Visual observation of the methane hydrate formation and dissociation process

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HIGHLIGHTS

- Visual observations of gas hydrate formation and decomposition on a microscopic level were conducted.
- Gas hydrate dissociation seems to be accompanied by liquid wetting of the solid phase at all times.
- The deducted model includes consecutive process of local decomposition, liquid diffusion and, nucleation in the liquid bulk.

GRAPHICAL ABSTRACT
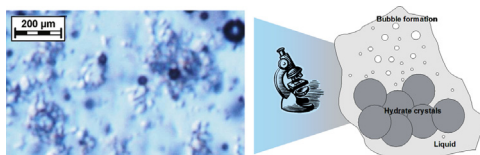
ABSTRACT

Studies regarding the microscopic processes taking place during the decomposition of methane hydrate under three phase conditions have been carried out using direct visual observations. Qualitative results regarding the formation and decomposition behavior of a dispersed hydrate phase are presented. Other author's previously published proposals regarding the location and manner of a vapor phase formation around the decomposing hydrates could not be confirmed in this work. Based on this work's observations it is proposed to model the process of gas hydrate dissociation as *consecutive* chain of *solid dissolution*, *guest diffusion*, and *vapor phase formation* and *growth*.

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1. Introduction

Gas hydrates are solid inclusion compounds formed by water and usually non to slightly polar gases. The water molecules form a cage like crystal lattice which is stabilized by engaging the guest molecules. Gas hydrates are thus water based, ice like solids also being able to form at temperatures above 0 °C but usually requiring elevated pressures. Besides the meanwhile well known equilibrium properties of gas hydrates (e.g., Sloan and Koh, 2007) experimental investigations of their phase change kinetics during decomposition by mechanical (e.g., Kim et al., 1987), thermal (e.g., Kamath et al., 1984) and chemical stimulation (e.g., Sira et al., 1990) have arisen scientific interest in the past years. Additionally, a differentiation between the terms dissolution (e.g., Rehder et al., 2004) and dissociation (e.g., Clarke and Bishnoi, 2000) has been established with the latter referring to gas hydrate decomposition under three phase (solid–liquid–vapor) conditions whereas no formation of a vapor phase occurs in contrary for the former. The state of the art dissociation model assumes the existence of a

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surrounding vapor cloud covering the solid during the dissociation process (e.g., Clarke and Bishnoi, 2000). The present work aims at investigating the microscopic processes taking place during gas hydrate dissociation using a direct visual observation technique.

2. Materials and methods

2.1. Experimental setup

This work's experimental setup was based on the concepts for examining gas hydrate decomposition kinetics originally developed by Kim (1985) and later improved by Clarke (2000). In Fig. 1 a schematic sketch of the experimental setup is given. The center piece of the test rig is a stainless steel high pressure autoclave reactor with an internal volume of approximately 500 ml. The reactor is equipped with a cooling jacket as well as a magnetically coupled blade stirrer with an operational range between 60 and 3080 rpm. In order to avoid vortex formation the possibility of mounting baffles inside the vessel has been foreseen. Besides one pressure sensor, two Pt100 temperature sensors were installed at different levels to enable simultaneous temperature measurement of the liquid and the vapor phase. In order to facilitate temperature control, the whole setup is shielded by thermal insulation. Two of the reactor's process nozzles were connected to an external temperature controlled capillary flow loop. Below the autoclave a high pressure pump was installed allowing pumping of suspensions with flow rates between 0 and 21.6 l/h via stroke length adjustment. Downstream of the pump a high pressure visual flow cell was installed. To avoid uncontrolled hydrate decomposition inside the flow loop, a temperature sensor was installed directly downstream of the flow cell. Its temperature level was controlled manually to a value equal to the autoclave's liquid phase value. The direct observation as well as particle size analysis of the aqueous

hydrate suspension was verified using digital macro photography (digital camera, macro lens, tube extensions) coupled with an industrial stroboscope for backlight exposure. Obtained pictures possessed a size of 10 megapixels with an effective spatial resolution of 1.4 μm per pixel. Typically a picture of the flow was taken every 10–20 s. For temperature control the whole flow loop was placed inside a tube in tube heat exchanger with aqueous glycol solution from the thermostat on the shell side. Constructional drawings of the autoclave reactor as well as the flow cell are given in Windmeier (2009).

For supplying and receiving gas to and from the autoclave reactor, two stainless steel pressure cylinders with a volume of approx. 1000 ml each were placed inside an aqueous glycol bath and connected to the reactor via a digital pressure control valve. Latter was able to operate in front- and back-pressure control mode. For more precise pressure measurements the internal gas supply vessels were also connected to one small bias cylinder with a differential pressure gauge each.

2.2. Experimental procedure

The basic idea of the experimental procedure is shown in Fig. 2. At the beginning of the experiment liquid water and a hydrate forming gas are brought into contact outside the respective hydrate stability area (1). The experiment is started by isothermally increasing the pressure slightly above the hydrate equilibrium pressure and letting the systems reach its solubility equilibrium (2). After equilibrium is reached the pressure is quickly increased isothermally to a desired point within the gas hydrate stability region (3). After some time hydrate will start to form and thus the crystallization heat will be rejected to the liquid phase accompanied by a decrease in system pressure. In order to ensure defined formation conditions an equivalent to the gas consumed by hydrate formation is supplied to the system by a pressure controller and the heat of formation is
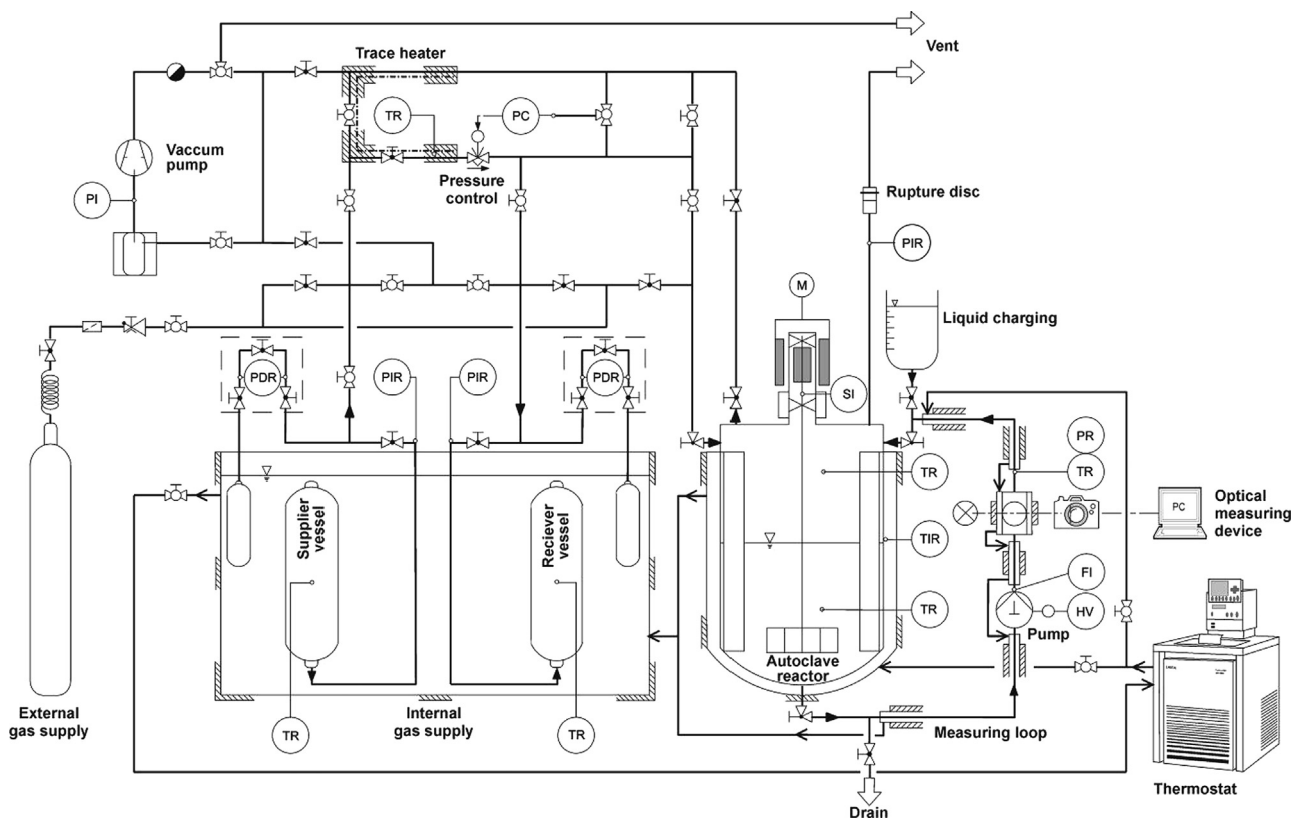

Fig. 1. Schematic description of the experimental setup.