

A NOVEL CONTINUOUS-FLOW REACTOR FOR GAS HYDRATE PRODUCTION

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ABSTRACT

Potential applications of gas hydrates, including carbon dioxide sequestration in the deep ocean, coal bed methane–produced water treatment, storage and transportation of natural gas, and gas separations, are based on continuous, large-scale production of gas hydrates. A novel three-phase injector/reactor was developed at Oak Ridge National Laboratory for the continuous synthesis of gas hydrates. The reactor receives water and a hydrate-forming species and rapidly forms hydrate with a residence time of a few seconds. The reactor was designed to maximize interfacial area between reactants, thus minimizing mass transfer barriers and thermal effects that negatively affect conversion of reactants into hydrate. The cohesiveness and the density of the hydrate product desired for specific applications can be controlled by slight variations in the geometry of an exchangeable internal piece of the reactor, the choice of the guest gas, and by the regulation of operating parameters such as pressure, temperature, reactant ratios, and degree of emulsification. In general, spraying one reactant into the other, within the jet-break up regime, results in the highest conversions. The reactor has been field tested for ocean carbon sequestration and in the laboratory for coal-bed methane produced-water treatment using liquid carbon dioxide. In this paper, the application of the reactor for ocean carbon sequestration will be discussed.

Keywords: CO₂ hydrates, hydrate reactor, continuous hydrate formation, carbon sequestration

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NOMENCLATURE

P operation pressure [MPa]

INTRODUCTION

Gas hydrates are ice-like crystalline structures formed by cages of hydrogen-bonded water molecules that are stabilized by the presence of a molecule of a guest gas species inside each cage [1]. With a ratio of 5 to 8 molecules of water per gas molecule, gas hydrates have a large capacity for the storage of gases in a stable, solid phase, which makes them an attractive medium for applications like gas transportation and storage [2], and ocean carbon sequestration [3]. However, the lack of a technology that will allow the production of hydrate in a continuous manner suitable for scale-up to industrial settings has hindered the utilization of gas hydrates in the above mentioned applications and others, such as gas separations [4] and produced water treatment [5].

Batch stirred-tank reactors are widely used in laboratory settings to perform fundamental studies on formation and dissociation of gas hydrates [4]. Only in recent years, the development of other alternatives has been pursued. One of such developments is the use of static mixers to promote hydrate formation, which enables the introduction of agitation in a semi-continuous or even a continuous manner [6,7]. Although the operation of such reactors is not batch, they present a similar limitation as in the batch stirred-tank reactors: the production of hydrate is limited by the degree of turbulence achieved during the mixing of water and the guest species [4,6,7].

The study of both stirred-tank and static-mixer reactors led to the conclusion that hydrate formation occurs at the interface between water and the guest species, which are in most cases immiscible [7]. Therefore, hydrate production can be enhanced via maximization of interfacial area in order to minimize mass transfer barriers and improve heat dissipation during hydrate formation [1,7]. Although various reactor designs have been since pursued to maximize the interfacial area between hydrate-forming species, none has been developed for continuous operation so far due to limitations imposed by scale of testing—for example, spraying of water in a chamber full of compressed gas [8–10]. Additionally, the utilization of surface-active or foaming agents has been pursued as well in a mixing-type of reactor design [11,12].

In the present work we discuss the design and development of a continuous hydrate reactor that produces hydrate from aqueous solutions and liquid CO₂. The reactor has been designed and tested for the purpose of carbon sequestration. However, other possible applications of the reactor and design modifications for each particular application are currently under investigation.

REACTOR DESIGN

It is expected that hydrate formation will take place when the components—i.e., water and guest species—are subjected to conditions of temperature and pressure inside the hydrate stability zone [1]. However, hydrate formation is usually controlled by the rate of crystallization, and, thus, it can be a slow process [1].

A successful way to accelerate the process is to form dispersions of one of the hydrate forming species into the other via vigorous mixing [4–12]. It is expected that hydrate formation will take place at the interface between the two hydrate-forming species, which also acts as a nucleation site.

The concept of creating very fine dispersions of water in liquid CO₂ via concurrently spraying a water stream into a liquid-CO₂ stream was developed at Oak Ridge National Laboratory (ORNL) a few years ago and successfully applied for the continuous formation of CO₂-hydrate particles at a small scale in both laboratory and field settings [13–17]. The original design was recently modified to allow, at a minimum, a ten-fold increase in the flow capacity of water and liquid CO₂ [18].

The new reactor design includes two parts: (1) an injector head piece and (2) the reactor mixing zone. The injector head piece includes a flow-distributing disk with single- or multi-capillary perforations that achieve the spraying of water in liquid CO₂ or vice versa at high velocities to form dispersions of very fine liquid droplets. The distributing piece is interchangeable, so different diameters and arrays of capillary perforations can be used as desired. Variations in design include multiple lateral injection points for the continuous phase.

The reactor mixing zone is attached to the injector piece and is also interchangeable, in order to control the residence time of the hydrate particles in the reactor as desired. Hydrate formation and further particle growth is promoted in the reactor mixing zone, as well as consolidation of the

particles into cylindrical composites that are several centimeters long, composed of CO₂-hydrate particles along with trapped unconverted water and liquid CO₂. The degree of conversion of hydrate-forming species into hydrate and the degree of consolidation of the final product are determined by the interchangeable pieces placed in the reactor as well as the choice of operation parameters [18].

APPLICATION OF THE REACTOR FOR OCEAN CARBON SEQUESTRATION

The concept behind the application of gas hydrates for ocean carbon sequestration is that CO₂-hydrate/liquid CO₂/water composites, with a composition of at least 25% hydrate, become heavier than sea water at ocean depths greater than 700 meters (equivalent to a pressure of 7.17 MPa) at ocean temperatures of ~4 °C [3,14]. Therefore, direct injection of CO₂ in the ocean leading to even partial formation of CO₂ hydrate would result in a sinking, slowly dissolving plume of hydrate particles with the following advantages when compared to other ocean carbon sequestration methods—for example, injection of a rising or sinking plume of liquid-CO₂ droplets: (1) increased residence time of sequestered carbon in the oceans, (2) reduced CO₂ pumping costs, and (3) less significant environmental impacts [19].

The ability of the scaled-up, continuous hydrate reactor to produce consolidated sinking CO₂-hydrate particles at pressures equivalent to ocean injection depths suitable for carbon sequestration and average ocean temperatures was tested first in the laboratory [18,20]. All the laboratory tests were performed in the Seafloor Process Simulator (SPS), a cylindrical Hastelloy C-22 vessel equipped with sapphire observation windows that can be maintained at pressures of up to 20 MPa [21]. During the experiments, the reactor was fully submerged in water to mimic the setup during possible ocean carbon injections. An experimental design targeting the individual and combined effects of the following variables and operation parameters was used: (1) design of capillary array in the distribution disk; (2) diameter of the capillary or capillaries on the distribution disk; (3) choice of dispersed phase—either liquid-CO₂ or water; (3) water/liquid CO₂ flow rate ratios; and (4) operation pressure or ocean depth of injection. A submersible pump (Seabird SBE 5T) was used to introduce water into the reactor at flow rates varying from 2.0 to 3.0 L/min, while the liquid

CO₂ was introduced to the reactor by a pulsed-flow Haskel pump at flow rates varying from 0.33 to 0.66 L/min. It should be noted that the water/liquid CO₂ flow rate ratios during all experiments were always kept higher than 2 in order to prevent the process from becoming reactant-limited. It should also be noted that the hydrodynamic conditions for all the experiments inside the reactor were always within the spray regime—that is, Weber numbers above 1000 [18,20]. Successful continuous production of CO₂-hydrate/liquid-CO₂/water composite particles was achieved at pressures as low as 4.8 MPa, and at temperatures as high as 4.1 °C (the equilibrium pressure at 4 °C is 3.75 MPa). However, consolidated, sinking hydrate-composite particles could only be obtained at pressures higher than 6.7 MPa at the same temperature. The reason for this is that the density of the final hydrate-composite product is a function of the conversion to hydrate achieved inside the reactor. Larger driving forces in terms of over-pressurization with respect to the required equilibrium pressure for hydrate formation are required to achieve larger conversions.

Figure 1 presents three examples of CO₂-hydrate composites obtained during the laboratory experiments that present different degrees of consolidation. The degree of consolidation and CO₂ hydrate composition of the final product can be controlled via the selection of the diameter of the capillary tube(s) of the distributing disk in the injector head; the operation pressure; the ratio of water to liquid CO₂ flow rates; the length of the mixing zone; and the choice of dispersed phase. In the case depicted in Figure 1, all experiments were performed with a multi-capillary injector with a capillary diameter of 119 microns. The different degrees of consolidation were achieved by regulating the injection pressure —P = 8.96 MPa for the case depicted in Figure 1(a) instead of P = 11.72 MPa for the cases depicted in Figures 1(b) and 1(c)—and by changing the water/liquid-CO₂ ratios. Upon completion of the laboratory tests of the reactor, it was decided that the multi-capillary distribution disks with a capillary diameter of 119 microns would be used for field tests.

Ocean carbon injections using the reactor described in this work were conducted at Monterey Bay, CA, more than 50 miles away from the coast [20]. A battery of four reactors was mounted in parallel on a remotely operated vehicle (the ROV *Tiburón*, property of the Monterey Bay

Aquarium Research Institute). However, due to pumping limitations, only one reactor was used during the experiments. The formation of CO₂-hydrate composite particles and the fate of the hydrate plume were monitored from the research vessel (RV) *Ventana* of the Monterey Bay Aquarium Research Institute. Details on experimental results and the performance of the reactor during the ocean carbon injection experiments can be found elsewhere [20].

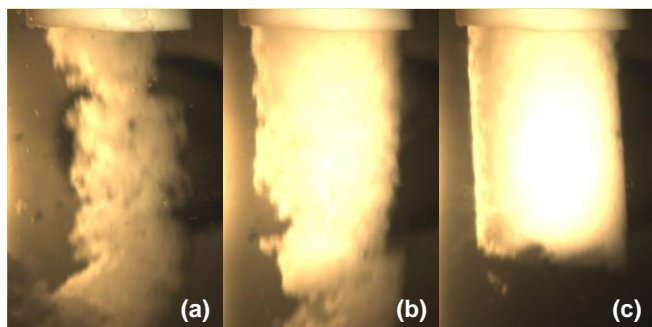


Figure 1 Examples of CO₂-hydrate composite product obtained with a 119- μ m diameter multi-capillary distributor with water as the dispersed phase at the following conditions: (a) P = 8.96 MPa and water/liquid-CO₂ ratio of 2.5; (b) P = 11.72 MPa and water/liquid-CO₂ ratio of 3.2; and (c) P = 11.72 MPa and water/liquid-CO₂ ratio of 2.0.

In conclusion, a novel continuous-flow reactor for the production of CO₂ hydrate was designed, constructed, and tested for its application to ocean carbon sequestration. The reactor successfully produces CO₂ hydrate/water/liquid CO₂ composites of varying degrees of consolidation and density. The consolidation and density can be controlled by regulation of operation parameters or slight variations in reactor design via interchangeable pieces. The utilization of the reactor and variations in the original design for other industrial applications are under development.

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