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Topological modeling of methane hydrate crystallization from low to high water cut emulsion systems

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ABSTRACT

Hydrate formation and remediation in oil flowlines facilities represent a major concern for oil industry in respect of capital and operational costs. It is necessary to have a better understanding on the hydrate formation process to be more efficient in hydrate prevention, especially in respect to additive dosage. This work is a contribution to enhance the knowledge of hydrate formation at high water cuts, by introducing new techniques of analysis in the *Archimede* flow loop: a Focus Beam Reflectance Measurement (FBRM) probe and a Particle Video Microscope (PVM) probe. These results will be supported by Pressure Drop, Flow Rate, Density and Temperature probes. From experimental observations, a method to determine the continuous phase (water or oil) of the system under flowing is proposed. It is based on the time evolution of the most representative chord class measured by the FBRM. In order to predict morphology and size of hydrates, a topological model was developed. It represents hydrate crystallization from different emulsion systems with and without low dosage of hydrate inhibitor additive (anti-agglomerant type). The key parameters are the gas transfer rate at the gas/liquid interface and at the hydrocarbon/water interface, and the role of the hydrocarbon as gas transfer phase. Gas/liquid transfer is low as water phase remains the continuous phase, but is enhanced as hydrocarbon content is increased. Hydrocarbon gas transfer property is depleted as continuous and rigid crust is formed around droplets, especially in well dispersed emulsions. This behavior is highlighted for experiments without anti-agglomerant additive (AA-LDHI) and at high water cut, as a small fraction of hydrocarbon is well dispersed in the water continuous phase. The maximum hydrate plugging risk is in between 70% and 30% water cut (intermediate and low water cut). In this work, experiments at high water cuts (more than 80%) never plug. In order to prevent agglomeration, the AA-LDHI works better if it shows a secondary surfactant benefit, well-dispersing the droplets (and later the formed hydrates) in the continuous phase, which was identified as being preferentially the hydrocarbon phase.

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1. Introduction

Gas clathrates hydrates, also called gas hydrates, are ice-like structures formed by crystallization process. Hydrogen-bonded water molecules cage a guest molecule, small enough to fit in different types of cavities and typically belonging to the lightest hydrocarbon group. Usually, methane, ethane, propane, butane, carbon dioxide and di-hydrogen sulfide act as guest molecule in hydrate formation. Gas hydrates can form during oil extraction in required conditions: low temperature and high pressure. These conditions are commonly found in subsea pipelines cases. After hydrate formation and agglomeration, pressure drop increase is observed and, in some cases, formation of impermeable plug can occur [1].

Methods to prevent hydrates formation and agglomeration are numerous but expensive, such as, maintaining the pipeline in a secure temperature zone by insulating the pipe, removing water from the system (dehydration), using additives as thermodynamic hydrate inhibitors (THIs) or, most recently, using low dosage hydrate inhibitors (LDHIs), including: kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs).

As oil field matures, the water fraction usually increases. Therefore, industry is facing systems where the emulsion continuous phase (oil or water) is unknown [2]. Since the last decade, this

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area became the focus of research because there is a clear interest on studying it to provide a better management of hydrate formation.

Emulsion is formed from two immiscible liquids, at least, where one liquid is dispersed in another which is called continuous phase. In this work, the determination of the continuous phase before and during crystallization will support our understanding of hydrate formation.

Experiments were performed in the *Archimede* flow loop equipped with several probes, among them a Focused Beam Reflectance Measurements probe (FBRM) and a Particle Video Microscope probe (PVM). The hydrate formation process in flow lines was investigated by evaluating the influence of different water cuts and varying flow rate. Sets of experiments were performed with and without the presence of a commercial AA-LDHI.

The FBRM probe has been already used to follow hydrate crystallization. *Clarke and Bishnoi* [3] used this tool to determine the intrinsic kinetic rate of CO_2 hydrate formation at different temperatures. In 2009, *Turner* et al. [4] used it to follow the hydrate growth at high water cut in crude oil without additive. During crystallization, they detected that water droplets behave as individual reactors to form hydrates; two different mechanisms of formation were identified: hydrate shell formation and water coating hydrate particle. In 2010, *Leba* et al. [5] proposed an algorithm to calculate the CLD (Chord Length Distribution) from a random and fractal aggregate in order to interpret experimental results in terms of primary particles number and fractal dimension. Their developed model was validated against experimental results from the *Archimede* flow loop.

The FBRM probe is often coupled with a PVM probe, providing more accurate results. *Greaves* et al. [6] found out that sizes obtained with the FBRM are larger than sizes from the PVM for glass particles in water, however, smaller when measuring droplets in an emulsion. This means that the FBRM probe has to be calibrated for different types of system. Following this study, *Boxall* et al. [7] proposed a correlation relating the measurements from the PVM and the FBRM. In this work, this correlation is not used, firstly, because it seems not to fit in the studied system. Secondly, it is hereafter proposed an analysis based on the PVM images and FBRM measurements, without numeric treatment.

The focus of this work is to monitor the hydrate formation mechanisms (mainly agglomeration) depending on the water cut (*i.e.*, the water volume fraction) and depending on the continuous phase, in absence and presence of anti-agglomerant (AA-LDHI).

For the performed experiments, the pipeline plugging was stated when no, or very irregular flow was observed. In regards to the additive dosage, the AA-LDHI is used at very low concentration, far below their real dosage in industrial facilities, where their concentration is sufficient to prevent agglomeration, whereas our objective is to observe it, and also other steps of the crystallization. If AA-LDHI concentration is too high, there is no more time evolution in the FBRM, PVM, Pressure drop, Density and Temperature data.

2. Experimental method

2.1. Materials

Experiments are performed with pure water, Kerdane®, methane and dispersant additive. Water is Ultra-pure-water (Type 1). The Kerdane® (organic liquid phase material) and the dispersant additive (commercial anti-agglomerant) are supplied by TOTAL Fluides®; more information is given in Table 1. Pure methane (99.99%) is supplied by AIR LIQUIDE.

2.2. Apparatus

The Archimede flow loop allows an appropriate scale-down of liquid/liquid flowing in deep sea pipelines. The temperature control ranges from 0 °C to 14° and pressure control up to 100 bar. The flow loop has a horizontal section of 36.12 m and internal diameter of 1.02 cm (2/5 inch), a riser of 10 m high going into a gas–liquid contactor/separator and a descending pipe of 10 m long going back down to the horizontal section. The vertical section has an internal diameter of 1.73 cm (2/3 inch). The FBRM is installed on the descending pipe and the PVM is installed on the horizontal section. Several temperature and differential pressure probes follow the time evolution of the experiment. The flow rate is monitored with a Coriolis flowmeter which is also able to measure the density. The *Archimede* flow loop layout with probes position is given in Fig. 1, more information is given in Fidel-Dufour [8].

The flow is induced by a multiphase pump (Moineau pump), which can work with flow rate between 72 L h^{-1} and 500 L h^{-1} (0.3 m s^{-1} to 1.8 m s^{-1}). The Moineau® pump is a kind of progressive cavity pump, consisted of a helical rotor turning inside a helical stator [9]. The rotational movement generates an axial displacement of the closed cells, transferring the product from the intake to the discharge without smashing the crystal. The gap for the liquid flow is the order of centimeters, while the largest hydrate aggregate measured has 200 μm. By this way, the particles, aggregates and agglomerates of hydrates will not be destroyed by the pump, an important factor considering the interest on evaluating hydrate formation and agglomeration.

2.3. Experimental conditions and protocol

In this work, water cut was varied from 30% to 90% and flow rate was fixed at either 200 L h^{-1} or 400 L h^{-1}. Experiments were performed with and without AA-LDHI (intentionally under-dosed for already mentioned reasons). Table 2 summarizes experiments conditions. During hydrate formation, pressure is maintained constant through a system of gas injection, composed of a pressure controller coupled to a gas flowmeter (see Fig. 1).

Experiment starts by feeding the flow loop with a mixture of water and Kerdane® (and additive when necessary). The emulsion is formed by shear between the liquid mixture and the pipe wall. When pressure drop and average chord length reach homogeneity and stability, the process of emulsion formation is considered as finished [10]. In sequence, the system is cooling down until the operative temperature reaches around 4 °C (sub cooling of 6 °C), then crystallization is induced by increasing the pressure up to 80 bar by methane injection. The methane is injected in the gas zone of the gas/liquid contactor/separator at the top of the flow loop. This contactor/separator prevents the gas to be flowed in the descending pipe and also acts as a gas/liquid exchanger. In fact, liquid (and solid if present), coming from the riser, forms a geyser that falls down by gravity to the bottom of the separator. The pressure is maintained constant by a pressure compensation system that injects gas at the top of the separator. The injected gas flow rate is monitored allowing the resolution of a mass balance, and then to calculate the experimental conversion of water into hydrates.

2.4. Experimental conversion

Conversion of water into hydrates is calculated from the gas consumption, normally identified by a sudden temperature increase. In order to calculate the conversion, it is assumed that all gas solubilizing into the system after hydrate formation beginning is consumed to form hydrates. Regarding methane hydrate

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