Applied Energy 113 (2014) 864–871

Contents lists available at ScienceDirect

Applied Energy

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

Clathrate-hydrate formation from a hydrocarbon gas mixture: Compositional evolution of formed hydrate during an isobaric semi-batch hydrate-forming operation

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HIGHLIGHTS

- Reports laboratory experiments of hydrate formation from synthetic natural gas.
- Shows how hydrate composition changes during each hydrate-forming operation.
- Compares the observed compositional change with thermodynamic simulations.
- Shows a PXRD result indicating simultaneous formation of sI and sII hydrates.

ARTICLE INFO

Article history:
Received 16 August 2012
Received in revised form 26 July 2013
Accepted 13 August 2013
Available online 7 September 2013

Keywords:
Clathrate hydrate
Gas hydrate
Mixed hydrate
Natural gas storage

ABSTRACT

The clathrate hydrate formation from a model natural gas, i.e., a mixture of methane, ethane, and propane in a 90:7:3 molar ratio, under a constant pressure was experimentally investigated, focusing on the compositional evolution of hydrate crystals formed inside a gas-bubbling-type reactor during each semi-batch hydrate-forming operation. The experimental system used in this study was specially designed for obtaining several hydrate samples formed at different, arbitrarily selected stages during each hydrate-forming operation. Each hydrate sample was analyzed by a gas-chromatograph to determine the mole fractions of methane, ethane and propane encaged in the hydrate. These analyses revealed a monotonic increase in the methane fraction and decreases in the ethane and propane fractions during each operation until a quasi-steady state was established. Powder X-ray diffraction analyses showed that both structure-I and structure-II crystals were simultaneously formed during the quasi-steady period. The compositional evolution of the hydrates formed during the early stages before the quasi-steady state was reached deviated from corresponding predictions based on the thermodynamic-simulation scheme previously reported. A hypothetical explanation for the discrepancy between the experimental and simulation-based results was provided.

1. Introduction

This paper describes an experimental study of the hydrate formation from a multi-component gas mixture. Understanding the behavior of such a hydrate-forming process is important for hydrate-based technology development for storing and transporting natural gas, separating undesirable (toxic or incombustible) species from biogases or natural gas with a high carbon-dioxide content, etc. Specifically, this paper focuses on the evolution in the composition of the hydrocarbon guest being captured in hydrates during their continuous formation from a hydrocarbon gas mixture simulating a natural gas. Such evolution originating from the nature of fractionation of hydrocarbons in forming hydrates possibly causes the lack of compositional uniformity of the hydrate products; hence it is of great importance concerning the industrial hydrate-forming operations for natural gas storage and transport [1]. For appropriately designing and controlling such operations, we need to have an insight into how the gas-phase composition in a hydrate-forming reactor, and hence the hydrocarbon uptake into the instantaneously formed hydrate, would change during each operation. Obviously, it is extremely difficult to find a solution fully satisfying the above task, because each hydrate-forming operation includes highly complicated multi-phase dynamic processes such as the convective

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0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.08.033

mass (hydrocarbons) transfer to, and heat transfer from, hydrate crystals thereby causing their growth, each dependent on the reactor design and the system-operational parameters (pressure, temperature, liquid stirring, etc.). However, it may be still possible and, if possible, should be valuable from an engineering viewpoint to find some practical means that allows us to estimate the compositional changes in the gas phase and the hydrate product during each hydrate-forming operation. As a tool for expeditiously estimating such compositional changes, Tsuji et al. [2] first presented a thermodynamic simulation scheme, in which the fluids and, if any, a hydrate confined in the reactor are assumed to form an open, instantaneously equilibrated system undergoing a quasi-static irreversible change in response to the successive discharge of the formed hydrate from, and the supply of the feed gas and water to, the reactor. Later, a modified, more sophisticated scheme for such simulations was constructed by Ogawa et al. [3]. These simulation schemes cannot predict the hydrate-formation rate in a given hydrate-forming system, hence they cannot predict how fast the gas phase and the hydrate product change their compositions with time; this is because the schemes are entirely based on the thermodynamics-based characterization of the system, and none of the rate-controlling factors (the size and geometry of the reactor, the gas–liquid interfacial area, the dynamics of the gas–liquid mixing, etc.) are taken into account. Instead, the schemes can predict, irrespective of the size and type of the reactor, how the gas phase and the hydrate product change their compositions with the progress in the fractional replacement of the gas phase with the fresh feed gas (a hydrocarbon mixture with a fixed composition) continuously supplied to the reactor in order to compensate the loss of each hydrocarbon species from the gas phase due to the hydrate formation.

Although the simulation schemes mentioned above can possibly be useful tools for designing hydrate-forming systems and their operations, we should be careful about possible deviations of the simulation-based estimates from the actual hydrate-forming behavior. Deviations possibly result from the modeling of hydrate-forming operations as thermodynamically quasi-static processes, which plays a key role in the simulation schemes [2,3]. A few attempts have been made at comparing simulation-based estimates to the corresponding experimental data concerning the change in the gas-phase composition during each hydrate-forming operation [4–6], which indicated a reasonably good agreement between them (except for the later stages of each hydrate-forming process in an unstirred semi-batch reactor containing a surfactant solution [6]). As for the compositional evolution in the hydrate product, however, no experimental examination corresponding to those for the gas-phase evolution [4–6] has been reported so far. For further clarification, this point may need a supplementary explanation, which follows. We find in the literature some previous studies in which the crystalline structures and hydrate-guest compositions in the hydrates formed from hydrocarbon mixtures were experimentally analyzed. See, for example, the papers by Uchida et al. [7], Schicks et al. [8], Hester et al. [9] and Seo et al. [10]. However, none of these studies demonstrated how the composition of the instantaneously-formed hydrate changed during each isobaric hydrate-forming process properly simulating industrial hydrate-forming operations for natural-gas storage.

In this paper, we describe our attempt at experimentally observing the compositional evolution of the hydrate formed in a gas-bubbling-type reactor to which a model natural gas (a mixture of methane, ethane, and propane in a 90:7:3 molar ratio) is continuously supplied to compensate for the loss of the gas due to hydrate formation, thereby maintaining the pressure inside the reactor constant. The hydrate-composition data obtained in these experiments are compared to the simulation-based predictions.

2. Experimental section

2.1. Experiment-design concept

The experimental work performed in this study was designed to extend our previous experimental study [5], in which we investigated how the gas-phase composition inside a gas-bubbling-type reactor changed during each hydrate-forming operation by continually sampling the gas from the reactor. The reason we selected a gas-bubbling-type reactor, instead of water-spray and other types [1], was simply for the convenience of obtaining gas samples which were free from water mist and uniform in composition. This time, we intended to obtain hydrate samples for their compositional analyses using the same reactor that we used for the gas-phase analyses [5]. The major technical difficulty in obtaining hydrate samples for compositional analyses was the fact that hydrate crystals formed at various stages of each hydrate-forming operation were inseparably mixed inside the reactor, hence we could not separately remove hydrate samples formed at specified stages from the rector. To overcome this difficulty, we installed a hydrate sampler (i.e., a detachable, small-capacity reactor) in parallel with the main gas-bubbling reactor for only a short period in order to obtain a hydrate sample representing the current stage. By repeatedly attaching and detaching the sampler during each hydrate-forming operation, we could collect hydrate samples representing different stages of the operation. The main reactor exclusively played a role of progressing the operation by continuously forming hydrates during every interval between successive hydrate-sample-forming procedures. The gas mixture thus *aged* in the main reactor due to the hydrate formation and the feed-gas supply that compensates for the gas consumption by the hydrate formation was circulated in a loop connecting the main reactor and the sampler during each hydrate-sample-forming procedure. This was to ensure that the hydrate sample was formed from essentially the same gas mixture as the one currently filling the main reactor. Technical details with which we realized the above experiment-design concept are described in Sections 2.3 and 2.5.

2.2. Materials used

The feed gas was a mixture of 90.07% methane, 6.93% ethane and 3.00% propane on a molar basis (synthesized and analyzed by Takachiho Chemical Industrial Co., Ltd., Tokyo, Japan). The deionized and distilled water was used for the hydrate formation. Sodium dodecyl sulfate (SDS) with a certified purity of 99.5% mass fraction (supplied by Nacalai Tesque, Inc., Kyoto, Japan) was added to the water at the concentration of 500 ppm (500 mg/kg) to prepare an aqueous SDS solution for use in forming hydrate samples for compositional analyses; this was just to promote hydrate formation, thereby shorten the period for forming each sample.

2.3. Apparatus

Fig. 1 illustrates the experimental apparatus used in this study. This apparatus was modified from that used in our previous study [5] by installing a device for forming hydrate samples for compositional analyses. Except for this device set in parallel with the main hydrate-forming reactor on the gas circulation loop, the layout of the apparatus as well as the components assembled in it are the same as those already reported [5]. For example, the main hydrate-forming reactor is the same coolant-jacketed gas-bubbling-type 754-cm^3 cell that we used in the previous study [5]. This reactor is equipped with a disk-type bubbler immersed in a water pool and a stirrer for providing a good mixing in the gas phase. The reactor is installed on the gas-circulation loop, through which the gas