

# Experimental Simulation of Methane Hydrate Extraction at High Pressure Conditions: Influence of the Sediment Bed

J R Agudo<sup>1</sup>, J Park<sup>1</sup>, G Luzi<sup>1</sup>, M Williams<sup>2</sup>, C Rauh<sup>3</sup>, A Wierschem<sup>4</sup> and A Delgado<sup>4</sup>

<sup>1</sup> Institute of Fluid Mechanics, FAU Busan, Busan, Republic of Korea

<sup>2</sup> Chair of Chemical Reaction Engineering, University of Erlangen-Nuremberg, Erlangen, Germany

<sup>3</sup> Department of Food Biotechnology and Food Process Engineering, Technical University of Berlin, Berlin, Germany

<sup>4</sup> Institute of Fluid Mechanics, University of Erlangen-Nuremberg, Erlangen, Germany

E-mail: jose.a.rodriquez@fau.de

**Abstract.** Being a clean alternative to other fossil fuels, Methane Hydrate (MH) is currently considered as one of the most important potential sources for hydrocarbon fuels [1]. In addition, the high energy density of MH and its stability at higher temperatures as compared to LNG (Liquefied Natural Gas) makes MH a potential greener method for energy transportation. At the same time, the low thermodynamic stability of MH strongly questions the future exploitation of gas hydrate deposits, turning its extraction into a possible geohazard [2]. Fluctuations in pressure, temperature, salinity, degree of saturation or sediment bed properties may cause methane gas release from the water lattice. We experimentally study the influence of the sediment bed geometry during formation-dissociation of MH. For this purpose, MH is synthesized within regular substrates in a 93 cm<sup>3</sup> high pressure vessel. The regular substrates are triangular and quadratic arrangements of identical glass spheres with a diameter of 2 and 5 mm, respectively. MH formation within regular substrate reduces the possibility of spontaneous nucleation to a unique geometrical configuration. This fact permits us to characterize the kinetics of MH formation-dissociation as a function of the sediment bed geometry. Preliminary experimental results reveal a strong dependence of MH formation on the geometry of the regular substrate. For instance, under the same pressure and temperature, the kinetics of MH production is found to change by a factor 3 solely depending on the substrate symmetry, i.e. triangular or quadratic.

## 1. Introduction

Methane Hydrate (MH) are formed spontaneously in appropriate physical conditions, i.e. low temperature, high pressure, appropriate amount of gas former and water [3]. Other phenomena, however, enhance hydrate formation and dissociation. It is well known that the nucleation sites, given by the geometrical properties of the sediment bed within which MH is formed, strongly affect the kinetics of MH formation-dissociation [4]. The formation and decomposition of MH within the sediment bed is thus of vital importance for realistic reproduction of the process occurring in Nature either in permafrost or in deep-sea sediments [5]. The structure of the sediment bed arrangement influences the kinetics of the process [5], the equilibrium conditions for MH formation [6], the internal fluid flow migration processes during formation-dissociation process [7] and the stability of the hydrate [8].



The literature is lacking in an experimental study for the kinetics of MH formation-dissociation within regular geometries. In irregularly arranged structures, as considered until now, the spontaneous MH nucleation is favoured in optimal local volumes inside the sediment bed. This results in a stochastic phenomenon with limited predictability for the onset of hydrate formation, which is strongly dependent on the laboratory equipment [9]. Studying the MH nucleation in regularly arranged sediment beds according to triangular or quadratic symmetries reduces the possibility of spontaneous MH nucleation to a unique geometrical configuration. This fact, therefore, permits us to characterize the kinetics of MH formation-dissociation as a function of the bed geometry.

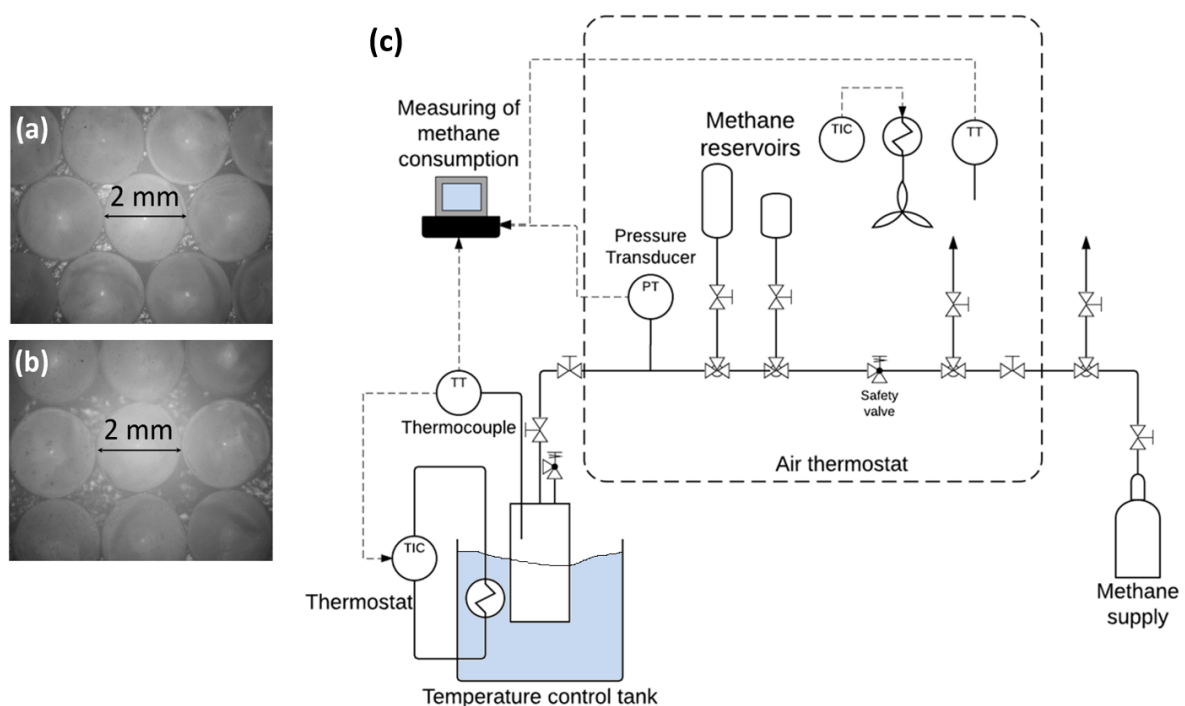
## 2. Experimental Set-up

Methane Hydrate is produced in regular substrates placed in a stainless steel vessel with a total volume of  $93.4 \text{ cm}^3$ . The regular substrates consist of a monolayer of uniform size glass beads of  $2 \pm 0.02 \text{ mm}$  and  $5 \pm 0.02 \text{ mm}$  in diameter, arranged and fixed in triangular and quadratic symmetries, respectively. To build the substrates, we follow a similar procedure as described in [10-12]. Figure 1(a)-(b) shows pictures of the different regular bed geometries. The vessel is filled with 6 mL of deionized water and is well distributed on the sediment bed surface. After flushing the system, high purity methane gas (99.90%) is injected into the vessel to achieve an initial pressure of 100 bar. The vessel is submerged into a water tank. A thermostat is used to control the vessel temperature, which is set at 273.5 K, for optimal conditions for MH nucleation inside the cavities of the sediment bed. The pressure on the system is continuously measured using a pressure transducer while the temperature is monitored using a thermocouple placed at the center of the vessel. Figure 1(c) depicts the experimental set-up.

We indirectly measure the methane consumption with time during MH formation via the pressure drop in the vessel in a similar experimental procedure as described in [5, 13]. The kinetics of MH formation are measured experimentally for each of the regular substrate geometries.

## 3. Experimental results and discussion

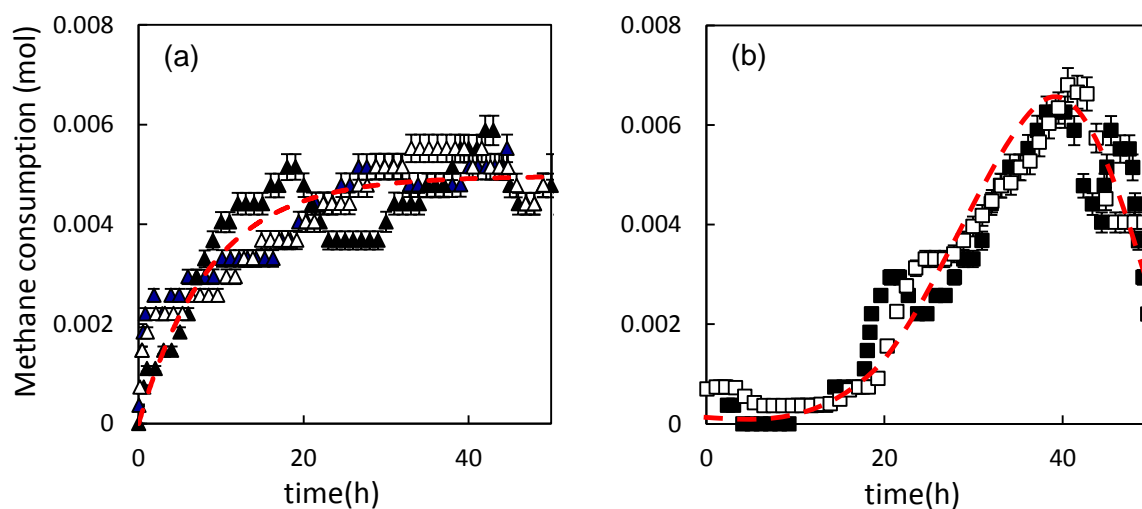
In isothermal conditions, the pressure gradually decreases as the gas phase is enclosed inside the MH cages. The increase of temperature due to MH formation is rapidly dissipated in the vessel by the temperature control tank.



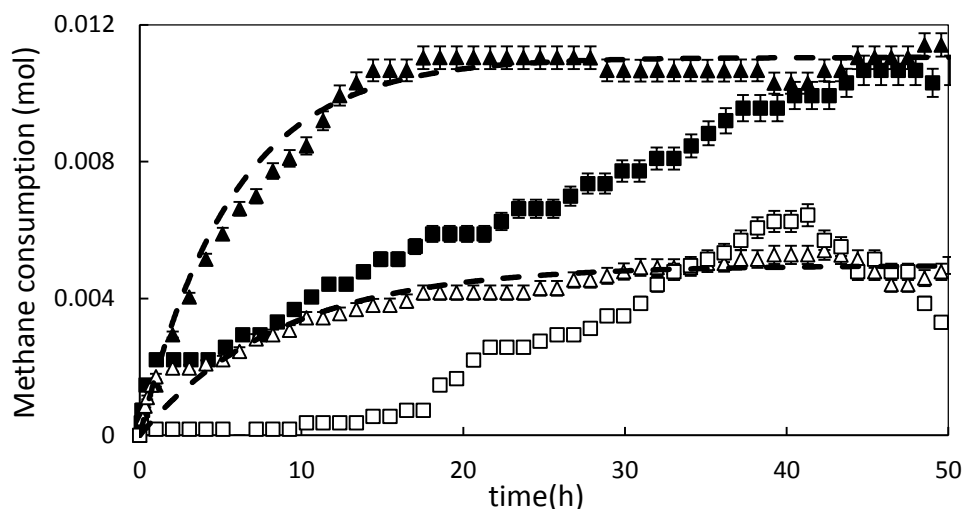
**Figure 1.** Substrates of identical and regularly arranged spherical glass bead. Triangular (a) and quadratic (b) configuration. Sketch of the experimental setup (c)

We record pressure and temperature every 2 minutes in order to study the progress of MH formation. To study the kinetics of MH formation for different regular geometries, the methane consumption was evaluated using ideal gas and Peng-Robinson equations of state as recommended by [13]. At the pressure and temperature considered, the choice of the equation of state hardly affected the mole of consumed gaseous methane. Figure 2 plots the methane consumption in moles as function of time for a triangular (a) and quadratic (b) substrate made of 5 mm diameter beads. Error bars in the figure represents the range of uncertainty of the measurements. The data for methane consumption are depicted every hour to simplify the diagram. (Red) dashed lines are drawn to guide the eyes. The experiments were repeated three times for the triangular substrate and twice for the quadratic one. Different symbol colours on the diagram represent different experiments performed under the same initial condition, i.e. temperature and initial pressure. As shown in Figure 2, the experiments roughly coincide on the diagram showing a good repeatability of the results. We observe a similar rate of MH production within the pores of the same size if other thermodynamic parameters remain constant. This fact corroborates that our experimental results remain independent of boundary effects.

Figure 3 shows the methane consumption as a function of time for each of the substrate geometries. The data are depicted again each hour and the error bars represent the range of uncertainty of the measurements. For the experiments performed using the substrate made of 5 mm, the average value of the repeated experiments is shown. Figure 3 reveals a strong influence of the substrate geometry on the MH formation. For same initial conditions, the total amount of methane consumed for MH formation was increased by a factor of two for the substrate of 5 mm beads, compared to the substrates of 2 mm beads (compare solid and open symbols in Figure 3). This increase in methane consumption represents a clear enhancement of the hydrate saturation level depending on the size of the sediment pores.



**Figure 2.** Kinetics of MH formation within the triangular (a) and quadratic (b) substrates made of 5 mm diameter beads. Different symbol colours represent different experiments performed under the same condition. The initial pressure was set at 100 bar and the temperature was fixed at 0.5°C. The error bars represent the range of uncertainty of the measurements. Dashed lines are drawn to guide the eyes.



**Figure 3.** Kinetics of MH formation within different regular substrates. Solid and open triangles: triangular substrates formed by beads of 2 and 5 mm in diameter, respectively. Solid and open squares: quadratic substrates formed by beads of 2 and 5 mm in diameter, respectively. For experiments performed using the substrate made of 5 mm diameter beads, the average value of repeated experiments is depicted in the figure. The initial pressure was set at 100 bar and the temperature was fixed at 0.5°C. The error bars represent the range of uncertainty of the measurements. Dashed lines represent a fit to the experimental data according to Eq. 1 for  $n^*$  equal to one as proposed in [5].

On the other hand, for substrates made of beads with the same size, the kinetics of MH formation strongly depends on the geometrical symmetry (compare triangles and squares in Figure 3). For the experiments performed with the triangular substrate made of 2 mm beads (solid triangles), the maximum methane consumption was achieved after around 15 hours. For the quadratic one, however, the maximum methane consumption achieved a plateau at around the same level but after 45 h. This fact corresponds to an enhanced kinetics of MH formation within the triangular geometry, by a factor of about 3, as compared to the quadratic configuration. Note that comparing triangular and quadratic substrates made of 5 mm beads, we also observe different kinetics of MH formation.

Moreover, MH formed in quadratic substrates made of 5 mm beads (open squares) showed a dissociation phase after around 40 h. This dissociation phase is not observed in triangular substrates with 5 mm beads (open triangles), pointing to a higher stability of the MH sample produced within the triangularly arranged substrate as compared to the quadratic one. This dissociation phase may be due to the decrease of pressure as methane changes from gas to solid phase. For the experiments performed with beads of 5 mm diameter, the final pressure drop achieved typical values of about 3 bar in the system. This decrease of pressure apparently affected the sample formed within the quadratic substrate, but did not affect the hydrate generated within the triangularly arranged one.

Kono *et al.* studied the dependency of kinetics of MH formation and dissociation on the sediment bed properties [5]. For that purpose, they formed MH in various custom-designed porous sediments with glass beads and cylindrical particles according to irregular arrangements. The glass bead diameter in their experiments varied from 0.1 to 5 mm. In order to characterize the different kinetics of MH formation within irregular beds, they defined an overall formation rate constant defined in terms of reaction engineering by the following equation [5]:

$$\frac{dn_{CH_4}}{dt} = -k_f n_{CH_4}^{n^*} \quad (1)$$

where  $n_{CH_4}$  is the number of mol of consumed methane,  $k_f$  is an overall formation rate constant that includes the effects of heat transfer, mass transfer and reaction and  $n^*$  is the overall order of MH formation process. While the overall order of the formation process  $n^*$  was found to be equal to one

independent of the sediment bed, the overall formation rate was observed to depend on the irregular bed configuration, which was varied on the experiments by the sediment shape and size but not by the arrangement [5]. Dashed lines in Figure 3 represent a fit of the overall kinetic model to our experimental data according to Eq. 1 for  $n^*$  equal to one. As shown in Figure 3, the overall kinetics of first order agrees within the range of uncertainty of our experimental data for MH formed in triangular substrates. Under the same pressure and temperature conditions, the overall formation rate constants are  $2.9 \times 10^{-3}$  and  $1.9 \times 10^{-3} \text{ min}^{-1}$  for the triangular substrates with 2 mm and 5 mm beads, respectively. Despite variation on the experimental set-up, these values are in accordance with the data obtained by Kono *et al.* for irregularly arranged sediment bed made of uniformly sized spherical beads of 0.1 mm in diameter,  $k_f = 2.6 \times 10^{-3} \text{ min}^{-1}$  [5]. We remark that operating pressure and temperature used during our experiments are similar to those performed in [5]. We hypothesize that the good agreement between our data for a triangular geometry and the overall first order kinetic model proposed by Kono *et al.* is due to the fact that a naturally arranged sediment may represent a close-packed sediment bed with a packing coefficient close to the maximum as in our triangular geometries. Note that the experimental data obtained for the quadratic substrate strongly differ from the overall first order reaction (fit is not shown in Figure 3).

#### 4. Conclusions and perspectives

We experimentally study the kinetics of MH formation as a function of the sediment bed geometry. For that purpose, MH is synthesized within the regular substrates, triangular or quadratic monolayers of glass beads of 2 and 5 mm in diameter, respectively. After placing the substrate into a vessel of 93.4 cm<sup>3</sup>, we added 6 mL of distilled water and injected high purity methane in order to achieve an initial pressure of 100 bar. The temperature was fixed at 0.5°C. Proper conditions for methane hydrate formation were, therefore, achieved inside the pressure vessel.

Experiments performed using the same regular substrate and under the same initial conditions showed a good repeatability of results. On the other hand, preliminary results pointed to a strong influence of the substrate geometry on the MH formation and the MH stability within the sediment bed. Under the same initial conditions, we measured a different total amount of consumed methane, by a factor of 2, depending only on the glass bead diameter. Furthermore, depending only on the substrate symmetry, we observed a favoured kinetics of MH formation, by a factor up to 3, for the triangular substrate as compared to the quadratic one. Finally, we observed dissociation phases in quadratic geometries but not in triangular substrates under the same initial conditions.

Further experiments for MH formation and dissociation must be performed in three dimensional regular structures with different width of the bed as suggested by [14]. In addition to the importance to quantify the role of the sediment bed geometry on the MH formation-dissociation, optimal configurations for MH stability within the sediment bed can be developed. An optimum bed configuration may permit to enclose a larger number of gas molecules per unit of volume within the MH (i.e. higher gas saturation), increasing the energetic density for transport purposes.

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