figure 1. Hydrate based gas separation process

A conceptual process flow sheet was presented for recovery of carbon dioxide from a flue gas and a fuel gas mixture in three stages [15, 16]. However, the operating pressures required for both the process are high. For the flue gas separation, the first stage requires 10 MPa. This would require about 75 % of the power output from a conventional plant [16]. While for the fuel gas separation process, the first stage required 7.5 MPa. One way to alleviate the problem of high operating pressures is the use of additives that will lower the hydrate formation conditions without affecting the kinetics and the separation efficiency or CO_2 recovery. The need for a lower pressure process was recognized early and the addition of tetrahydrofuran (THF) was recommended for the flue gas separation [11]. The addition of THF even in small quantities considerably reduces the operating pressure. For example a gas mixture of 16.9% CO_2 and rest N_2 forms hydrate at 7.7 MPa at 273.7 K. With the addition of 1 mol% THF, the mixture readily forms hydrate at 0.345 MPa.

For the separation of CO_2 from the fuel gas mixture, a suitable additive is propane. Kumar et

al. [17] reported that hydrate formation pressure at any given temperature reduced by almost half on addition of just 3% of propane to the CO_2/H_2 mixture. Finally, Linga et al. [16] presented two metrics to assess the hydrate-based separation process. These are the separation efficiency or CO_2 recovery and the separation factor.

The objective of this work is to present a medium pressure process for pre-combustion capture of CO_2 and also present a large scale apparatus which will be used to test the hydrate processes at a larger scale. A key objective of the new apparatus is to enhance the rate of hydrate formation and also to increase the CO_2 recovery or separation efficiency of the process

CAPTURE OF CO_2

Linga et al. [1] presented thermodynamic and kinetic data obtained from a semi batch stirred tank reactor studying the effect of THF on the hydrate process to capture CO_2 from a flue gas mixture. They also presented a medium pressure clathrate process operating at 273.7 K and 2.5 MPa which combines three hydrate formation stages with a membrane separation stage to recover CO_2 from a flue gas mixture. Nearly 50% of CO_2 is recovered in the first two hydrate stages and 37% in the third one. The process uses 1 mol % THF. Even though, the operating pressure is reduced significantly, the rate of hydrate formation and the overall gas consumption for hydrate formation was less compared to the high pressure process without THF [1, 16].

Hence there is a need to improve the rate of hydrate formation and the separation efficiency of CO_2 in order to reduce the load on the membrane unit that will deal with the CO_2 lean phase coming out of the hydrate process unit. This can be accomplished by a better contact of water and gas to form hydrates.

Hydrate formation experiments were carried out for the fuel gas mixture with the presence of 2.5 % of propane at 3.8 MPa and at 273.7 K for two hours. The hydrates were decomposed and it was found to have a composition of 83.0 mol % CO_2 while, the composition of propane and hydrogen are 6.5 % and 9.9 % respectively. The key is to enrich the CO_2 stream with another hydrate formation stage. This can be accomplished with another hydrate formation stage. The second stage

operate can be operated at 3.5 MPa. Our results indicate that the CO₂ rich stream coming out of the second stage is 98.0% CO₂. Hence, a CO₂ rich stream of 98% CO₂ can be obtained in two stages and is shown in figure 2. In order to complete the separation a hybrid membrane/hydrate process as shown in figure 2 is suggested. The CO₂ recovery calculated for the first stage and the second stage hydrate process are 0.47 and 0.32 respectively.

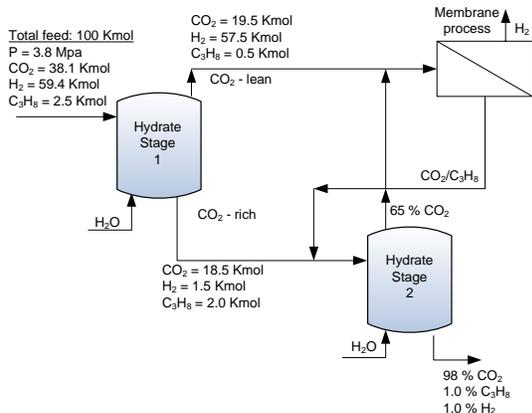


Figure 2. Block flow diagram for a hybrid hydrate-membrane process for CO₂ recovery from fuel gas.

There is a need for examining the hydrate process for the separation of CO₂ from fuel and flue gas mixtures at a larger scale. Some of the key areas to improve are the rate of gas consumption and also overall gas consumption.

A New Large Scale Hydrate Apparatus:

The schematic of the new apparatus is given in Figure 3. It consists of the crystallizer (CR) and reservoir (R), which is used to supply gas during hydrate formation experiments and also to collect the decomposed gas during hydrate decomposition. Both CR and R are immersed in a water bath. The temperature of the water bath is controlled by an external refrigerator. The apparatus is instrumented with pressure transmitters and thermocouples which are connected to a data acquisition system to record the pressure and temperature data. The apparatus also consists of a control valve coupled with a PID controller.

Figure 4 shows the cross section of the crystallizer. It is a modular type crystallizer with two removable sections connected together with top and bottom flanges. The crystallizer is equipped with a stirrer. The shaft of the stirrer has a special

arrangement with the propeller so that when the experiment is run under a pressure it allows the flow of gas through the shaft and then releases it in the liquid through the propeller blades. Hence it enables proper mixing as well as internal circulation of gas into the liquid. The crystallizer is also connected to a high pressure pump. The crystallizer can also be operated as continuous mode by circulating the liquid contents from the bottom of the crystallizer using the pump and spraying it through two nozzles connected at the top of the crystallizer as shown in figure 3 and 4. This can be done at high pressures.

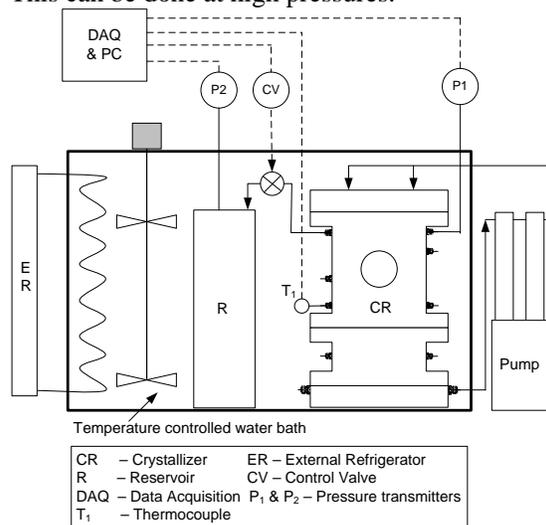


Figure 3. Schematic of the apparatus

Hydrate formation procedure for “closed-system operation”

1.1 L of 1.0 mol% THF is added into the crystallizer. The pressure in the crystallizer is then set to the desired experimental pressure (2.5 MPa) and the temperature is allowed to reach the experimental temperature. The stirrer is set at the desired speed setting and is started. This is time zero for the formation experiment. Data is then logged in the computer for every 20 seconds. All hydrate formation experiments are carried out with a fixed amount of water and gas (closed system). The temperature in the crystallizer is maintained constant by an external refrigerator. When hydrate formation occurs, gas will be consumed and hence the pressure in the closed system drops. The experiment is allowed to continue for 120 min. Pressure and temperature data are used to calculate the moles of methane consumed in the crystallizer (gas uptake) for hydrate formation.

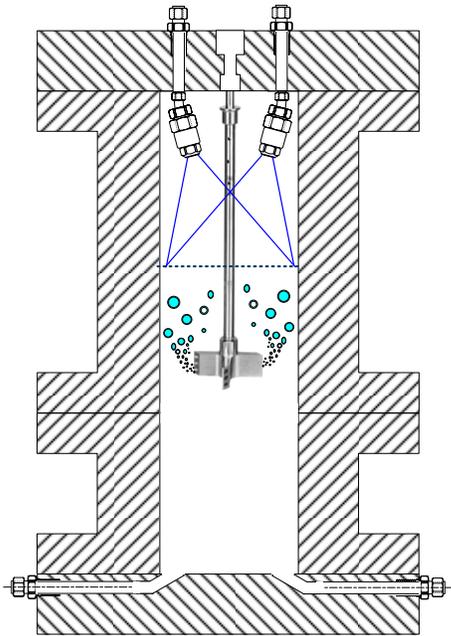


Figure 4. Cross section of the crystallizer with the stirrer and nozzle arrangement.

Hydrate formation experiment for 16.9% CO₂/ rest N₂ gas mixture was carried out at 275.3 K and at an experimental pressure of 2.5 MPa. The experiments were carried out at three stirring rates of 200, 300 & 400 rpm, respectively, to study the effect of mixing on hydrate formation and also to determine the optimum mixing speed for the new experimental apparatus. Figure 5 shows the gas uptake measurement curve obtained for the experiment conducted at a mixing rate of 400 rpm. Hydrate formation started as soon as the mixing commenced. Hydrate formation is a crystallization process and an exothermic reaction. Hence, heat is released when nucleation occurs and this is represented by an increase in temperature at <1 min. This point is referred to as induction point or turbidity point.

Figure 6 shows a comparison of the gas uptake measurement curves obtained for all the three experiments carried out at the same temperature and experimental pressure but at different stirring rates. As it can be seen from the figure, the gas uptake was considerably higher for the experiment conducted at 400 rpm compared to the one conducted at 200 and 300 rpm. The hydrate formation rates were calculated for the first 20 min of hydrate formation [1, 18]. The rates were found to be 0.126, 0.146, and 0.329 mol/hr for the

mixing speeds of 200, 300 and 400 rpm, respectively.

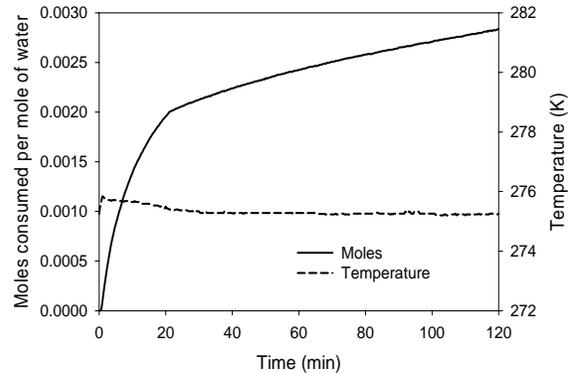


Figure 5. Typical gas uptake measurement curve obtained at 275.3 K and at a starting pressure of 2.5 MPa. (The mixing speed was 400 rpm)

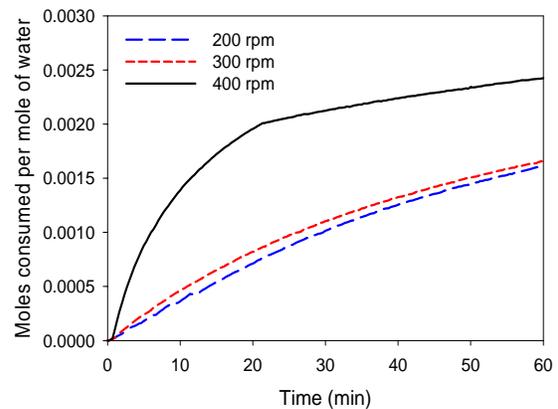


Figure 6. Effect of mixing on hydrate formation.

Research is under way to test other contact modes like spraying water into the gas environment and also to simulate all the contact modes like mechanical stirring, bubbling gas in the water environment and also spraying water in the gas environment with the focus of improving the hydrate formation rates and also to demonstrate the separation process at a larger scale.

CONCLUSIONS:

A medium pressure process for pre-combustion capture of CO₂ from fuel gas has been presented. It consists of two hydrate stages operating at 273.7 K and at 3.8 and 3.5 MPa, respectively. A fuel gas mixture (39.2/60.8) CO₂/H₂ is separated into nearly 98 % CO₂ and H₂ streams. In order to enhance the rate of hydrate formation and scale up

the CO₂ capture process a new hydrate formation apparatus was built. The optimum mixing rate for the system was selected to be 400 rpm. The mole consumption rate at the optimum mixing was found to be 0.329 mol/hr. Further work is underway to study the effect of other gas/water contact modes.

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