High pressure hydrate detection in a stirred vessel

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ABSTRACT

Measurements have been undertaken in a stirred vessel on pressurised saturated hydrocarbon/water mixtures from the North Sea.

Hydrate formation and dissociation was detected, and the increase in mixing torque was quantified.

Stirred vessels, fitted with suitable pressure and temperature control facilities, can be used to characterize many of the important parameters coupled to the presence of hydrates in production systems.

The measurements have been undertaken on pressurised systems containing hydrocarbon liquid, mixed with saline water and saturated with hydrocarbon gas. The oil/water dispersions have then in turn been tested in a stirred vessel of volume 500 ml with pressure and temperature control. Typical test pressure has been 50 bars, and the temperature during hydrate formation typically 2 °C.

INTRODUCTION

Clathrate hydrates[1, 2] may form in oil production facilities when the pressure and temperature favour the growth of hydrate crystals. Typically, at a pressure of 50 bar hydrates may form when the temperature falls below approximately 20 °C. The presence of hydrate crystals in the fluid may cause a significant increase in viscosity. From a production point of view this poses a threat to both production capacity and possible blocking of the production pipeline if the hydrates form a plug. The strength of pure clathrate hydrates can be 20 times stronger than ice[3], but this may not be comparable with the strength of solidified dispersions containing hydrate particles.

The presence of hydrates in oil and gas transport systems poses a threat to the continuous production process. It is therefore of great importance to be able to characterize dispersions containing hydrates with respect to both flow properties and strength. The present work focuses on saturated oil/water system where the water volume fraction is less than 50%, thus forming a water in oil dispersion or a partially stratified system before hydrates are formed. Similar hydrate tests have also been made in rheometers[4].

The flow of hydrate dispersions in pipelines has been investigated by several authors[5, 6]. Hydrate growth is often inhibited by the addition of Methanol or Glycols affecting the thermodynamic equilibrium. Kinetic hydrate inhibitors, slowing down the rate of hydrate growth or delaying hydrate formation, have been investigated by several authors[2, 5]. Some oils also seem to contain components that act as natural inhibitors[7, 8] that prevent the formation of hydrates. Published information on the rheology of hydrate dispersions include characterization of hydrate suspensions[9], investigations on the flow properties of hydrate in water

Figure 1: The Dispersion Characterization Rig with the Dispersion Characterization Probe (DCP) in the centre.
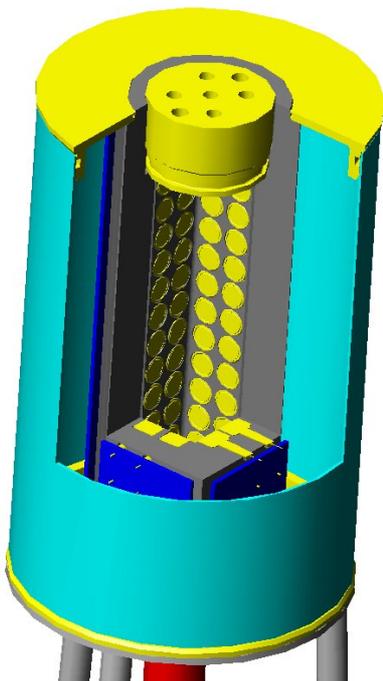
Figure 2: DCP with wall cut-out showing the circular capacitance sensors.
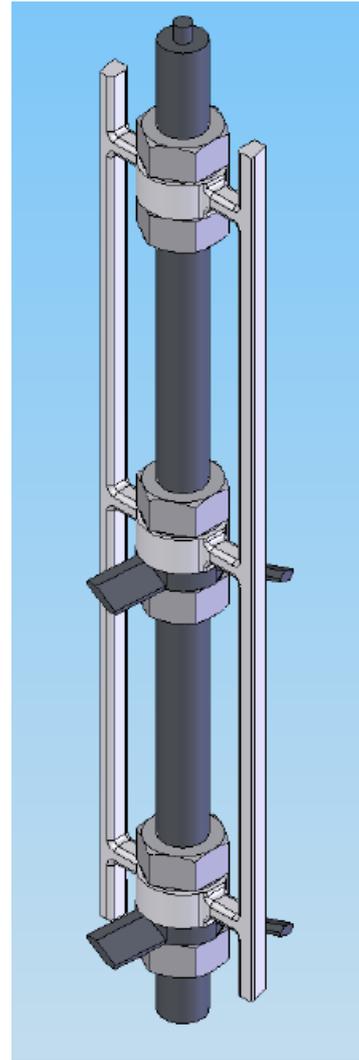
Figure 3: Mixer geometry with anchor and two three-bladed propellers.

systems[10] and viscosity measurements on crude oil systems[11, 12].

The focus in this work was placed on the use of a stirred vessel for determination of rheological behaviour of dispersions containing hydrates.

MATERIALS AND METHODS
The DCP

The Dispersion Characterization Probe (DCP) is a 500 bar test cell with a volume of 500 ml. It has previously been used to investigate the separation of North Sea oil and saline water[13]. The test cell is made of Titanium and is fitted with 92 internal SeCaP™ electrodes (Single electrode Capacitance Probes[13-18]) monitoring the

content in the vessel. The high pressure rating of the cell is required to perform separation tests on actual down hole well samples. The cell is fitted with a channel through the Titanium body and is placed in a temperature-controlled environment, thus controlling the temperature during the test runs. Pressurized bottom-hole hydrocarbon samples can be transferred to the test cell without any contamination with oxygen or other unwanted compounds. The DCP is shown in Figure 1 and Figure 2.

The test cell has a square cross section with side 45 mm and a height 247.8 mm, making a total volume of 500 ml. Each SeCaP™ electrode has a diameter exposed to the fluid of 15 mm. To distribute all 92 electrodes over the cell height, the electrodes overlap, making an electrode vertical resolution of 5 mm.

The cell also contains a variable speed mixer. An external motor drives the shaft. The mixing unit is driven by a frequency controlled motor, through a magnetic coupling, and both the torque and the rotational speed is measured, thus knowing the mixing power input to the test volume. This is an important parameter to control since it is desired to match the mixing power per unit volume in the cell to the normal power dissipation per unit volume in real processes such as pressure drop due to friction in pipes, pressure drop across valves and so forth. The design of the mixer/stirrer used in the hydrate studies is shown in Figure 3.

Experiments
Creation of hydrates in the DCP:
The DCP was filled with the required amount of water[*] and hydrocarbon liquid. The DCP will normally not be completely full, but have a gas volume at the top.

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[*] Synthesized salt water: NaCl: 25.09 g/l, $CaCl_2 * 2H_2O$: 2.191 g/l, $MgCl_2 * 6H_2O$: 12.064 g/l, KCl: 0.982 g/l, $NaSO_4 * 6H_2O$: 8.900 g/l

Normally the cell will be between half and 2/3 full (250-300 ml).

The DCP was closed and the gas volume flushed with nitrogen, and a hydrocarbon gas mixture was then added to a pressure of approximately 2 bar.

The complete DCP assembly was then cooled down to 0-5 °C by means of a cooling system (KRYOMAT). The steady state temperature was normally approximately 2 °C.

When the temperature was steady, the pressure in the DCP was increased to 50 bar by the controlled addition of gas, thus entering the hydrate region.

The mixer was started at a speed of 150 rpm.

Hydrate growth consumes gas, so more gas must be added in order to keep the pressure at 50 bar during hydrate formation.

The presence of hydrates in the DCP can be detected in the following ways:

- The hydrate formation process is exothermic, so an increase of local temperature indicates hydrate formation.
- Increased torque on shaft
- The SeCaP™ measuring system should identify the presence of hydrates by a lower than water signal strength. The dielectric constant of hydrates is lower than that of water. The SeCaP™ system is also able to register a possible dispersion formation as a result of hydrate formation.
- The consumption of gas.

Dissociation of hydrates in the DCP:
Dissociation of hydrates was initiated by pressure reduction, or in combination with a slow increase of temperature to the surrounding temperature level.

The pressure was reduced slowly (in a matter of minutes) to 1 bar by the opening of discharge vents.

The dissociation is an endothermic process that absorbs energy. It may

therefore be possible to observe local reductions in temperature where hydrates dissociate.

The temperature in the DCP was monitored at each SeCaP™ element.

CFD Calculations

The flow behaviour in the DCP was studied by means of the computational fluid dynamics (CFD) code Fluent[†].

Simulations with different water cuts (water volume fraction) (0, 10, 50 and 100%) and rotational speeds (100 and 200 rpm) were performed. The results show that the convective transport was mainly in the tangential direction in all the cases. Minor mixing was observed in the radial and axial directions. The flow patterns for the different cases were similar, and no significant discrepancies were observed.

The velocities were largest at the tips of the impellers and anchors, and in the area between these. Stagnant zones were observed in the corners of the cell. These stagnant zones were caused by the geometrical layout. The oil and water had the same velocity magnitude, and no major discrepancies in the flow pattern could be observed between the 2 phases.

The shear rate was in the range 40-80 s^{-1} in most of the cell at 200 rpm as shown in Figure 4. This is the same order of magnitude as flow through pipelines and bends in offshore plant.

However, in the boundary layer at the impeller tip, anchor and walls, and between the wall and rotor the shear was significantly larger. The shear rate was caused by the large velocity gradients in these regions, and is hard to avoid due to the geometry.

A summary of the results is shown in Table 1.

RESULTS

Experimental results

A typical set of experimental results is shown in Figure 6 and Figure 7. A height in the DCP versus time diagram is shown in Figure 6. The system is initially separated with water at the bottom, but at time 22:15 hydrates form and the system changes to a hydrates in oil dispersion. The driving torque on the motor shaft also increases at the same time due to the increased viscosity of the fluid system in the DCP as seen in Figure 7.

Figure 6 is a raw data plot of the capacitance values from the SeCaP™ system. No filtering has been applied. Specific numerical values have bee assigned a specific colour, and intermediate numerical values are given colours based on linear mixing on the colour palette.

The results show that the formation of hydrates is easily detected, and a significant increase in viscosity (or mixer driving torque) is observed when hydrates are formed. The hydrate dissociation (or melting) temperature is also easily detected by the SeCaP™ instrumentation.

DISCUSSION

The flow conditions in the DCP must be close to those of real flowing systems. The CFD-calculations were therefore performed with Fluent in order to determine the typical conditions in the stirred cell. A summary of the main parameters from these calculations is shown in Table 1.

The average shear rate at 200 rpm is between 30 1/s and 40 1/s, and it increases with increasing water cut. The maximum shear rate, occurring near the outer parts of the rotating anchor, is larger by a factor of approximately 20.

[†] http://www.fluent.co.uk/
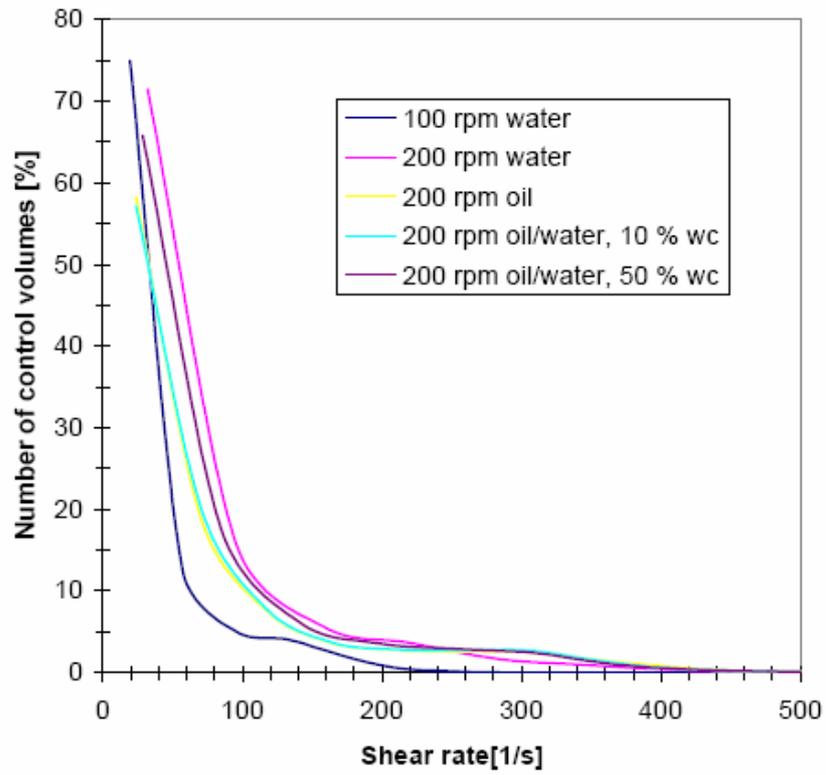
Figure 4: Shear rate distributions in the DCP at different speeds and water cuts.
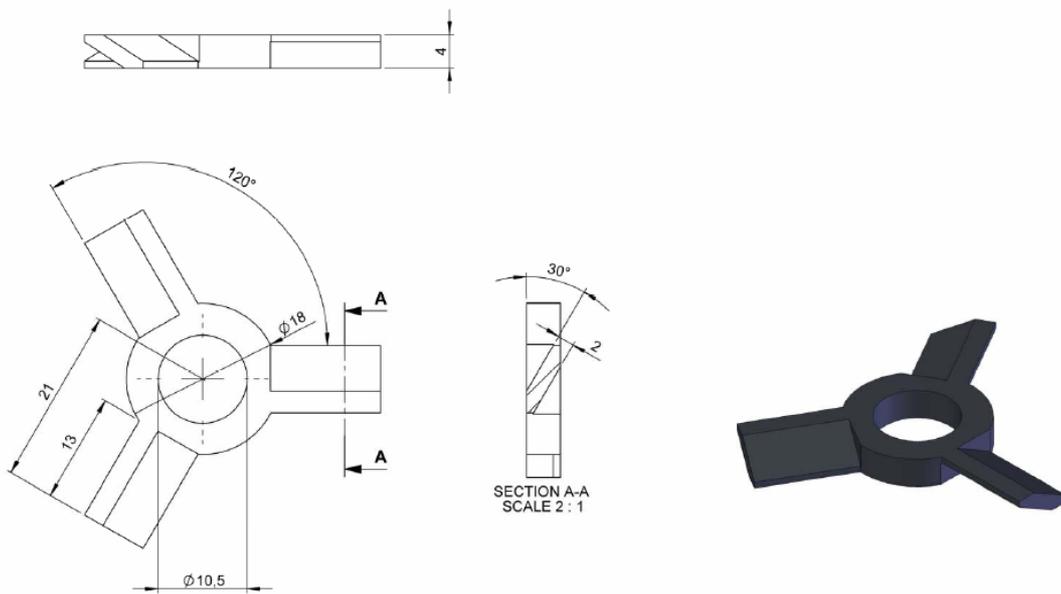
Figure 5: Detailed view of propeller design.

Table 1: Results from CFD calculations.

	100 rpm, water	200 rpm, water	200 rpm oil	200 rpm oil/water 10 % wc	200 rpm oil/water 50 % wc
Averaged velocity magnitude [m/s]	0.075	0.148	0.133	0.135	0.141
Averaged absolute tangential velocity [m/s]	0.067	0.137	0.122	0.123	0.130
Averaged absolute axial velocity [m/s]	0.017	0.032	0.027	0.029	0.030
Averaged absolute radial velocity [m/s]	0.016	0.027	0.024	0.026	0.026
Averaged shear rate [1/s]	18.8	33.1	37.6	34.5	35.6
Maximum shear rate [1/s]	494	1200	709	769	1080
Averaged turbulent kinetic energy [m^2/s^2]	0.0006	0.0019	0.0032	0.0032	0.0028
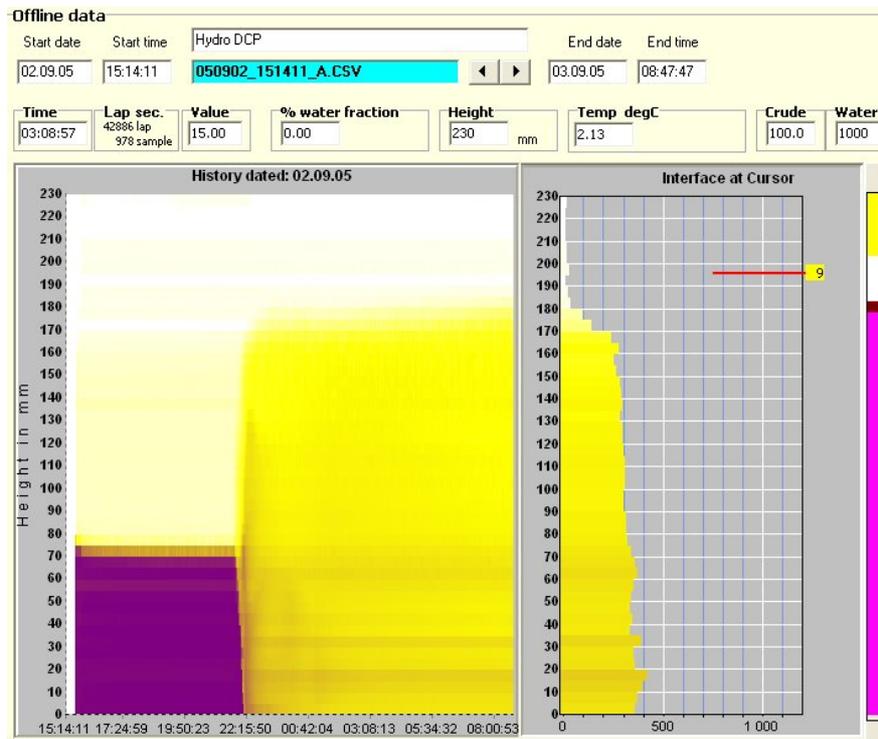
Figure 6: Hydrate formation as seen by the SeCaP™ probes in the DCP. A height versus time diagram on the left and an instantaneous profile shown on the right.

Torque plot
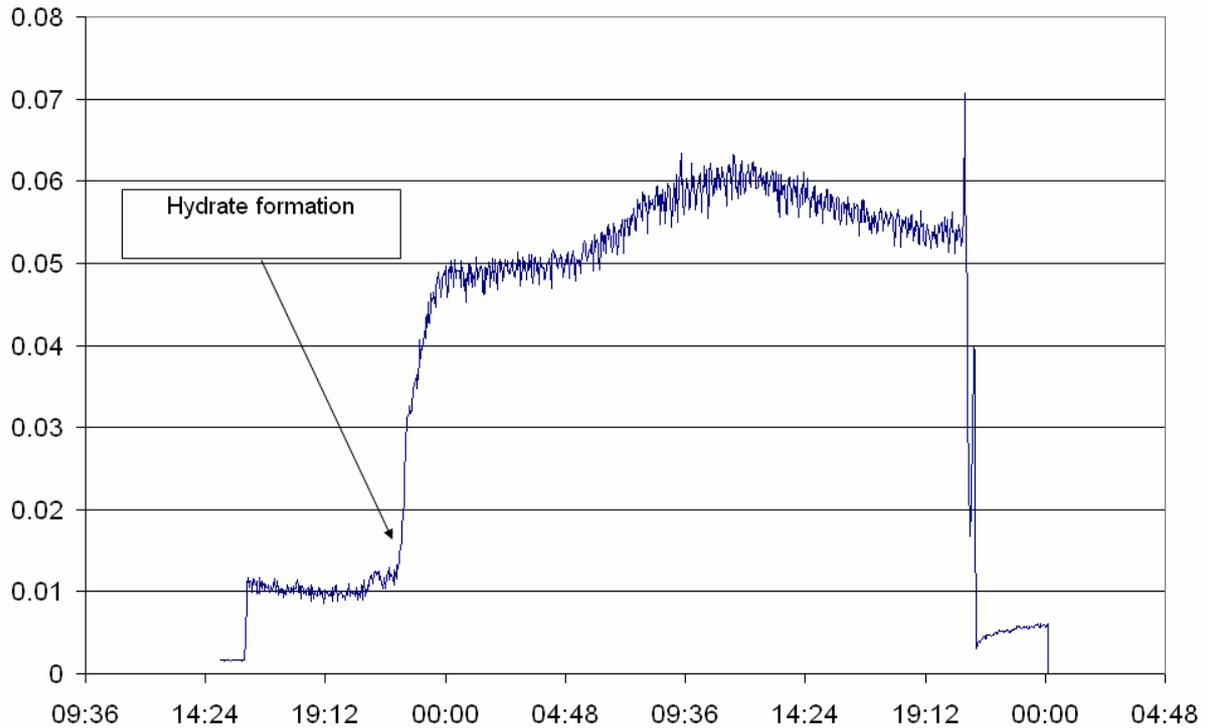
Figure 7: Torque plot during hydrate formation.

The tangential velocity is the larger of the velocity components in the stirred vessel. The total average velocity is approximately 0.13 m/s at 200 rpm. At a speed of 150 rpm the values can be approximated to be 75% of the 200 rpm-values.

The rotational speed used in the series of tests was 150 rpm, corresponding to an average shear rate of approximately 27 1/s and a maximum shear rate of approximately 800 1/s. All the fluid particles in the DCP will over a period of time be exposed to the maximum shear rate and it is therefore likely that dispersed particle sizes is correlated to this maximum value.

CONCLUSIONS

The conclusions from the DCP tests in 2005 can be summarized as follows:

A tests method for hydrate detection and characterization has been established using the Dispersion Characterization Probe (DCP).

The DCP can be used to repeatedly form hydrates.

The relative increase in torque during hydrate formation can be quantified giving rheological information on the hydrate slurry.

The delay time for hydrate formation seems to decrease with increasing water cut.

The delay time for hydrate initiation in the DCP is typically below 24 hours.

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