

## **A HIGH YIELD PROCESS FOR HYDRATE FORMATION**

**Carlo Giavarini\***

**Chemical Engineering Department  
University of Roma "La Sapienza"  
Via Eudossiana 18, 00184, Roma  
ITALY**

**Filippo Maccioni**

**Chemical Engineering Department  
University of Roma "La Sapienza"  
Via Eudossiana 18, 00184, Roma  
ITALY**

### **ABSTRACT**

A new procedure was studied to obtain concentrated methane hydrates in bulk, at medium-low pressure, avoiding the use of the spray process. Methane hydrate was formed at about 5 MPa and 2 °C in a reaction calorimeter with the volume of two liters. The clathrate concentration was about 30% and the final reactor pressure was 2.7 MPa. Any further repressurization at 2 °C had no noticeable effect on the hydrate formation. However, by repressurizing the vessel again to 4 MPa and increasing the temperature near the decomposition value (about 6° C) more clathrate was formed. Repressurizing again the reactor at 4 MPa and controlling the temperature at the same level, a concentration of 88% hydrate in the bulk was reached. Respect to the hydrate produced by the spray process, this procedure takes more time, but it can be sped up and made continuous by using two reaction vessels, one for hydrate formation and the other for hydrate concentration. The advantage is the production of concentrated hydrates, by a simple equipment, working at relatively low pressures.

*Keywords:* gas hydrates, high conversion, equilibrium curve.

### **INTRODUCTION**

Methane hydrate is important because of the huge amount of natural gas stored in deep ocean hydrates, so that hydrate reservoirs have been considered as a substantial energy resource [1]. Because hydrates concentrate methane by as much as a factor of 164, a number of transportation and storage systems for natural gas using gas hydrates have been investigated and some of them are nearing practical use [2, 3] In these systems the hydrate is produced (as a slurry) by a spray process at about 7 MPa, and then shaped into

pellets [3]. The use of a spray process, instead of a conventional stirred vessel is necessary in order to reach high hydrate concentrations (nearly 90 % water converted to hydrate) in the hydrate-ice system.

In previous unpublished experiments, we have noticed an apparently anomalous behaviour during the hydrate decomposition process. By increasing the temperature, a pressure decrease was detected near the equilibrium curve, indicating that some hydrate had formed just before the decomposition. In fact, the pressure increase is an indicator of the

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\* Corresponding author: Phone: +39 6 44585565 Fax +39 6 44585416 E-mail: carlo.giavarini@uniroma1.it

hydrate decomposition, while temperature increase is linked to hydrate formation [4].

Such an effect was also present in the experimental procedure adopted by E. Behar et al.[5] to study the plugging problem during hydrocarbons production and transport, but it was not emphasized by the authors (Figure 1).

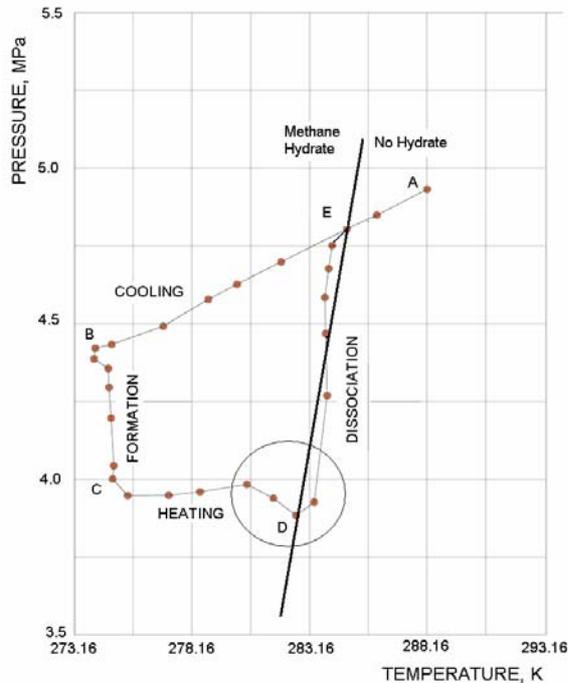


Figure 1. Experimental procedure for hydrate equilibrium curve measurement [5], which shows hydrate formation just before decomposition (point D).

During the study of HCFC141b hydrate growth process, Xie Yingming et al. [6] noticed the hydrate continuous formation along the surface of the heat transfer tube; they also described the phenomenon of fast nucleation of hydrate from melting ice. According to these experiments, they suggested the possibility of forming hydrates from melting ice or/and along a heat transfer surface. A nearly complete conversion of ice to CO<sub>2</sub> hydrate was obtained by S. Circone et al.[7] as the temperature of the sample was cycled through the melting point of ice.

Following our previous experiments and the literature data, in the present work we have studied a new procedure to produce a bulk of concentrated methane hydrate in a static traditional reactor at moderate pressure, controlling pressure (4 ÷ 5 MPa) and temperature in the interval between ice

melting (273.16 K) and the hydrate equilibrium curve (about 279.16 K).

The importance of having due control over the experimental parameters, especially the heating gradient near the equilibrium conditions, has been previously underlined [7, 8].

## EXPERIMENTAL

### Apparatus

The experimental apparatus for the formation tests (Fig. 2) consists of a jacketed stainless steel reactor (RC-1 Mettler Toledo) with an internal volume of about 2 L, equipped with a stirrer.



Figure 2. The reactor used for the experiments.

Pressure, temperature, and stirrer revolutions are transmitted to a computer through a data acquisition board and are recorded at 3 s intervals. For hydrate formation, CH<sub>4</sub> gas (99.9 %) is supplied from a cylinder bottle in the reactor containing the required amount of distilled water. An external oil circulation loop is attached to the chamber; the rate at which cold oil flows through this loop is controlled by a plunger pump. During all experiments it is possible to control the rate of heat transfer to the reactor by varying the

temperature difference between the jacket fluid ( $T_j$ ) and the reactor interior ( $T_r$ ).

### Hydrate formation.

The normal procedure adopted in our laboratory for producing hydrates from gas and water consists in purging the reactor chamber (containing about 560 g of water, at 283.16 K) and pressurizing it with methane to about 4-5 MPa. Stirring is then started and the temperature is lowered to 275.16 K to enter the hydrate stability zone in the equilibrium diagram. Hydrate formation begins immediately and is detected by a pressure decrease and a temperature increase (Figure 3).

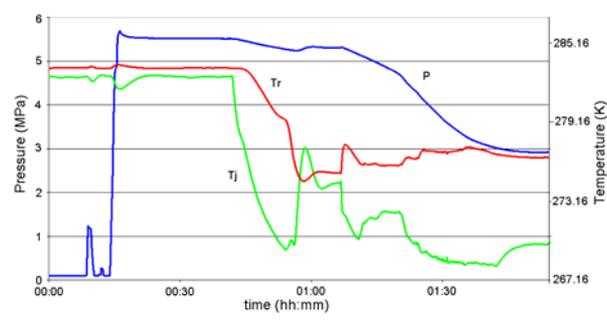


Figure 3. Typical pressure and temperature trend during hydrate formation. (normal experimental procedure)  $T_r$  : reactor temperature;  $T_j$  : cooling jacket temperature;  $P$  : reactor pressure.

The concentration of the produced hydrate in the system ice-hydrate is normally about 30-35 % and the final reactor pressure is about 2.8 MPa. Any further repressurization at 275.16 K has no apparent effect on the formation of new hydrate.

Figure 4 shows the normal formation procedure (step 0  $\rightarrow$  1) and the other steps of the new procedure. Following the first step, the reactor is repressurized with methane to about 4 MPa (step 1  $\rightarrow$  2); the temperature is then increased to near the decomposition value, at about 279.16 K, (step 2  $\rightarrow$  3). The pressure drop clearly indicates a new formation of gas hydrate (step 3  $\rightarrow$  1); in this step the temperature is decreased at a rate of 1 K/hour to obtain pressure and temperature values close to the hydrate dissociation conditions. In order to further increase the hydrate conversion, the reactor is pressurized again to about 4.4 MPa at 275.16 K and the conversion cycle 1-2-3-1 is repeated.

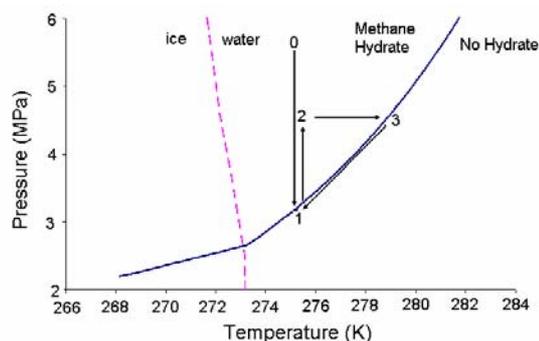


Figure 4. hydrate production near the equilibrium curve.

## RESULTS AND DISCUSSION.

Figure 5 shows an example of the P-T experimental curve relating to the proposed formation procedure: the formation steps are indicated by the same numbers of Figure 4.

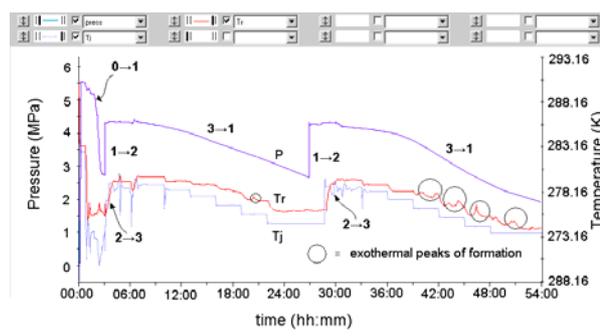


Figure 5. Experimental P-T curves of the hydrate formation following the procedure of hydrate production near the equilibrium curve.

The first hydrate formation (0  $\rightarrow$  1) occurs at 5 MPa and 275.16 K when the stirrer is started; the pressure drop is about 2.5 MPa. The reactor is repressurized to 4.3 MPa (1  $\rightarrow$  2) and then heated to a temperature close to the equilibrium curve (step 2  $\rightarrow$  3). During heating, the reactor pressure increases up to 4.4 MPa and the temperature to 279.16 K, where an inversion of the pressure trend is noticed and the formation of new hydrate starts (step 3  $\rightarrow$  1).

During the hydrate formation in this step, the temperature of the jacket is held at about 278.16 K for 3 hours and then gradually decreased in order to reach a temperature of 274.16 K inside the reactor, where the pressure is just under 3 MPa. The reactor is then repressurized to 4.3 MPa and

the formation cycle is repeated (from step 1 to step 3). The new hydrate formation is shown in Figure 5 by a pressure drop and by various (circled) exothermal peaks on the  $T_r$  curve. After 3-4 cycles, about 90 % of the free water is converted to hydrate. In the described example the formation of "new hydrate" (steps 1  $\rightarrow$  3) is about 53 %; by adding the conversion obtained with the normal procedure (step 0  $\rightarrow$  1), total conversion is 88 % water converted to hydrate.

## CONCLUSION

This procedure seems suitable for the development of a gas hydrate storage and transport technology methane hydrate is produced with "unreacted" interstitial water.

The formation near the equilibrium curve can possibly be explained in terms of surface free energy which is in favour of hydrate formation at the borderline between the hydrate stability zone and no hydrate zone [6]. The hydrate film on the liquid-liquid interface is a kind of porous media so that gas and water can permeate into the other side of this film [9]. Near the equilibrium curve the film is weakened and water (and gas) permeation is facilitated. Respect to the spray process this procedure takes more time, but it can be sped up and made continuous by using two vessels: one for hydrate formation and the other for hydrate concentration. The advantage is the production of a concentrated hydrate, using a simpler equipment and working at lower pressures respect to the spray process.

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