

# Identification of a New Experimental Method to Measure the Induction Time for Gas Hydrates.

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**Abstract** - The gas hydrate formation process is divided in two main phases: the initial nucleation and the following massive growth phase. The time required for the production of a quantifiable quantity of hydrates is referred as “induction time”. Different solutions have been proposed to measure this interval; however, the low accuracy of the measure and the difficulties in evaluating it in the medium – scale lab reactors, have been not still solved. The most diffused technique consists of the visual confirmation of the production of a numerable quantity. In this work, a new alternative approach was proposed and experimentally validated. Being the formation process exothermic, the formation of the target quantity of hydrates leads to the appearance of peaks in temperature in a confined environment. These peaks cannot be exploited, due to their casual occurrence, associated to the stochastic nature of the process. Differently, the quantity of heat produced, can be directly used to calculate the moles of hydrates formed; thus, it allows to characterize the induction period for the process. In this research, the induction time was evaluated during the formation of methane and carbon dioxide hydrates, in order to detect any potential difference between the two species.

**Keywords:** natural gas hydrates; carbon capture; carbon storage; induction time; energy production.

## 1. Introduction

Gas hydrates consists of ice – like crystalline compounds, whose structure is composed by water molecules, also called “hosts”. This structure form around specific gaseous molecules, referred as “guests”, which remain trapped within the cavities of the hydrate lattice [1]. Different types of cavities have been observed, as a function of the pressure and temperature conditions and the characteristics of the gaseous species involved in the process. The combination of those cavities leads to the formation of three different structures: the cubic Structure I (sI), the cubic Structure II (sII) and the hexagonal Structure H (sH) [2]. The naturally occurring gas hydrates mainly contain methane, or the main component of natural gas, and preferentially form the first typology of structure [3]. The hydrate formation process is the sum of two different phases: the nucleation and the catastrophic growth [4]. The nucleation phase describes the formation of the first clusters of hydrate. These clusters are initially diffused in the bulk liquid phase and can grow or dissociate, depending on the possible collision with surrounding clusters (this phenomenon explains the stochastic nature of the process). As soon as the cluster reaches the so called “critical size”, which corresponds to the maximum of the Gibbs free energy, its growth continues spontaneously and the system enters in the massive growth phase [5, 6]. Before reaching the maximum of Gibbs free energy, the process is deterministic and it is common believe that it can be significantly affected by the type of guest compound. It has been already asserted that, when the guest consists of carbon dioxide molecules, the probability that the first nuclei dissociate immediately after their formation, is higher than the probability of their massive growth. According to it, carbon dioxide hydrates would never form. Several theories were formulated to theoretically prove the feasibility of CO<sub>2</sub> enclathration, such as the “Local Structuring Nucleation Hypothesis” [7] and the “Blob Hypothesis” [8]. The peculiarity observed for carbon dioxide is mainly associated to the not hydrophobicity of its molecules. For that reason, it was suggested that the nucleation phase for hydrates containing such species could be longer than what observed for other species, as methane, thus leading to a longer induction period. The induction time is defined as the time needed to form a detectable quantity of hydrates [9]. It includes the nucleation phase and part of the following growth phase [10, 11]. It may assume a key role in practical applications: for instance, it may affect the efficiency of replacement processes because the formation of carbon dioxide hydrates might occur in delay and the dissociation of methane hydrates could be faster. A similar delay could be responsible for the re – formation

of methane hydrates, with the consequent reduction of the exchange efficiency [12 – 14]. In this work, an original method for the evaluation of the induction period, was proposed and experimentally verified for methane and carbon dioxide hydrates. Finally, a direct comparison between the results obtained for the two respective species was carried out, in order to validate what theoretically asserted in literature.

## 2. Materials and Methods

### 2.1. Experimental apparatus

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The experiments were carried out in a lab – scale unstirred reactor, equipped with appropriate pressure and temperature sensors and inserted in a cooling room to control the internal temperature. The reactor was designed in order to obtain the same internal characteristics of a previous device, sited in the same laboratory and used for the same scopes and, at the same, to carry out the hydrate formation and dissociation processes with a higher degree of accuracy [15, 16]. Detailed information of the apparatus can be found elsewhere in literature; in this section, only the scheme of the reactor (Figure 1) and of the assembled experimental apparatus (Figure 2) are provided.

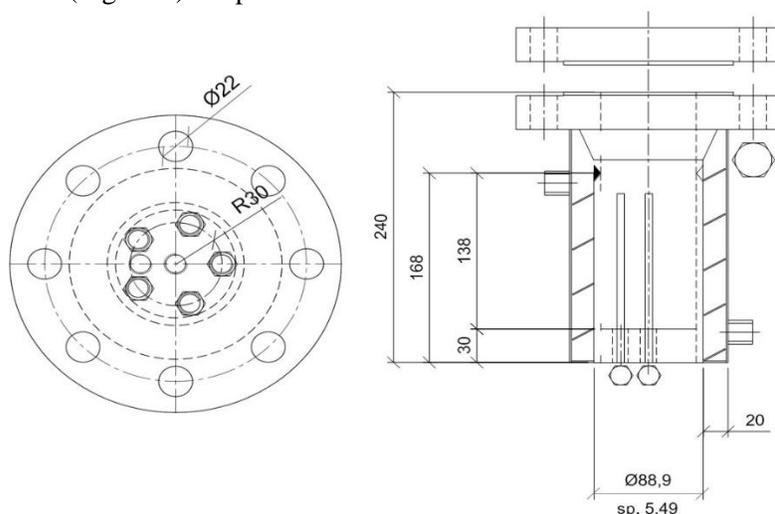


Fig. 1: Technical scheme of the reactor used in the present research [17].

The reactor was equipped with six Type K thermocouples, having class accuracy 1, and with a digital manometer, model MAN-SD, having class accuracy equal to  $\pm 0.5\%$  of full scale.

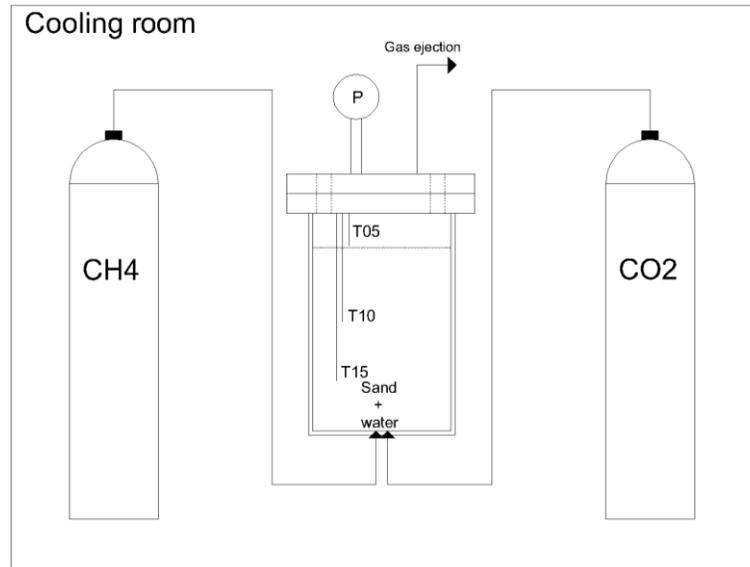


Fig. 2: Scheme of the whole experimental apparatus [17].

Finally, all the measures were collected and elaborated with LabView. A more detailed description of the data acquisition system can be found in [18].

## 2.2. Materials

The reactor was filled with a mixture of 800 cm<sup>3</sup> of pure quartz porous sand and 270 cm<sup>3</sup> of demineralised water. The sand consists of spherical grains having diameter ranging from 150 to 250 μm and porosity equal to 34% (this parameter was measured with a porosimeter, model Thermo Scientific Pascal). Ultra – High – Purity (UHP) methane and carbon dioxide were used for the experiments.

## 2.3. Methods

The formation of gas hydrates was performed by following the same procedure executed in previous researches [19, 20]. The injection of the guest compound in the formation environment, was carried out after lowering the local temperature at 2 – 2.5 °C. In this way, as soon as the gas was injected, the local conditions were immediately suitable for the process. In tests involving methane, the internal pressure was fixed at 50 bar, while in presence of carbon dioxide, 33 – 37 bar were reached (the conditions required for carbon dioxide hydrates formation are milder than those required for methane hydrates). Due to the favourable conditions, the process started spontaneously and caused an initial peak in temperature, due to the exothermicity of the reaction (the enthalpy of formation is equal to – 54.49 kJ/kg for methane hydrates and to – 57.98 kJ/kg for carbon dioxide hydrates). Differently from the techniques traditionally used [21 – 23], here the induction time was measured by considering the quantity of heat released during the formation process: as soon as the heat release became quantifiable, the delta – time was measure and considered as induction period. The quantification of the heat produce was made by considering the following quantities: 1.252 kg of sand, having specific heat equal to 0.837 kJ/kg, and 0.236 kg of water, having specific heat equal to 4.186 kJ/kg. The heat absorbed in the gaseous phase was not considered, being this phase negligible if compared with the other masses. The moles of hydrates formed during the induction period, were calculated according to Equation 1:

$$n_{H(peak)} = \left| \frac{Q}{\Delta H^{\circ}} \right| [mol] \quad (1)$$

In the equation, the enthalpy of formation can assume the two values cited above. Finally, the moles of hydrates formed along the whole formation process, were calculated with Equation 2:

$$mol_{HYD} = \frac{V_{PORE}(P_i Z_f - P_f Z_i)}{Z_f (RT - P_f / \rho_{HYD})} [mol] \quad (2)$$

In the equation,  $V_{PORE}$  is the volume available for the growth of hydrates, P, T, R and Z respectively indicate pressure, temperature, gas constant and compressibility factor (this latter parameter was calculated with the Peng – Robinson equation) and “ $\rho_{HYD}$ ” is the molar density of hydrates, calculated by assuming 100% of cage occupancy. Finally, subscripts “i” and “f” represent the beginning and the ending of the process.

### 3. Results and Discussion

This experimental section shows two group of experiments: the first is related to methane hydrates, while the second to carbon dioxide hydrates. Being the production of clathrate hydrates an endothermic process, because of the stochastic and not deterministic formation of the first clusters, the induction time was defined by considering the heat released during the process.

The evolution of temperature over time was measured and plotted for each test; the results are shown in figures from 3 to 5 for methane hydrates and figures from 6 to 8 for carbon dioxide hydrates.

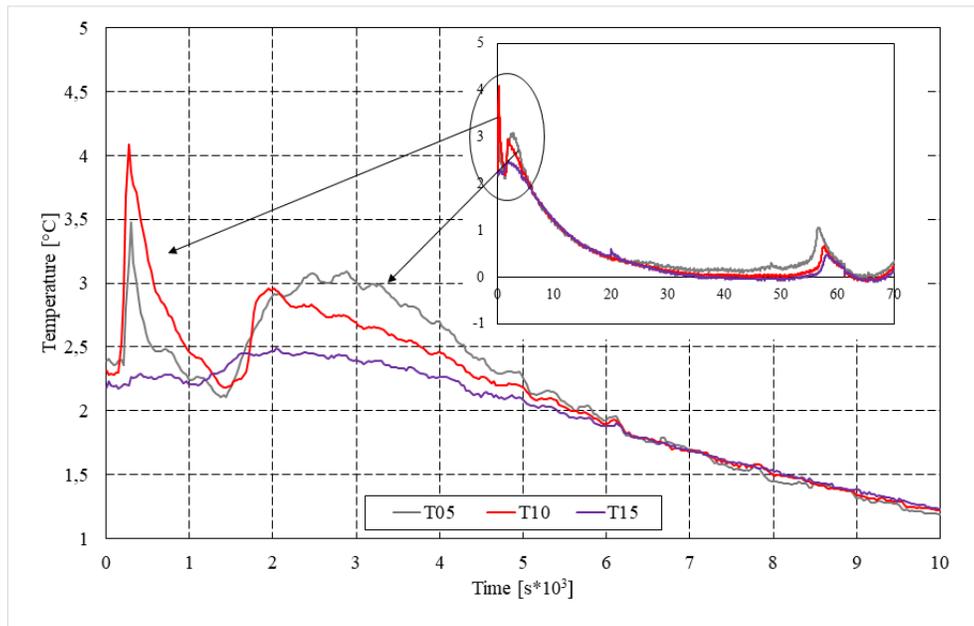


Fig. 3: Temperature over time in Test 1, carried out with CH<sub>4</sub>.

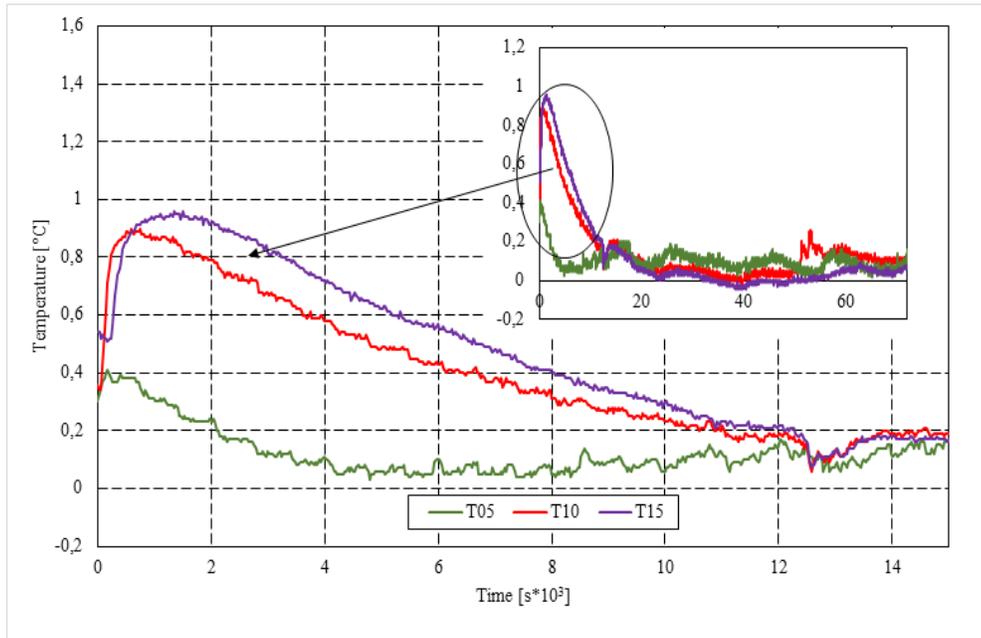


Fig. 4: Temperature over time in Test 2, carried out with CH<sub>4</sub>.

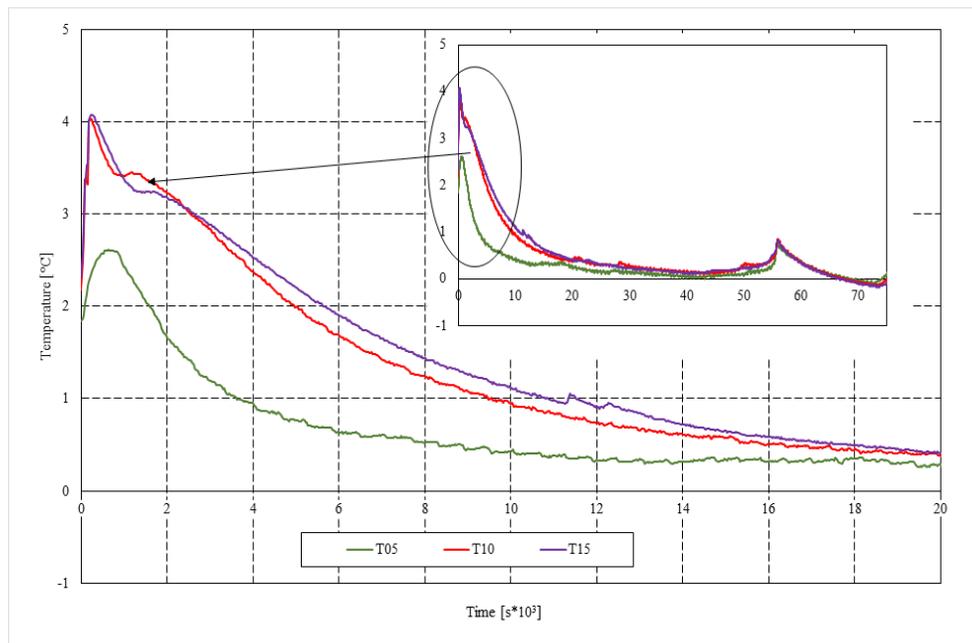


Fig. 5: Temperature over time in Test 3, carried out with CH<sub>4</sub>.

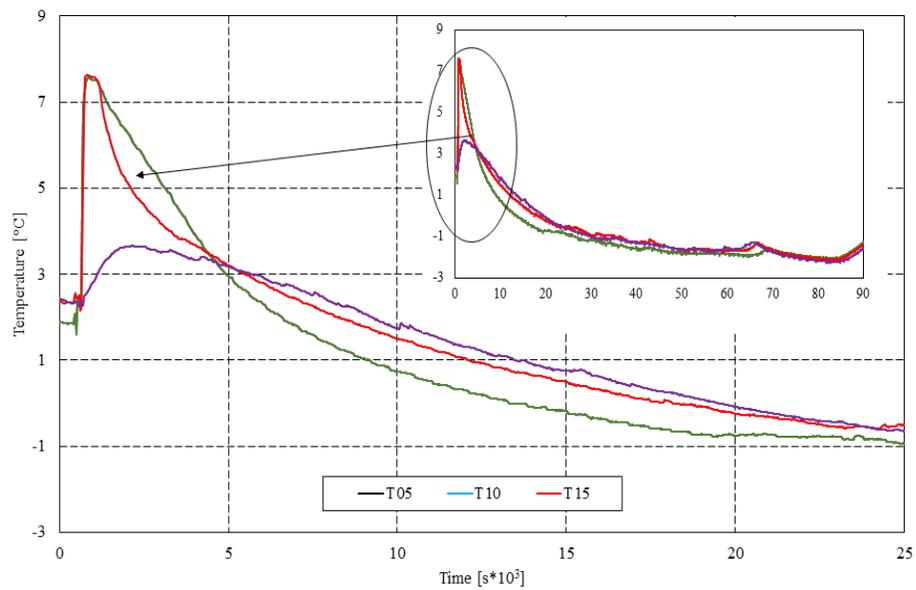


Fig. 6: Temperature over time in Test 4, carried out with CO<sub>2</sub>.

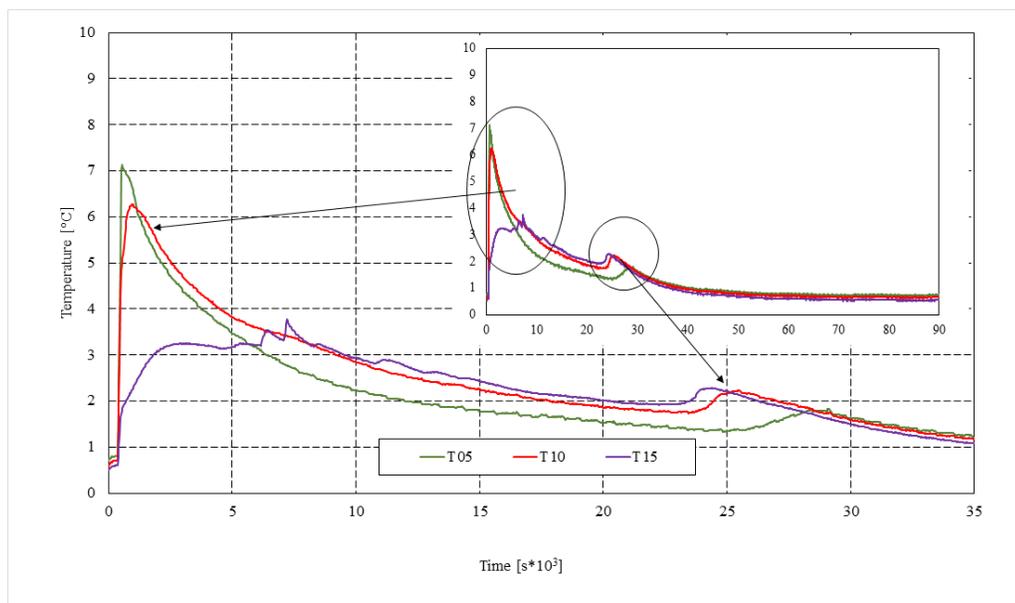


Fig. 7: Temperature over time in Test 5, carried out with CO<sub>2</sub>.

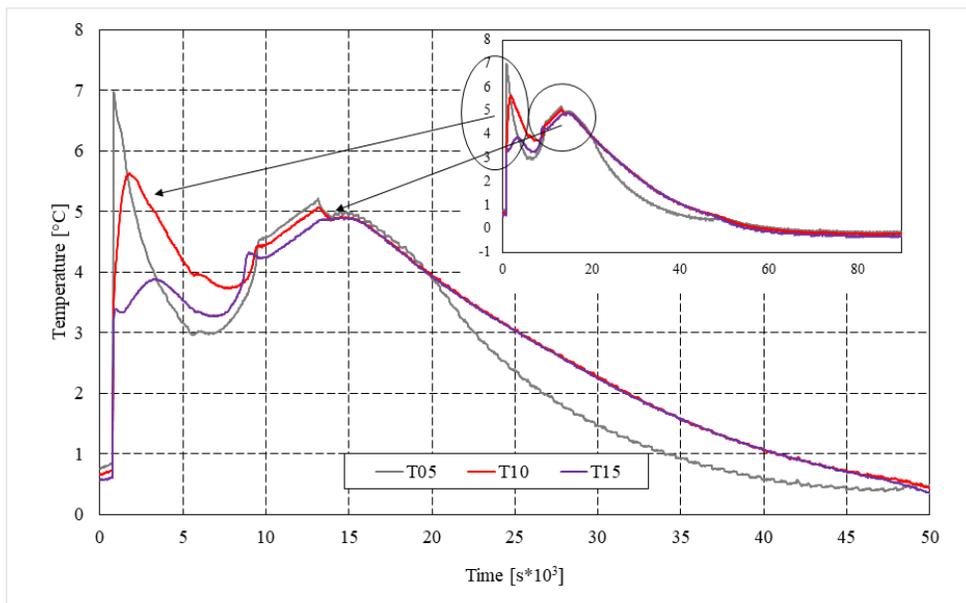


Fig. 8: Temperature over time in Test 6, carried out with CO<sub>2</sub>.

As showed in the scheme of Figure 2, the temperature was measured at different depths: respectively at 5, 10 and 15 cm depth from the top of the reactor. The first temperature describes what happens in correspondence of the gas – liquid interface; the others were used to monitor the process within the porous sediment. Each figure shows two diagrams: the smallest one represents the whole hydrate formation process, while the largest consists of an enlargement of the first one and allows to better visualize the initial peak in temperature associated to the beginning of the process.

The diagrams proved that the process began at different depths as a function of the gaseous species present inside the reactor. In the presence of carbon dioxide, the highest variations were noted in correspondence of T05, while, in the presence of methane, the most relevant peaks were measure with the thermocouples T10 and T15. In both the cases, the trend of temperature confirmed that the process was not homogeneous: it occurred at different times and with different intensities. For that reason, by its own, the temperature cannot be considered to accurately evaluate the induction time. Differently, the heat released allows to reach a good level of accuracy, because it is normalized along the whole internal volume of the reactor. Table 1 contains, for each test, the mean variation of temperature, the heat produced and used to measure the induction time and the associated quantity of hydrates produced (calculated with Equation 1).

Table 1: Heat released during the induction period and the associated quantity of hydrates formed.

	Guest	$\Delta T/^\circ\text{C}$	Q/kJ	$n_{\text{HYDP}}/\text{mol}$
Test 1	Methane	0.85	1.737	0.032
Test 2	Methane	0.41	1.234	0.028
Test 3	Methane	1.44	2.932	0.054
Test 4	Carbon dioxide	3.62	7.371	0.128
Test 5	Carbon dioxide	4.23	8.612	0.148
Test 6	Carbon dioxide	4.54	9.244	0.159

The peaks of temperature were significantly more pronounced in the tests involving carbon dioxide as guest and are clearly associated to a more abundant production of hydrates. This result confirms what observed in previous studies where, regardless of the induction period, the formation process for carbon dioxide hydrates was found to be faster than the one for methane hydrates [24].

The heat released and the associated quantity of hydrates produced, were then used to calculate the induction period. This parameter was considered as the time elapsed from the beginning of the formation process to the production of  $n_{HYDP}$  moles of the two respective species. The results are provided in Table 2.

Table 2: Values of the induction time for each test, obtained with the proposed method.

	Guest	Induction time/s
Test 1	Methane	$2,4 \cdot 10^2$
Test 2		$2,7 \cdot 10^2$
Test 3		$1,5 \cdot 10^2$
Test 4	Carbon dioxide	$6,6 \cdot 10^2$
Test 5		$3,9 \cdot 10^2$
Test 6		$8,1 \cdot 10^2$

The stochastic nature of the process led to visible difference also between tests belonging to the same group; however, the differences in induction time between methane and carbon dioxide hydrates appeared clearly. The results proved that the induction time is considerably longer for  $CO_2$  hydrates and confirm what asserted in literature [25, 26]. Future researches will be focused on evaluating the induction period for the same type of hydrates, obtained with the same procedure, by using the conventional techniques, for then carry out a direct comparison and verify the reliability of the proposed technique.

Finally, the process was not time limited and continued until the stabilization of pressure, which represents the spontaneous completion of the process. The total amount of hydrates formed was calculated with Equation 2. The relationship between the quantity of hydrates formed during the induction period ( $n_{HYDP}$ ) with, respectively, the total quantity of hydrates formed ( $n_{HYDtot}$ ) and the initial quantity of gas injected ( $n_{INJ}$ ), is shown in Table 2.

Table 3: Relation between the moles of hydrates formed in the induction period, with the total quantity of hydrates formed and with the initial amount of gas injected.

	$n_{HYDtot}/mol$	$n_{HYDP}/n_{HYDtot}$ [%]	$n_{HYDtot}/n_{INJ}$ [%]
Test 1 ( $CH_4$ )	0.3	10.67	51.72
Test 2 ( $CH_4$ )	0.28	10	45.9
Test 3 ( $CH_4$ )	0.3	18	51.72
Test 4 ( $CO_2$ )	0.31	41.29	59.62
Test 5 ( $CO_2$ )	0.23	64.34	52.27
Test 6 ( $CO_2$ )	0.24	66.25	54.55

As expected, the difference observed for the induction period did not affect the production of hydrates. Even if carbon dioxide hydrates showed a longer induction time, the tests based on their formation has a higher production of hydrates, if compared with the tests involving methane. The induction time is a kinetic parameter and, because the process was not time limited, it did not alter the final quantity of hydrates. Finally, the last column of Table 2, confirmed what observed in previous studies [27]: once the process started, the formation of carbon dioxide hydrates is significantly more intensive than the one of methane hydrates. It mainly depends on the higher mixing degree between water and guest molecules, which is related to the elevated dissolution of carbon dioxide in water. Conversely, the dissociation of methane is extremely low and can be neglected.

#### 4. Conclusion

This research deals with the experimental definition of the induction time for methane and carbon dioxide hydrates, by considering the heat released during the formation of the first clusters as identifying element. The heat released was then used to evaluate the quantity of hydrates formed during the induction period. This method was proposed in order to achieve

comparable or, if possible, more accurate results, than the ones achievable with the current solution and to extend, the possibility of measuring this parameter, also to medium – scale closed reactors.

The results demonstrated that the induction time is longer for carbon dioxide hydrates than for methane hydrates and confirmed what asserted in literature. The reason probably stays in the non – hydrophobicity of the CO<sub>2</sub> molecule and in the consequent higher maximum of Gibbs free energy, which must be overcome to proceed with the massive growth phase.

The process was not time limited, and the longer induction time did not affect the quantity of hydrates produced during the whole formation phase. The comparison between the hydrates formed during the induction period, the total quantity of hydrates obtained and the initial quantity of gas injected inside the reactor, revealed that, once the process started, the growth of carbon dioxide hydrates was faster and more abundant, due to the higher mixing between host and guest molecules, which is consequence of the high dissolution in water of carbon dioxide molecules.

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