Chemical Engineering Journal 172 (2011) 144–157

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetics of CO_2 hydrate formation in a continuous flow reactor

Dali Yang[a,*], Loan A. Le[b], Ronald J. Martinez[b], Robert P. Currier[b,**], Dwain F. Spencer[c]

[a] Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States
[b] Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States
[c] SIMTECHE, 13474 Tierra Heights Road, Redding, CA 96003, United States

ARTICLE INFO

Article history:
Received 5 January 2011
Received in revised form 23 May 2011
Accepted 23 May 2011

Keywords:
Mass transfer
CO_2 hydrate
Hydrate formation
Kinetics
IGCC

ABSTRACT

In a previous paper, we examined heat transfer issues during CO_2 hydrate formation in a tubular continuous flow reactor (Energy & Fuels 22 (2008) 2649–2659). In this work, the CO_2 hydrate formation dynamics are examined from a chemical kinetics perspective. Mixtures of CO_2 and argon, or helium, are used to mimic the composition of shifted synthesis gas (typically ~40 vol% CO_2 in hydrogen). The kinetics of CO_2 hydrate formation are reported at high fluid velocities and at high gas volume fractions (exceeding 85%). The effects of the gas carrier, fluid velocity, slurry concentration, and temperature on the hydrate formation rate are investigated. The CO_2 hydrate phase likely forms at the interface between aqueous and gas phases and can be well-represented by a first-order reaction rate law under each of the distinct flow conditions considered. At the highest velocities and gas volume fractions tested, vigorous inter-phase mixing reduces heat and mass transfer resistances and the global reaction rate may ultimately approach the intrinsic CO_2 hydrate formation rate. Under many other conditions, the global hydrate formation rate appears to be heat transfer-limited. Under heat transfer-limited regimes, the higher heat transfer rates associated with helium/CO_2 mixtures (relative to argon/CO_2) give apparent overall rate constants higher than those obtained from a Ar/CO_2 mixture under similar flow conditions. However, even in the presence of thermal transport resistances, the hydrate formation rate remains rapid under industrially relevant processing conditions and the apparent kinetics can still be represented reasonably well by a simple first-order model, which should prove useful in process simulation and assessment studies.

1. Introduction

Fossil fuels currently supply over 85% of the energy in the United States of America. Use of these fuels is projected to increase significantly in the first half of the 21st century. However, combustion of these fossil fuels is responsible for ~90% of the greenhouse gas (GHG) emissions in the United States [1,2]. In an era of heightening concern over carbon dioxide-induced global warming, continued use of resources such as coal may soon require near-zero emissions in power plant applications. One promising technology for achieving this goal is the integrated gasification combined cycle (IGCC) design [2–7]. IGCC technology effectively converts coal into its chemical constituents using gasification which is followed by a water-gas shift reaction to generate "shifted" synthesis gas. The shifted synthesis gas consists of pressurized hydrogen fuel (60 vol%), carbon dioxide (37–39 vol%), and trace gases such as hydrogen sulfide. At this point, it provides an attractive basis for pre-combustion carbon capture at the industrial-scale. A key element in this, or any, carbon capture and sequestration scheme is the ability to economically separate the carbon dioxide and provide pipeline pressure gas for transport to the sequestration sites. A viable, economic, and efficient carbon dioxide separation technique will thus prove essential in implementing carbon capture and sequestration at the industrial scale.

The SIMTECHE process is designed to separate and pressurize CO_2 from IGCC power plants [8,9]. This flexible process can be configured to reduce CO_2 emissions from such plants by 65–90 vol%, or more. The process makes use of the fact that high pressures are being designed into the IGCC flow sheets, motivated by both gasifier and gas turbine performance considerations. These higher processing pressures are exploited in the process to remove the CO_2 (and hydrogen sulfide derived from sulfur in the feedstock) at elevated pressures by forming gas hydrates. The gas hydrates are ice-like inclusion compounds (illustrated in Fig. 1), which are used as a separation agent. These inclusion compounds can incorporate light hydrocarbon gases, such as methane, CO_2, and/or hydrogen sulfide (H_2S) into their crystalline structures [10]. Specifically, "guest" molecules (e.g. CO_2) are physically captured within polyhedral cages of hydrogen-bonded water molecules primarily by means of van der Waals forces. Crystalline gas hydrates have the capacity to incorporate large amount of gas. For example, in a CO_2 hydrate,

---

* Corresponding author. Tel.: +1 505 665 4054.
** Corresponding author. Tel.: +1 505 665 3601.
E-mail addresses: dyang@lanl.gov (D. Yang), currier@lanl.gov (R.P. Currier).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.05.082

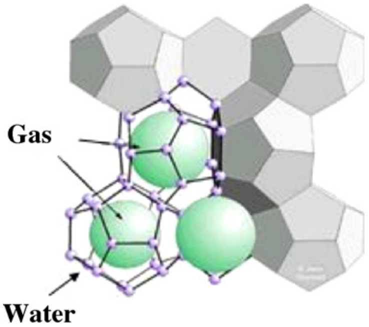

Fig. 1. Polyhedral gas–hydrate cages (comprised of hydrogen-bonded water) enclosing guest molecules.

carbon dioxide represents up to 30% of the gas hydrate by weight [10]. The basis for CO_2 separation from shifted synthesis gas is the fact that hydrogen does not readily form gas hydrates under these conditions, thus it is largely excluded from the crystalline phase, remaining in the gaseous state [8,9,11–15]. An advantage of using gas hydrates as the separation agent is that upon decomposition of the hydrates, elevated pressure CO_2 can be produced [15,16]. This is especially important if pressurized CO_2 is required for geologic disposal or for use in enhanced oil recovery [9]. Gas hydrates have also attracted attention as a potential means of disposing CO_2 into the deep sea [17–22]. Numerous process engineering and economic studies have been conducted aimed at understanding the thermodynamic and kinetic mechanisms of water–CO_2 hydrate formation and to investigate the effect of hydrodynamics on formation and dissociation [14,23–30]. However, virtually all of these studies were conducted in batch reactors using liquid CO_2 injection into water or made use of a water ice phase to promote hydrate formation. It is important to also investigate CO_2 hydrate formation from gas mixtures and liquid water at high flow velocities and high gas volume fractions in a continuous flow reactor (CFR). These conditions are directly relevant to industrial application of hydrates as separation agents.

A major advantage of a hydrate-based process is the ability to regenerate CO_2 at elevated pressures which greatly reduces compression costs required to produce pipeline pressure gas [31]. A block diagram of the process is shown in Fig. 2. Another advantage of this process over chemical scrubbing techniques is that no chemical agents are added to absorb the CO_2. The only working fluid is CO_2-saturated cold water, which is re-circulated. As a consequence, the CO_2 hydrate separation process does not add new byproducts or wastes. Gas hydrate formation does involve some energy intensive steps in that gas hydrate formation is exothermic while gas hydrate dissociation is endothermic. However, close integration of the heat-of-formation with the heat required for CO_2 regeneration from dissociating the hydrate can lead to an energy efficient process. In the SIMTECHE process, the refrigeration system is designed so that the hydrate formation reactor (where the hydrate heat-of-formation must be removed) is the evaporator while the slurry flash unit (where the hydrate heat-of-decomposition must be supplied) is the condenser. This design provides excellent heat integration between the process unit heat duties. Only ~10% of the process heat, primarily derived from refrigerant compression, must be disposed of in wet cooling towers. In addition, the hydrate-liquid-vapor phase equilibrium boundary is such that 75–80% of the total CO_2 obtained from hydrate decomposition can be regenerated at 650–700 psia (4.48–4.83 MPa), with the remainder being regenerated at 275–300 psia (1.9–2.1 MPa). This is a major advantage over the competing scrubbing processes, which reportedly regenerate CO_2 at 50–100 psia (0.34–0.69 MPa) [2,7]. Thus the parasitic energy losses associated with CO_2 compression energy can be greatly reduced. Relative to conventional scrubbing, where low pressure CO_2 is typically obtained upon regeneration of the scrubbing solution, the process in part shifts the task of compressing all the captured CO_2 to pipeline pressure to one of moving the hydrate heat-of-formation between the formation and flash reactors in order to enable regeneration of high pressure CO_2 from hydrate decomposition. Moving the heat-of-formation is accomplished by way of the refrigeration system. While the refrigeration loop still involves PV work of compression, the large latent heat of the refrigerant (ammonia) lessens the total amount of PV work required relative to simply compressing a full charge of low pressure CO_2 to pipeline pressures, namely ~2200 psia (1.52 MPa).

A number of technical challenges were present in developing the hydrate process. First, gas hydrates are well-known for plugging pipes. This plugging tendency remains an on-going problem in petroleum production operations and in natural gas transmission [10]. Thus, the potential for plugging must be addressed as part of demonstrating continuous hydrate production. Second, reports exist suggesting that batch systems often must be held under hydrate formation conditions for extended periods (up to hours) before bulk quantities of hydrate form. Thus, short induction times must be demonstrated if industrially applicable hydrate formation rates are to be achieved. Finally, key engineering process design parameters such as kinetic rate constants and heat transfer rates were not accurately known for CO_2 hydrate formation in continuous flow systems, since the process fluid becomes a three-phase mixture. Initial bench-scale experiments using a Venturi mixer followed by an actively cooled tail tube demonstrated clearly that with a large thermodynamic driving force, e.g. a CO_2 partial pressure of 400 psia (2.76 MPa), good inter-phase mixing, and effective removal of the heat-of-formation, the hydrate formation rate can be very rapid [32–35]. The ability to operate at the bench-scale for extended periods, without plugging, was also established. Subsequently, a larger-scale experiment was deemed necessary in order to obtain better steady-state operating data, to confirm CO_2 separation performance, and to develop confidence predicting the performance of the process. Thus, a larger "Engineering Test Model" (ETM) unit was designed and constructed. The ETM has operated with 2 different tail tubes, having internal diameters (ID) of 0.457 and 0.8 cm and using both CO_2–Ar and CO_2–He feed gases to simulate CO_2–H_2 mixtures without the attendant safety issues, such as hydrogen flammability. The ETM configuration with a ~23 m long tail tube allowed hydrate experiments to be conducted at a high gas-to-liquid ratio (gas volume fraction >85%) and high fluid velocity (>4 m/s). As with the prior bench-scale unit, vigorous mixing conditions showed that with just a few seconds of "reaction" time (i.e. residence time), up to 30 vol% of the CO_2 was captured into hydrates. A lowering of the CO_2 partial pressure to values expected along the hydrate-liquid-vapor phase equilibrium line (i.e. equilibrium conversion) was also achieved in the ETM system at several temperatures [34,36]. The properties of the carrier gas were also found to impact the overall heat transfer coefficient obtained by treating the process fluid side, tube wall, and shell-side heat transfer resistances as resistances-in-series [36]. Specifically, when the carrier gas argon was replaced with helium, experiments at similar operational conditions gave an overall heat transfer coefficient in the He/CO_2 system at least 50% higher than that obtained from the Ar/CO_2 system [35]. However, with vigorous mixing the hydrate formation rate appeared to still become heat transfer-limited. As a continuation of the previous work focused on heat transfer issues [35], we now report on how flow conditions impact the apparent kinetics of CO_2 hydrate formation in a continuous flow reactor under temperature and pressure conditions where CO_2 is sub-critical and the carrier gases are above their critical temperature.