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# The use of FBRM probe during hydrate particles agglomeration

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## Abstract:

Gas hydrates formation from water in oil emulsion is of particular interest in the context of crude oil production. Once hydrates form in the pipeline, individual gas hydrate particles agglomerate together and form a plug preventing fluid flow. This work shows the main advantages of using a Focused Beam Reflectance Measurement (FBRM) probe for in situ chord lengths analysis during hydrate particles agglomeration for a better understanding of this process within the pipe. The formation of gas hydrate was studied in a flow loop. Experiments were carried out at 278K and 7.5 MPa. This paper provides a systematic study of the FBRM probe signal. It also underlines the links between the shape of the CLD and the morphology of agglomerates carried inside the flow. This is particularly useful to understand the agglomeration process.

Keywords:

*FBRM ; Focused Beam Reflectance Measurement ; hydrate particles agglomeration ; water ; oil emulsion*

## I. Introduction

In the context of offshore oil-fields, long production lines operate under high pressure and low temperature conditions which are favorable for the formation of gas hydrates that can cause severe production disruptions. Therefore, an understanding of the variation of the particle size during the crystallization process of methane hydrates is necessary.
Experiments were performed in order to evaluate the influence of two parameters on the agglomeration effects: the water fraction and the content of an Anti-Agglomerant Additive. The first experiment set shows that the size of droplets in the emulsion is influenced neither by water-cut nor by the additive concentration. Nevertheless, the second experiment set evidences the effect of the water-cut and the additive content on hydrate agglomeration.
To model crystallization, the Particle Size Distribution (PSD) is currently used. Unfortunately, the FBRM does not provide a particle size distribution but a Chord Length Distribution (CLD): chord length is a straight line between two points on the edge of a droplet, primary particle or agglomerate. Therefore, several studies have focused on evaluating the PSD from the CLD, and also comparing the FBRM technique with another sizing technique, such as laser diffraction and microscopy (PVM) (Li., 2005), (Pons, 2006), (Greaves, 2008).
From the works of Camargo (Camargo, 2002) and Fidel-Dufour (Fidel-Dufour, 2006) hydrate aggregates are modelled as fractal-like objects characterised by a fractal dimension $D_f$, a number of droplets/primary particles $N_p$ of individual radius r (= $D_p$ /2, $D_p$ is the primary

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particles diameter) and a radius of gyration $R_g$. Those characteristics are related through the following statistical scaling relationship with $k_f$ the structure factor (Filippov, 2000):

$$N_p = k_f \left( \frac{R_g}{r} \right)^{D_f} \quad (1)$$

In a previous work (Le Ba *et al*, 2008) a model was developed to evaluate the CLD from the construction of theoretical aggregates with geometric characteristics $N_p$, $D_f$, $k_f$ and $D_p$. In the work of Le Ba *et al* (Le Ba *et al*, 2008) the aggregate is constructed from a suspension of monodispersed spheres. This permitted to compare the calculated CLD with the experiment by fitting $N_p$ and $D_f$. In the work of Camargo (Camargo, 2002) the fractal dimension was found from experiments equal to 2.5.
The algorithm used for building 3D fractal aggregates and simulating CLD from a monodispersed suspension presented in a previous work (Le Ba, 2008) is extended to a polydispersed suspension in this work.
This study focuses on modelling the CLD by fitting the calculated CLD with the experimental one by varying the primary particles size, the polydispersity, and the fractal dimension of the aggregates formed from a suspension of polydispersed spheres.

## II. Experimental apparatus and procedure

### II.1. Materials

The organic phase is a C10-C13 cut delivered by TOTAL Fluids under the commercial name Kerdane. As this oil does not present any natural emulsifying property, an Anti-Agglomerant Additive (IPE 202, patented by IFP) is added. The gas used was pure methane (99.99%) from AIR LIQUIDE. The water was ultra pure (Type 1).

### II.2. Experimental apparatus

Crystallization of water-in-oil emulsion to hydrate slurries under shear stress was studied in the Archimede loop located at Saint-Etienne School of Mines. A scheme of the apparatus is given on Figure 1. The test section is a 36 m long of 1 cm of internal diameter temperature-controlled with a pipe-in-pipe heat exchanger. More details on this equipment can be found in Fidel-Dufour *et al.* (Fidel-Dufour, 2005).The test section is equipped with a FBRM probe for *in situ* chord size analysis.

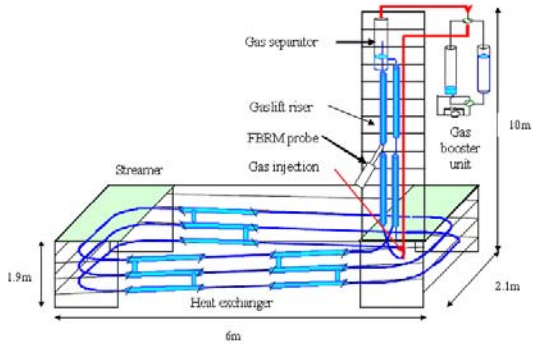



*Figure 1 : Archimede flow loop.*

The FBRM probe is an in situ chord size measure provided by Lasentec. This apparatus consists of an infrared LASER, with a wavelength of 785 nm and a scan speed of 2 $m.s^{-1}$. During the analysis of a suspension, the laser emitted from the probe is reflected when it encounters a particle. The chord length is deduced from the reflection time multiplied by the laser scan speed. The probe is capable of measuring chord lengths between 0.5 and 1 000 µm. In this work each 20 s, the probe provides a CLD (Chord Length Distribution), giving the

number of chord lengths counted for each chord length range. For more information on the probe and the analysis technique see the FBRM User's Manual (Mettler-Toledo Lasentec®).

### II.3. Experimental procedure

Emulsion is created in a reactor with an Ultra-Turrax impeller at 8000 rpm during 3 minutes. After loading the liquid phase into the loop, the emulsion is cooled down while flowing in the pipe. Once the operative temperature is reached, the methane gas is injected up to a pressure of 7.5 MPa. The methane dissolution in the oil induces a pressure drop which is compensated with a second gas injection of methane, then pressure decreases down to a constant value corresponding to the saturation of the phases (water and oil).
The methane hydrate crystallization begins and pressure starts to decrease to reach the liquid/gas/hydrate equilibrium pressure, dependent on the operative temperature. Because crystallization is an exothermic phenomenon there is a sharp increase in the temperature at the beginning of crystallisation.

## III. Results and Discussion

### III.1. Modelling

The model suggests that water droplets in the emulsion convert to primary hydrate particles maintaining their size (Camargo, 2002) and then agglomerate each other.
In order to interpret the CLD, the first step is to build 3D theoretical aggregates from a population of polydispersed spheres.
The particle size distribution (PSD) of the emulsion (PSD of spheres) is supposed to be characterized with a lognormal distribution (Equation 2). In order to evaluate correctly the PSD, the emulsion experimental CLD must be interpreted.
In fact, the FBRM probe measures at the beginning of the experiment the CLD of the emulsion. Supposing a lognormal distribution function (Equation 2), with two inputs: the average particle size $\overline{D_p}$ and the standard deviation δ, the PSD can be calculated and transformed into CLD. Comparing both CLD from experiment and calculated from PSD, $\overline{D_p}$ and δ are fitted (Figure 2).

$$f(D) = \frac{1}{\delta\sqrt{2\pi}}\frac{1}{D}\exp\left(-\frac{1}{2}\left(\frac{\log(D)-\log(\overline{D})}{\delta}\right)^2\right) \qquad (2)$$

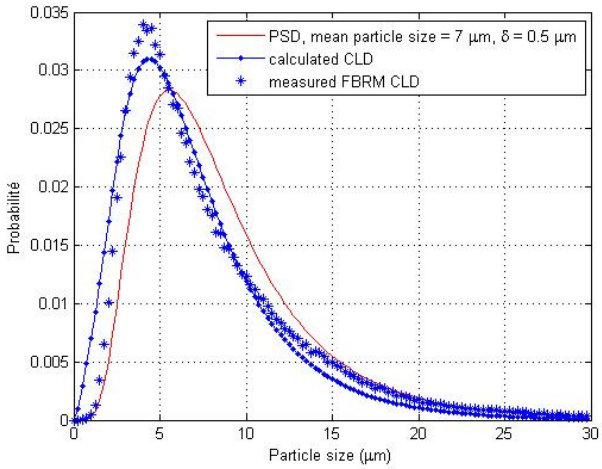



*Figure 2 : Comparison between CLD calculated and from experiment.*

From Equation1 the same can be written with the average primary particles size $\overline{D_p}$ and a radius of gyration $R_g$ following the statistical scaling relationship:

$$N_p = \left( \frac{R_g}{\overline{D}_p} \right)^{D_f} \quad (3)$$

Once the PSD of the emulsion has been evaluated, the theoretical random agglomerate is built using the method proposed by Le Ba *et al* (Le Ba *et al*, 2008). The result is a 3D aggregate, for example the one presented in Figure3 with 100 particles, an average particle size equal to 7µm, a standard deviation equal to 0.5 and a fractal dimension equal to 2.5.

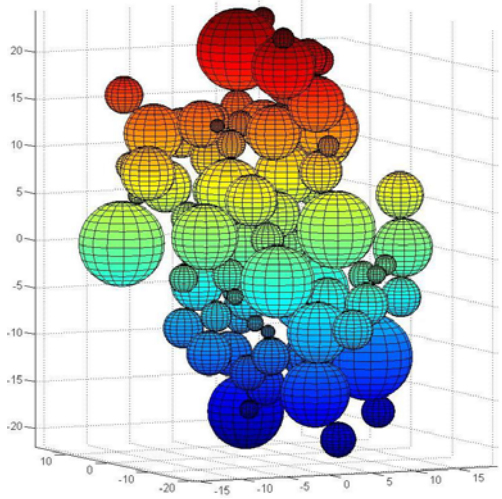


*Figure 3 : Example of aggregate with 100 particles (Np = 100, $\overline{D}_p$ = 7 µm, δ = 0.5, Df = 2.5)*

When the aggregate is built, it is projected in a plan and scanned as FBRM does to calculate the CLD. This procedure is repeated 200 times after rotating randomly the aggregate. At the end, a mean CLD is calculated. For more details about the model see Le Ba *et al* (Le Ba *et al*, 2008)

### III.2. Modelling

An hydrate slurry was formed from an emulsion with 20% of water (v water/v liquid) and 2% of additive (m/m water). Hydrate crystallization started 40 minutes after the injection of methane in the system.

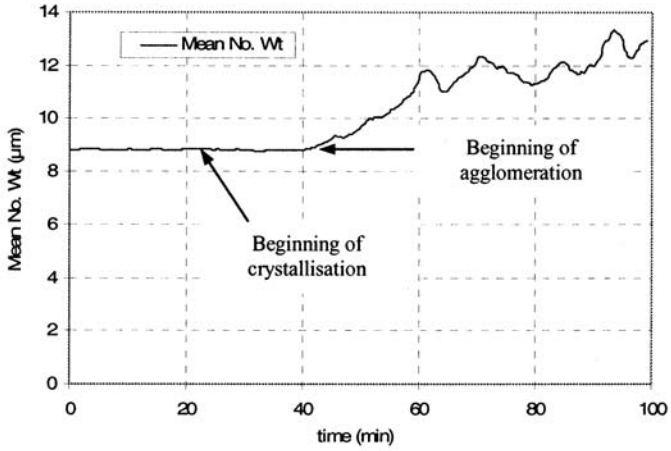



*Figure 4 : Mean chord length during a gas hydrate crystallization*

The onset of agglomeration phenomena is associated to a sharp change in the mean chord length estimated by the FBRM probe (Figure 4) and to the appearance of shoulders in the chord length distribution (Figure 5).
From Figure 5 one can see in the CLD before the beginning of crystallization, a main peak at 7µm corresponding to the water droplets in the emulsion (primary particle size). When hydrate crystallizes, the shape of the CLD is very different from the shape of the emulsion because the main peak decreases and the maximal chord length increases due to the agglomeration between water droplets. The beginning of crystallisation is accompanied by a step increase in temperature and a decrease in pressure. In the CLD, secondary peaks appear when agglomeration begins (62 min) and increase during agglomeration (95 min).

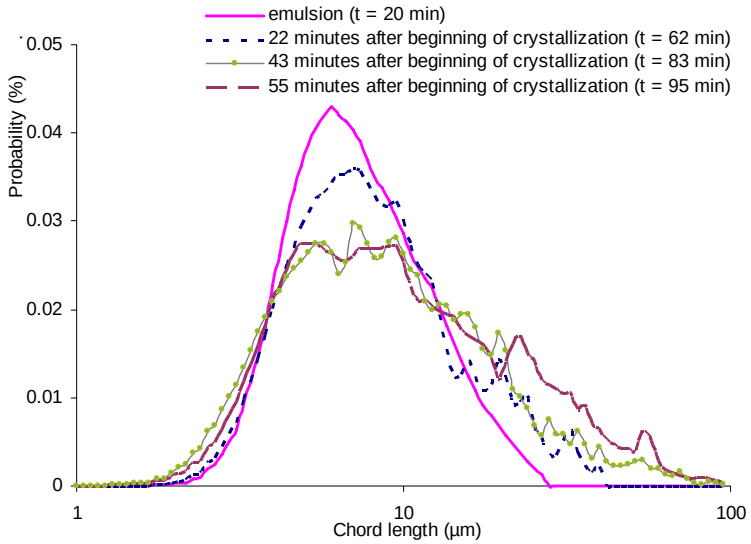
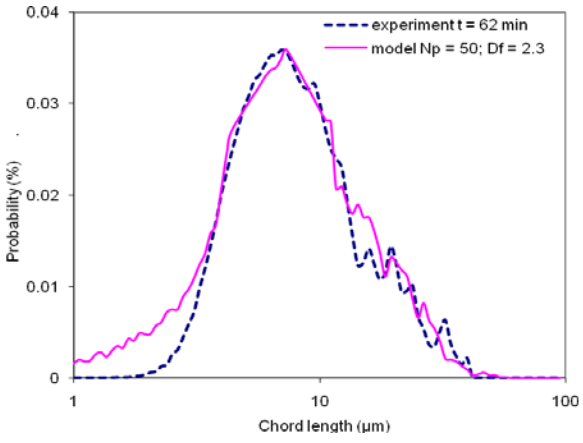
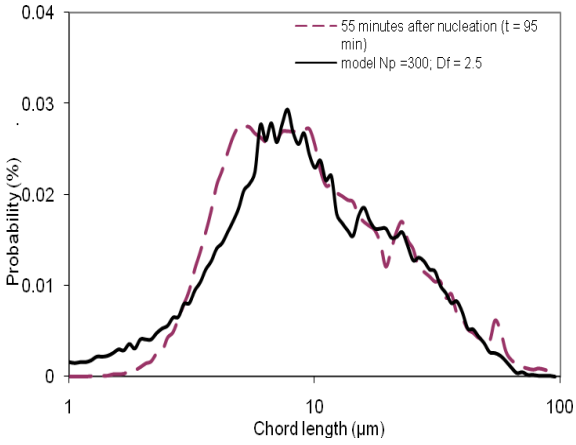



*Figure 5 : Evolution of CLD during hydrate crystallization.*

In order to construct an aggregate from a polydispersed suspension, the PSD of the emulsion at 62 min was determined by Equation 2. From this PSD several agglomerates have been constructed with varying number of primary particles and fractal dimensions in a way to fit the calculated CLD with CLD from experiment. The comparison between calculated and experimental CLD is shown in Figure 6.
For the first 62 minutes after the beginning of crystallization (Figure 6a), the simulated CLD was fitted for an aggregate with 50 primary particles and fractal dimension equal to 2.3. At 95 min (Figure 6b) agglomeration is finished but agglomerates become more and more compact due to rearrangement of particles. This was confirmed by simulation as the fitted fractal dimension increases from 2.3 until 2.5, this value is the same found by Camargo (Camargo, 2002).




(a)




(b)

*Figure 6 : Comparison between simulated CLD and experimental CLD a) t = 62 minutes, b) t = 95 minutes.*

## IV. Conclusions

An algorithm was developed in order to assess the geometrical characteristics of gas hydrate aggregates circulating in a pressurized loop from the CLD measured with the FBRM probe. Agglomerates were built from a monodispersed population of spheres (Le Ba, 2008). The same algorithm was used to build random aggregates from a polydispersed population of spheres characterized by their fractal dimension, average primary particles diameter and number of primary particles. After the corresponding CLD distributions were computed and compared with experiment.

This procedure has permitted to estimate the fractal dimension and number of primary particles of aggregates during experiments made in Archimede flow loop.

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