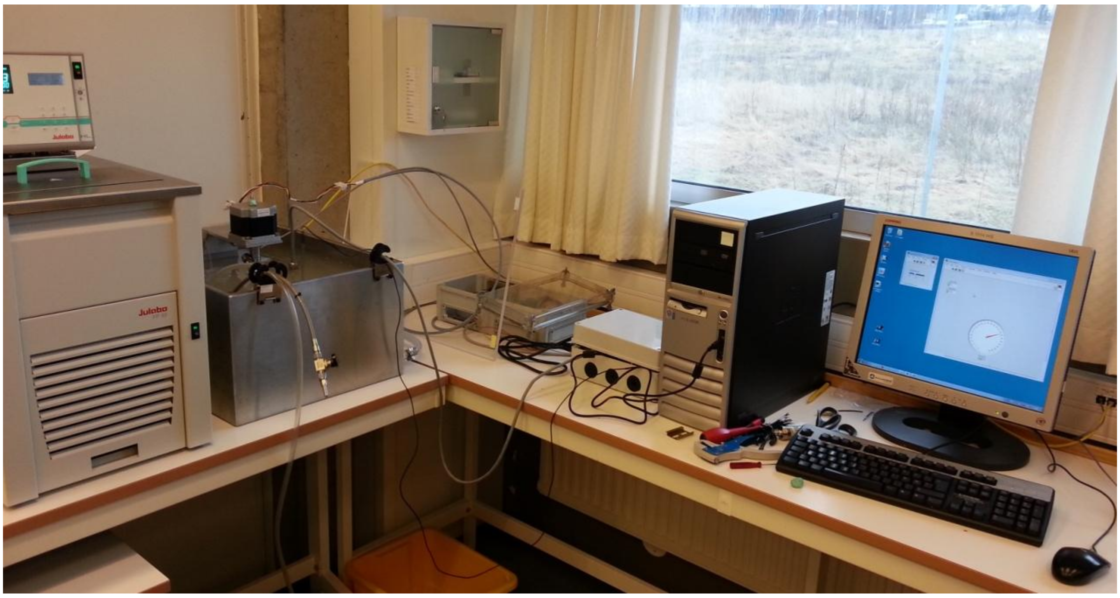
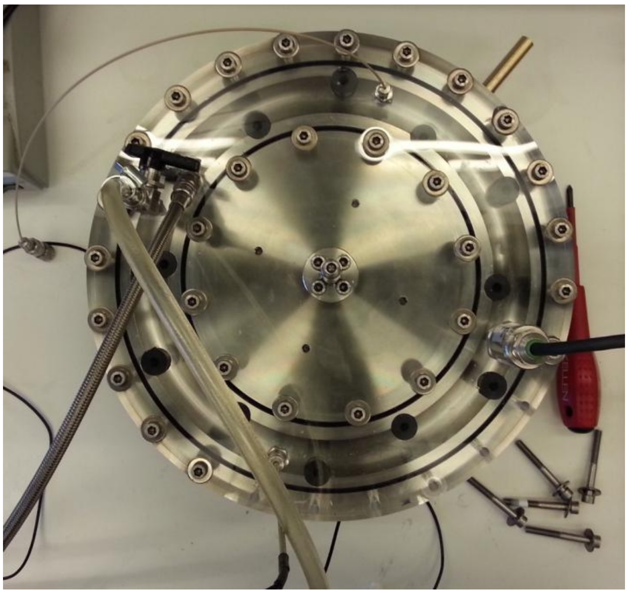
ESTABLISHMENT OF NEW EQUIPMENT FOR TESTING LOW DOSAGE HYDRATE INHIBITORS





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It has been an interesting journey to be a part of and to observe this apparatus progression. To have been the first to conduct experiments on this prototype apparatus, have proven to be both informative and exciting.

ABSTRACT

Gas hydrate formation posses a notorious concern for the oil and gas industry, and it only gets bigger because of that the never-ending pursuit of oil and gas compels the industry into deeper and colder waters. Here gas hydrate can from and agglomerate into plugs, jeopardizing pipelines and process equipments. Therefore a variety of methods have been developed to inhibit gas hydrate formation, one of them being to utilize low dosage hydrate inhibitors, which consists of kinetic hydrate inhibitors and anti-agglomerants. Low dosage hydrate inhibitors are relatively expensive, and it is therefore important to determine effective concentrations in laboratory apparatuses. Test apparatuses and methods are numerous, and the majority are THF rigs, rocker rigs, autoclaves, pipe wheels and flow loops. Prior methods for assessing hydrate inhibitors performance concentration tend to suffer form not being repeatable in addition to be inconsistent. Thus there are always possible for new hydrate inhibition test methods and apparatuses.

A prototype table top wheel was developed for testing low dosage hydrate inhibitors. It consisted of a wheel submerged in a water bath. Unique features of the table top wheel was its small size, the acrylic top disk and the mode of moving the liquid in the apparatus. A swirling circular motion made the liquid move based on the "Euler disk" mechanical movement, hence no pumps or internal equipment for propelling the liquid was utilized.

Preliminary tests were conducted to approve the apparatus for future experimental work, by providing a gas hydrate formation method of a consistent manner. The result for the same anti-agglomerant range in both 1.5wt% NaCl solution and distilled water, obtained in the table top wheel was compared to the rocker rig RCS20. This was done to confirm if this apparatus indeed could be used to rank inhibitors, thus a validation of the apparatus.

It was confirmed that the table top wheel result for the same anti-agglomerant range in both 1.5wt% NaCl solution and distilled water had the same trend as the results from the rocker rig. The table top wheel was thereby validated and approved at least for this anti-agglomerant range. However, the concentration required for an adequate inhibition was higher in the table top wheel compared to the rocker rig, hence the table top wheel was a more conservative test apparatus than the rocker rig.

Unfortunately the table top wheel could not be operated safely after 59 pressurized experiments, due to cracks in the acrylic top disk. This was a severely design flaws which must be sorted out for the apparatus to progress.

However, as far as being a prototype the table top wheel approved to be adequate. It yielded reliable and predictable test results and provided a consistent method for both hydrate formation and inhibitor testing.

CHAPTER 1: THEORY

1.1 The physical properties of water

Since gas hydrates, or clathrate hydrates, consist mainly of water, it is essential to understand the physical properties of water both in its liquid and solid phase.[1]

Most of the physical properties of water are dominated by the formation of hydrogen bonds between water molecules. Hydrogen bonds is therefore the principal interaction in liquid water and the same holds for ice and clathrate hydrates.[2] The oxygen atom carries a negative charge, while the hydrogen atoms carry a positive charge. Furthermore the number of lone pairs on the oxygen atom that can form the negative ends of hydrogen bonds, equal to the number of hydrogen atoms in a water molecule that can form the positive ends. This charge distribution is the reason for water being a strongly dipolar molecule, and the water dipole molecules attract each other and form aggregates through hydrogen bonds. This results in an extensive three-dimensional network in which each oxygen atom is tetrahedrally bonded to four hydrogen atoms by means of two covalent bonds and two hydrogen bonds. The hydrogen bonding allows the attachment between water molecules due to mutual acceptance and donation of hydrogen bonds. This is done in such a way that the central water molecule is surrounded in a tetrahedral manner by the other four. Bonds that form in this way are relatively strong and give the structure rigidity, thus there is more space between molecules than there would be in the liquid phase. Hydrogen bonds are much stronger interactions than dipole-dipole interactions are, which goes under the common name van der Waals forces. These dipole-dipole interactions make it possible for most materials to form condensed phases. However, hydrogen bonds are many times weaker than chemical bonds. The existence of hydrogen bonds makes it possible for water to be in a liquid phase at room temperature, although its molecular weight alone should dictate a gas phase. Without these bonds, water would be even more difficult to condense than oxygen, nitrogen and carbon dioxide. Also, water would melt about −100°C and boil at about −90°C. [1,3,4,5,6,7]

One particular peculiarity of water is its capability to expand upon freezing, thus the liquid phase is denser than the solid phase. This clearly shows that water in its solid phase have a more “open” structure than in its liquid phase. When water freezes, ice is formed, and this substance have a more open lattice, hence substantial lower density, than the liquid water it came from. The formation of water in its solid phase (ice) is energetically (enthalpy) favored process, because of the extraordinary amount of energy that is releases as heat as additional hydrogen bonds form (exothermic process). The formation of ice is however not favored by the entropy because the water possesses a more ordered structure in the solid phase.[1,7]

When energy is introduced to ice, it melts. In the melting process monomeric water molecules occupy holes in the remaining “icelike” lattice, hence causing the density of water to be greater than that of ice. More hydrogen bonds are broken and the open structure partially collapses, but at the same time the kinetic energy of molecules increases as the temperature is increased. Therefore the elevated kinetic energy decreases the density of water because the molecules occupy a greater volume. But at the same time this will cause more water molecules to be trapped. Initially the trapping of monomeric water molecules outweighs the expansion in volume due to the increase in kinetic energy. Thus the density increases from 0°C to 4°C. So at 4°C the increase in density due to the collapsing of the hydrogen-bonded clusters of water molecules is overtaken by the decrease in density due to the increasing molecular motion resulting from the rise in temperature. Beyond this temperature the density decreases with increasing temperature, because of predomination of expansion.[3,7]

There are similarities as well as distinct differences in the thermophysical and mechanical properties of ice and gas hydrates, although the physical appearance and refractive index between them are very similar. Therefore gas hydrates and ice have a different phase behavior, and the thermal conductivity of gas hydrates is over four times lower than ice. Provided adequate pressure, gas hydrates will be stable at temperatures above and below the freezing point of ice. Thus pressure have a tremendous impact on gas hydrate. Ice on the other hand are normally stable at low temperatures, therefore virtually independent of pressure (except at very high pressures).[8,9] There are nine known ice crystal types, hence it is no surprise that there are three known gas hydrate structures.[7] Gas hydrates allow a solid water phase to form at an elevated temperature above the normal freezing point of water.[6]

1.2 Gas hydrates in general

The definition of clathrate is as a substance in which atoms or molecules are trapped within the crystalline framework of other molecules. The name clathrate is derived from the Latin word *clathratus*, meaning “enclosed behind bars”. Clathrates made up of gas and water is called gas clathrates of water or simply gas hydrates. The word gas hydrate is a little deceptive in its meaning, and not strictly correct. The term hydrate usually implies some intermolecular attraction between the surrounding water molecules and the substance. Warming the crystals causes immediate release of the gas, thus there exist no chemical interaction between the water molecule and the gas. Therefore the gas atoms are simply locked into cavities in the hydrogen-bonded ice structure and are free to rotate and vibrate but have limited translation. With the exception of H_2, there exist no experimental evidence that guest atoms can diffuse from one cavity to another. The cavity structure collapses and the gas atoms are released, as the ice melts. A significant point is that the presence of a “guest” within the ice structure plays a decisive role in the stabilization of the crystal lattice, and increases the melting point if the ice several degrees above 0°C (figure 1.1).[3,4, 10] One explanation for hydrate formation is that the entrance of the gaseous molecules into vacant lattice positions in the liquid water structures causes the water to solidify at temperatures well above the freezing point of water.[11]

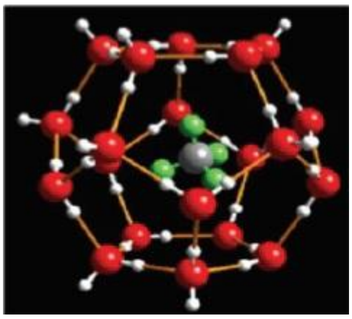


Figure 1.1. Schematic of methane hydrate surrounded by a water molecule cage.[5]

Gas hydrates are nonstoichiometric, snow-like, crystalline solids where gases of certain-molecular-weight stabilize the hydrogen-bonded water molecule cages. These inclusion compounds mainly consist of water, therefore it have many similarities with ice. If certain low-molecular-weight hydrocarbons combine with water under specific conditions of temperature and pressure, favoring conditions being low temperatures (typically < 20°C) and high pressure (typically > 30bar), which must be thermodynamically appropriate to that specific gas, gas hydrates will form (figure 1.2). van der Waals-type interactions between the water lattice and the trapped guest molecule causes the stability of hydrates. For this reason, in the absence of the guest, hydrates are unstable. The guest molecules are small gas molecules entrapped in the cavities of the solid water molecule lattice. A delicate balance between hydrophilic and hydrophobic interactions among water molecules and guest molecules causes the stability of gas hydrates. Gases that form gas hydrates are light, generally have low solubility in water and are nonpolar. Usually they are C1 to C4 inclusive and may be olefins or paraffins. In addition to this other gases found in oilfield fluids, such as N_2, H_2S and CO_2, will also form hydrates given the favorable conditions.[4,12,13,14,15,16]

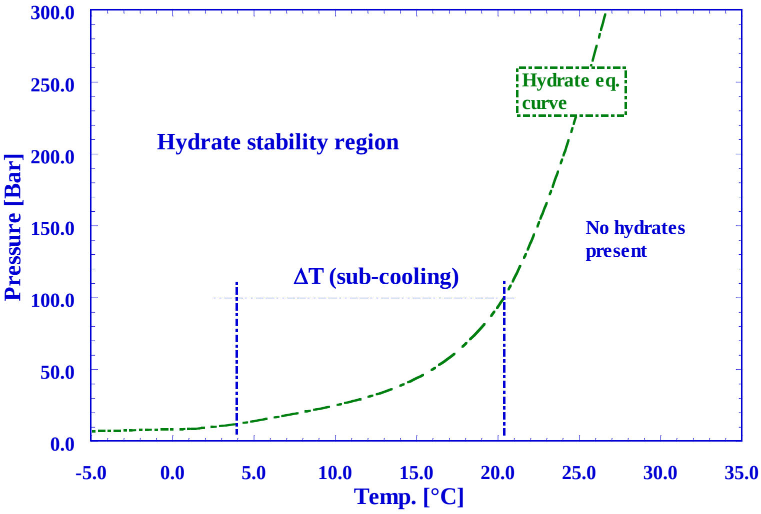


Figure 1.2. A general pressure against temperature graph for natural gas hydrate. These curves are made by the dissociation because hydrate formation is stochastic.[17,18]

In the case of gas hydrates the water molecules form a repetitive geometric lattice, commonly referred to as a cage, around a central molecule of a low molecular weight gas. This gas can be methane, ethane, propane, iso-butane, H_2S, N_2, CO_2, SO_2 and others which commonly constitute natural gas. More than 100 formers have been identified, with n-butane as the maximum size. Given the right conditions of temperature and pressure, the water molecule-based cage forms a geometric structure in the presence of the central gas molecule. This structure usually have 12, 14 or 16 sides and is stabilized by the additional van der Waals forces, acting between the gas molecule and the surrounding water molecules. The highly organized cage structure would be in dynamic equilibrium with free flowing water molecules, perpetually forming and collapsing, without the central gas molecules. Gas hydrates can coexist with ice and/or liquid water over a wide range of temperatures and pressures.[4,15]

Methane and water solidify under pressure:[11]
$CH_{4(V)} + 6H_2O_{(L)} \rightarrow CH_4 \bullet 6H_2O_{(S)}$

Gas hydrate are ice-like compounds belonging to a class of inclusion compounds called clathrates. They consist of cages composed of hydrogen-bonded water molecules, called the host lattice, which is stabilized by small molecules, called guests, that reside in the cages. Thus ,the gas molecules play, both figuratively and literally, only a supporting role. However, without this support, the whole structure collapses. For instance $1m^3$ of hydrates may contain as much as 180SCM (standard cubic meters) of gas.[6,19,20,21]

The discovery of the existence of gas hydrates was done in 1810 by Sir Humphrey Davy when he was studying chlorine. It is possible, however, that it the discovery took place in 1778 by Priestley. In the beginning gas hydrates was looked upon as mere scientific curiosity, until it was realized in 1934 by Hammerschmidt that it were gas hydrates and not ice formation that plugged natural gas pipelines on cold days. This event captivated the scientific and engineering interest, and caused a large series of investigations on gas hydrate stability conditions, gas hydrate structures and on gas hydrate prevention. This resulted in methods for calculating gas hydrate equilibrium conditions for any gas composition, and by addition of inhibitors or gas dehydration prevent gas hydrate form forming.[9,10,19,22,23]

1.3 Gas hydrate structure

Gas hydrates can crystallize in several different structures.[20,24] There exist three known gas hydrate structures, namely Structure I (sI), Structure II (sII) and Structure H (sH). These structures differ in type of water cages present in the crystal lattice.[9] Structure I and Structure II have a cubic shape and are made up of two kinds of cavities (small and large), while Structure H have a hexagonal shape and are made up of three kinds of cavities (small, medium and large).[4,25] This refers to how the water cages are joined to each other and held together by van der Waals forces (figure 1.3). It is the gas molecules, their size relative to the cavity and the relative stability of the structures that decides which structure to be formed. In addition to this, the shape and chemical nature of the guest molecules may also influence on the type of structure formed.[26] The gas composition determines not only which of the structures that will develop, but also at which temperature and pressure it will crystallize. Thus, every structure have its very own temperature and pressure equilibrium curve. The formation of the gas hydrate structures are therefore related to the ratio of the guest molecule size to the cavity size, and to the thermodynamic conditions of pressure, temperature and gas composition. The resulting regular geometric arrangement, or crystal lattice, which is formed, is the one that is most thermodynamically stable. This is the structure with the lowest free energy.[12,15]

It is not necessary for all the cages to be occupied by a guest hydrocarbon molecule for the crystal to be stable. At maximum occupation however, all the cages are occupied by only one guest molecule, 1mole of gas hydrate of either structure yields about 0.15mole hydrocarbon gas and 0.85mole water (15mole% hydrocarbon gas and 85mole% water).[9,12,27,28,29]

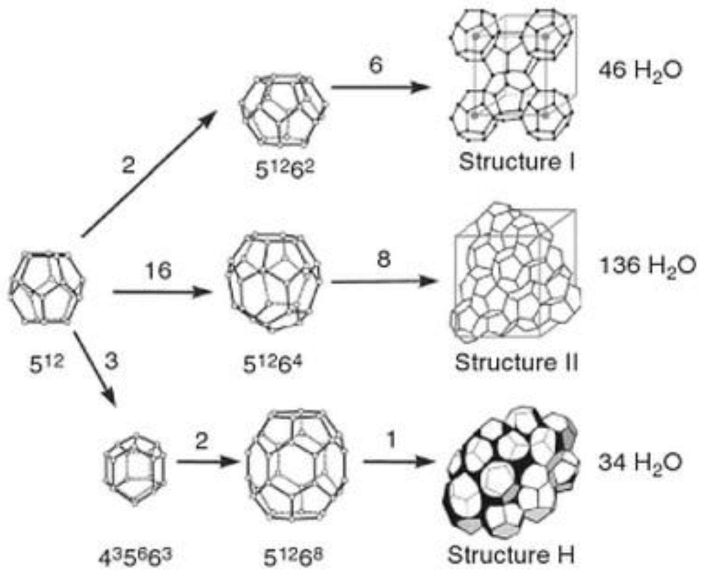


Figure 1.3. The three repeating hydrate unit crystals and their constitutive cages.[30]

Structure I consists of two types of cavities, a small pentagonal dodecahedral cavity and a large tetrakaidecahedral cavity. The small pentagonal dodecahedral cavity is denoted 5^{12} (12 pentagonal faces in the cavity), while the large tetrakaidecahedral cavity is denoted $5^{12}6^{2}$ (12 pentagonal faces and 2 hexagonal faces in the cavity). Structure II also consists of two types of cavities, a small pentagonal dodecahedral (5^{12}) cavity and a large hexakaidecahedral cavity. The large hexakaidecahedral cavity is denoted $5^{12}6^{4}$ (12 pentagonal faces and 4 hexagonal faces in the cavity). Each form is therefore a combination of the small cages in addition to either of the larger cages. Structure H consists of three types of cavities, the small 5^{12} cavity, a midsized $4^{3}5^{6}6^{3}$ cavity and a large $5^{12}6^{8}$ icosahedral cavity.[9,27]

The unit cell formula of Structure I gas hydrate is $(S)_2(L)_6{\bullet}46H_2O$, with the water framework consisting of two small (S) 12-sided (5^{12}) cages and six large (L) 14-sided ($5^{12}6^{2}$) cages. This means that the unit cell contains a total of eight cavities (six small and two large) made up of 46 hydrogen-bonded water molecules. The unit cell have a dimension of 12.03Å. The unit cell formula of Structure II gas hydrate is $(S)_{16}(L)_8{\bullet}136H_2O$, with the water framework consisting of 16 small (S) 12-sided (5^{12}) cages and 8 large (L) 16-sided ($5^{12}6^{4}$) polyhedral cages. This means that the unit cell contains a total of 24 cavities (16 small and eight large) made up of 136 hydrogen-bonded water molecules. The unit cell have a dimension of 17.31Å. The unit cell formula of Structure H gas hydrate is $(S)_3(M)_2(L)_1{\bullet}34H_2O$, with the water framework consisting of three small (S) 12-sided (5^{12}) polyhedral cages, two medium (M) 12-sided ($4^{3}5^{6}6^{3}$) polyhedral cages and one large (L) 18-sided ($5^{12}6^{8}$) polydedron cage. This means that the unit cell contains a total of 6 cavities (three small, two medium and one large) made up of 34 hydrogen-bonded water molecules. Thus the small (S) cage of pentagonal dodecahedron (5^{12}) is the common unit lattice cage of all these gas hydrate structures (figure 1.4).[2,12,24,31]

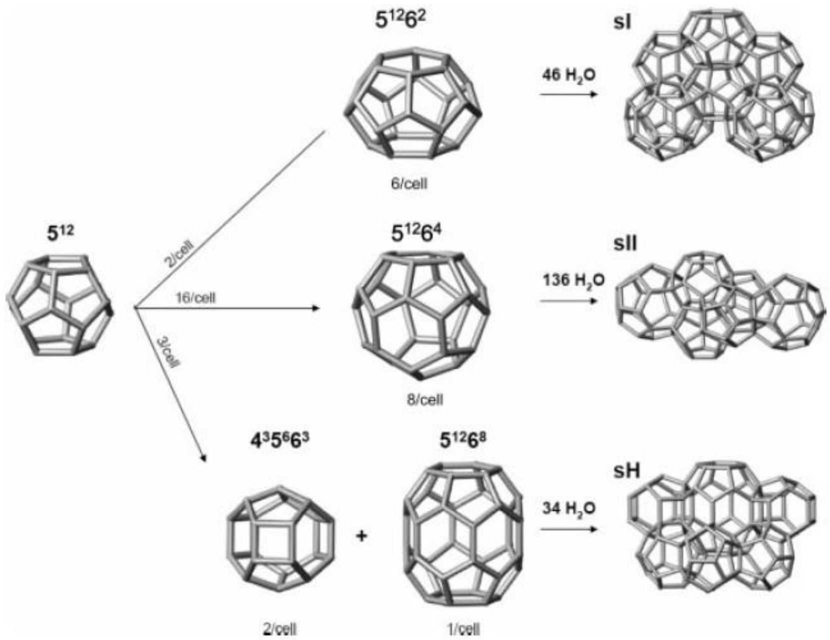


Figure 1.4. Polyhedral water cavities comprising Structure I, II and H.[32]

Structure I is a body-centered cubic structure, and Structure II is a diamond lattice within a cubic framework. Normally gas hydrates form in one of two small, repeating crystal structures. From a basic "building block" water cavity that have 12 faces with five sides per face (5^{12}), the two hydrate structures are formed. Linking the vertices of the 5^{12} cavities, with interstices of large cavities composed of 12 pentagons and two hexagons ($5^{12}6^{2}$), results in Structure I. Linking the faces of the 5^{12} cavities, with interstices of large cavities composed of 12 pentagons and four hexagons ($5^{12}6^{4}$), results in Structure II. The ratio of water molecules to hydrocarbon molecules would be 5.67 to 5.75 depending on which structure formed and all the cages occupied.[27,33]

To form the small pentagonal dodecahedron (5^{12}) cage it takes 20 water molecules, 24 water molecules to form the large tetrakaidecahedral ($5^{12}6^{2}$) cage and 28 water molecules to form the other large hexakaidecahedral ($5^{12}6^{4}$) cage. Each water molecule is hydrogen-bonded to three neighbor water molecules within the cage and one water molecule outside the cage. At each vertex in the structure there is one water molecule which is hydrogen-bonded to other water molecules within the cage. The water molecule donates two hydrogens to two of the four neighboring water molecules and accepts two hydrogens from the other two. The 5^{12} cavity can entrap methane, oxygen, nitrogen and other small molecules. Ethane, carbon dioxide and other similarly sized molecules can be encased in the $5^{12}6^{2}$ cavity. The $5^{12}6^{4}$ cavity can enclose propane, n-butane, iso-butane and other similarly sized molecules. Most of the cavities are occupied by gas molecules. With the increasing fugacities of the species in the natural gas from which the hydrate formed, the occupancy rate increases as well.[2,5,29]

Structure I is formed when the natural gas blend contains molecules smaller than propane, with diameter less than 0.6nm, mainly methane and are virtually free from C3−C4 hydrocarbon units. If as little as 0.5% propane should be in the natural gas blend, then Structure II will be formed. It is formed when natural gases or oils contain molecules smaller than pentane but larger than ethane, with diameter between 0.6 and 0.69nm. The physical properties of the two structures do not differ much, their chemical properties do however. Structure H will be formed by even larger molecules such as methylcyclohexane with a small help guest for instance methane. Mostly Because of the normal distribution of hydrocarbons in petroleum, Structure II will be the most frequently occurring of the structures in the field. It commonly occurs in both production and processing conditions. Structure I can occur in natural gas fields of almost pure methane, and Structure H have, except for in extremely rare cases, yet to be found outside the laboratory.[9,17,27,33,34]

Thus there exist size requirements that the guest molecules must possess in order to stabilize cavities in the gas hydrate structures. For both Structure I and II, if the diameter is below 0.35nm the molecules become too small to stabilize any cavity. If the diameter is above 0.75nm the molecules become too big to fit into any cavity in the structures. Hence, a guest molecule must be big enough to provide stability for the cavity, but not so big that it cannot fit into the cavity. A guest/cavity size ratio of approximately 0.75 is necessary for the stability of a single guest hydrate. When the ratio exceeds unity only by a few percent, however, the molecule will not be able to fit within the cavity and the structure will not form.[35]

On the other side of the scale, if the ratio is significantly less than 0.75, the molecule cannot lend enough stability to the cavity to cause formation.[35]

The occupancy of the hydrate cages by the guest molecule is essential for the mechanical stability of the hydrate lattice.[2] The hydrate structure will eventually transform to a more stable structure if the former structure is not the most stable. For a given composition, temperature and pressure the actual structure of hydrates that form depends on kinetics as well as thermodynamics.[29] Because Structure II is the most stable of the structures, it is probably the one that is produced by the highly selective nucleation process. Growth proceeds in a less selective, perhaps even hectic and chaotic manner once the Gibbs free energy barrier has been surpassed for the nucleation process.[35]

1.4 Hydrate formation

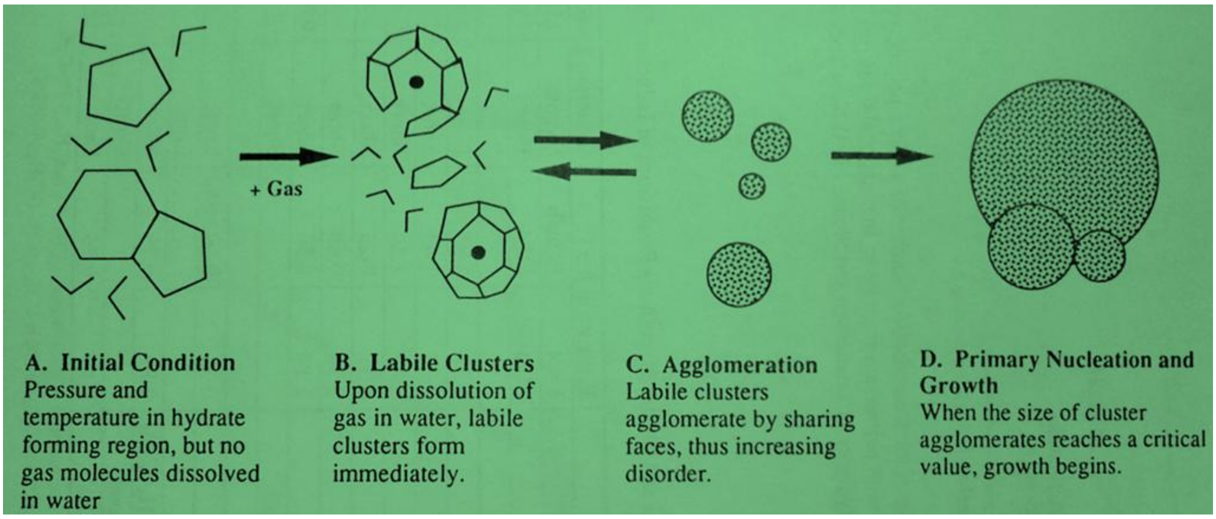
When it comes to hydrate formation, there are four stages:[36]

1. Diffusion of gas into water (gas-liquid mass transfer).
2. Nucleation.
3. Crystal growth.
4. Agglomeration.

Both hydrate nucleation and crystal growth are a kinetic process. This means that with the onset of thermodynamically favorable conditions, hydrates do not instantaneously appear. There is thus a lag time between the time when the system enters thermodynamically favorable conditions for hydrate formation and the appearance of hydrates, and it is known as induction time.[15] Induction time is in other words defined as the duration beginning when the system enters the hydrate forming region until the onset of hydrate formation.[37]

Gas hydrates are formed when small gas molecules, < 9Å, comes into contact with free water under high pressure and low temperature, typically around 6−15MPa and 277K respectively.[4,9,38] It is believed that the mechanism for the kinetics of gas hydrate formation follows a two step process. First, around a non-polar core of different sizes of apolar molecules there are formed clusters of hydrogen bonded water molecules. This is then followed by the formation of gas hydrate nucleus by the joining of these clusters. Hydrate formation usually occurs at the interface between vapor and liquid. There are two reasons for this. One is that the concentrations of both host and guest molecules are high enough at the contact surface, so therefore it is the most likely place for crystals to conduct nucleation and growth. This is because of the large amount of each constituent present. Thus there are a large amount of gas hydrate relative to the dissolved amount of gas in the liquid. The other is that the contact area decreases the Gibbs free energy of nucleation (figure 1.5). At temperatures closer to the freezing point of water the formation is usually favorable for gas hydrate. Under sufficient pressure however, gas hydrates will form at elevated temperatures as well.[12,35,39,40]

Hence, hydrate formation requires extensive contact between water and one or more of the hydrate forming gases under suitable conditions of both pressure and temperature. The resulting solids can form plugs that restrict or blockage the gas flow during oil and gas production. [12,35,39,40]



A. Initial Condition
Pressure and temperature in hydrate forming region, but no gas molecules dissolved in water

B. Labile Clusters
Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration
Labile clusters agglomerate by sharing faces, thus increasing disorder.

D. Primary Nucleation and Growth
When the size of cluster agglomerates reaches a critical value, growth begins.

Figure 1.5. Overview of the hypothesis of hydrate formation.[35]

1.4.1 Mass transfer

Mass transfer is the net movement of mass from one location to another. In chemical engineering there are two means of mass transfer, either by diffusion or convection:[41]

- Diffusion is the spread of molecules or particles from regions of higher concentration to regions of lower concentration through random motion.
- Convection (advection) is the concerted, collective movement of ensembles of molecules or particles within fluids due to the bulk motion of fluid.

Gas-liquid mass transfer is a diffusive process, by movement of molecules over the gas-liquid interface. A number of mass transfer theories have been proposed over the past 50 years in order to explain the mechanism of gas transfer across gas-liquid interfaces. Among them are the two-film theory (proposed by Lewis and Whitman (1924)), the penetration model (proposed by Higbie (1935)) and the surface-renewal model (proposed by Danckwerts (1951)). The two-film theory is the most commonly used, because of its simplicity and in more than 95% of the situations encountered, the results obtained are essentially the same as those obtained with the more complex theories. Even in the 5% where there is some deviation between the two-film theory and other theories, it is not clear which approach is more correct. Both the penetration model and the surface-renewal model are more theoretical and take into account more of the physical phenomena involved.[41]

The two-film theory is used to explain how gases are transported from a gas phase to a liquid phase, through film thicknesses of varying resistances. It is based on a physical model in which two films exist at the gas-liquid interface. The resistance to the passage of gas molecules between the bulk-liquid and the bulk-gaseous phases is provided by the two films, one being liquid and one being gas. Molecular diffusion through the films is the driving force, and the rate limiting step is changes in gas transfer as the mode of flow changes. Diffusion of gas through the liquid phase is generally slowest under perfectly quiescent or stagnant conditions, and fastest under turbulent conditions. The gas-liquid interface is controlling the process if the liquid is sufficiently agitated either by natural turbulence or by induced mechanical mixing. When an equilibrium is established between the bulk-liquid and the interface, the mass transfer flux terminates. One important note when it comes to the application of the two-film theory is that the assumption of uniform partial pressure and concentration in both the bulk phases, that is mixed completely, are valid.[41]

1.4.2 Nucleation, an induction period

There exist two types of nucleation, namely homogeneous nucleation and heterogeneous nucleation. Homogenous nucleation is a process that only takes place in the absence of impurities. A bimolecular collision by an autocatalytic nature is most likely to proceed, since the nucleation process involves too many molecules that everyone can collide at once. Heterogeneous nucleation on the other hand, takes place in the presence of a foreign object or a surface. Also, the required subcooling is lower than that by homogenous nucleation. Water solutions prepared at the laboratory can contain more than 10^6 particles per cm^3. On this basis it would be virtually impossible to achieve a solution completely free of foreign matter, although careful filtering can reduce the contamination to some extent. Hench, homogenous nucleation is unusual, while heterogeneous nucleation occur much more frequently.[42] Subcooling (ΔT) is defined as the difference between the equilibrium hydrate temperature (hydrate dissociation temperature) and the operation temperature at a fixed pressure and composition.[6,37]

There are some conditions that must be present for hydrate nucleation to occur:[43]

- ✓ At the point of nucleation the water must be saturated with gas.
- ✓ In order for the removal of latent heat from fusion, subcooling must be present.[44]
- ✓ The chemical potential of water in the liquid water phase must equal that of water in a hydrate lattice.

Like any other phase transition process in nature, hydrate nucleation is random. Nevertheless, the process is highly controlled by the magnitude of the driving force expressed as displacement in temperature and/or pressure from the corresponding values at equilibrium. In addition to this, hydrate nucleation is also influenced by the type and size of the guest molecules, degree of turbulence, impurity and water history.[2]

Nuclei can be formed from clusters of fine particles chemically unrelated to the precipitate but with some similarity of crystal lattice structure. A nucleus is a fine particle on which the spontaneous formation or precipitation of a solid phase can occur.[1] The hydrate crystal nucleation process occurs at the interface of water and gas, it is thus an interfacial process, and the crystal growth may take place both in the liquid phase and the gas phase. Generally hydrate formation requires extensive contact between water and one or more of the hydrate-forming gases under suitable conditions of temperature and pressure.[12] The hydrate former could be in a liquid or a vapor phase, in addition to being either miscible or immiscible with water. The formation is controlled by parameters as: Availability of open gas-water interface, intensity of creating free gas-water interface, temperature, degree of subcooling, pressure, the composition of water and gas, thermodynamic conditions, fluid composition, diffusive properties of medium, rate of heat removal and sorption activity of the forming hydrates.[43] Therefore formation and growth of hydrates are a complicated mix of kinetic and thermodynamic factors.[20] The large cavities of Structure I and Structure II, the tetrakaidecahedral ($5^{12}6^{2}$) and the hexakaidecahedral ($5^{12}6^{4}$) respectively, initialize the hydrate nucleation. This means that the small cavities, the pentagonal dodecahedral (5^{12}), is not essential for the initialization process.[2]

During this induction time (the time required to form nuclei), or nucleation, there is a critical radius that the hydrate nuclei must reach in order to sustain their further growth and form hydrate. This required radius must be greater than the critical radius to enable both stable nuclei and continued growth of the hydrate. Hence, any nuclei with radius smaller than the critical radius will re-dissolve in the liquid medium.[44] Thus, clusters of these molecules can either grow or shrink until they reach the critical size. Until they exceed the critical size, the agglomerates are in quasi equilibrium with each other and the labile clusters.[35] When clusters possessing the critical size, monotonic growth occurs. This phenomenon can also be interpreted as an excess in Gibbs free energy, ΔG, between the small dissolved solid particles and the solvent in the solution.[42] ΔG becomes negative and the growth becomes spontaneously or catastophic.[40] Small aggregates are formed in the course of nucleation, which become seeds for hydrate growth. The critical size is thought to be between 20−50nm (8−30nm)[15] .[29] The critical size depends inversely on the thermodynamic driving force, which is the free energy of formation and directly on the interfacial energy. For small driving forces the rate of crystal formation is low. The rate rapidly becomes larger at intermediate driving force and reaches a limiting value at very high driving force.[6] Under dynamic conditions, the presence of free gas/water surface and intensive heat removal usually makes the formation rate of hydrate several times higher than under static conditions. For any given pressure and temperature there exist a maximum rate of massive type hydrate accumulation. Where the conditions allow the rate of gas-water surface renewal equals the radial rate of hydrate crystal growth on that surface corresponds to the maximum rate of hydrate accumulation.[43]

By random movement, a number of growth units may come together, a growth unit in this context is a gas molecule and the sphere of water molecules it keeps arranged around itself. The assembly will become stable and begin to grow if enough growth units come together.[6]

1.4.3 Crystal growth

There exist four essential elements that must be present on order to get hydrate nucleation and growth:[45]

1. Around dissolved apolar natural gas molecules, labile clusters of water molecules with particular coordination numbers exist.
2. By joining these clusters together, hydrate is formed.
3. Upon joining, clusters can transform from one coordination number to another.
4. Structure I have no distinguishing alternatives for joining hexagonal faces, structure II have two alternatives. This leads to competing structures, thus slows down hydrate nucleation and growth.

After hydrate formation at the gas-water interface, hydrates form in the liquid phase from the dissolved gas in water. This will cause the content of the dissolved gas in water to decrease significantly.[43]

The gas/water interface is the most likely location for hydrates to initiate forming, because the interface is always mutually supersaturated with both phases. Consequently, the role of mixing is only limited to control the rate at which the bulk water reaches saturation with the gas phase. With continuous mixing it appears that regardless of the saturation state of the bulk water, the phase transition always initiates at the surface of the vortex (gas/water interface). However, free gas have to dissolve in the bulk water and diffuse to the crystal surface for adsorption for any further growth in the formed hydrate crystals. At this stage mixing controls the extent and rate of hydrate formation.[2]

1.4.4 Agglomeration

Nuclei come in contact with other nuclei and join to form larger particles. This process is called agglomeration, and is caused by the relationship attraction between neighboring apolar molecules inside the cages of water molecules.[15]

Very small particles have a higher surface energy than larger particles, the solution concentration in equilibrium with small particles will be higher than that in equilibrium with larger particles. Thus, in a mixture of particle sizes, the larger particles will continue to grow because the solution is still supersaturated with respect to them. Through the growth of the larger particles the solution concentration is decreased. This will lead to the dissolving of the small particles because the solution concentration is now below their saturation value. By the agglomeration of particles to form larger particles, the enhancement of conversion of small particles into larger particles is conducted.[1]

Even at temperatures well above the freezing point of water, these agglomerates are thermodynamically favored.[46]

1.4.5 Hydrate formation in the pipelines

The most complex multiphase flow problems, involving water, liquid hydrocarbon, gas and hydrates as solids, occurs from formation and transport in flowlines. A conceptual representation of hydrate blockages in both oil-dominated and water-dominated systems is given in the following (figure 1.6):[28,47]

A. Before hydrates are formed, the phases are emulsified from the flow turbulence, possibly creating gas bubbles entrained in the oil and water, oil emulsified in water and water emulsified in oil. As the result of oil chemistry and shear, water is entrained in an oil-continuous-phase emulsion as droplets of typically 50µm in diameter. The surface area for hydrate formation is created by the entrained/emulsified droplets/bubbles.

B. When the temperature and pressure conditions are within the hydrate stability region, hydrates will most likely form at the water and hydrocarbon fluid (water and oil) interface. Hydrates grows rapidly (approximately 1mm/3sec) at the oil/water interface as the flowline enters the hydrate formation region. Here they form thin (10−30µm thick) hydrate shells around the water/oil droplets emulsified in oil/water. The particles remain the same size as the original water droplet, despite the formation of hydrate shell. Further, on the pipe walls is another possible location for hydrates to initially form. This is because the walls are constantly exposed to the gas in addition to being wet.

C. As a function of mass transfer of the guest through the oil and the hydrate shell, as well as heat transfer dissipating the energy from hydrate formation, shrinking-core droplets continue to grow inward within each hydrate shell. The process of continued hydrate growth is typically mass or heat transfer limited. In the former, water and/or gas must diffuse to the interface. In the latter, heat must be removed because of the fact that hydrate formation is an exothermic process. Strong capillary attractive forces between the hydrate droplets are enabled by possible free water coating each droplet. Hydrate growth will be limited by either the availability of water, gas or temperature.

D. The hydrate slurry will change the rheology (flow behavior) of the system once a sufficient amount of hydrates are present. The hydrates can either be deposited on the solid surface or be suspended in the fluid phase.

E. The interaction of hydrate particles will largely depend upon the continuous fluid phase. The binding force between the hydrate particles are minimal, thus they will remain dispersed if the hydrate particles are dispersed in a water continuous phase. It is likely that the hydrate particles will bind to form large aggregates because of the water capillary bridging formed between the particles, if the hydrate particles are dispersed in an oil continuous phase. Hence, once hydrates are present, the hydrate particles may interact either by agglomerate into larger aggregates or continually grow on the existing deposits on the pipe wall.

F. Hydrate deposition on the pipe wall is an important phenomenon. It may even be responsible for eventual hydrate blockages under steady state operation, because these deposits can build slowly up over time. Not surprisingly, hydrate deposits on the wall can narrow down the flow channel, similar to wax/asphaltene deposition.

G. Finally, the jamming of hydrate particles, which causes the blockage of the system. This comes from the agglomeration of the hydrate droplets that eventually can plug the pipeline.

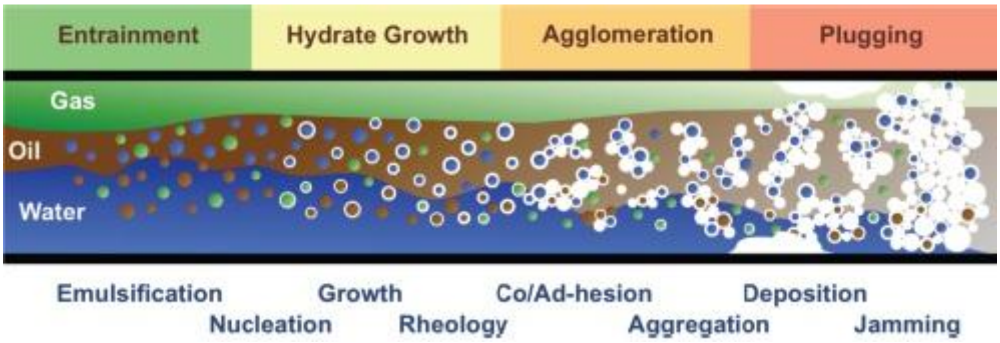


Figure 1.6. Conceptual representation of hydrate formation, agglomeration and plugging in an oil- or water-dominated system.[47]

There arises six rules of thumb for flow assurance in an oil- or water-dominated system:[28]

1. One key to prevent blockage formation is to keep the formation of emulsions/dispersions high enough to sustain the water/hydrates suspended in the oil phase.
2. High shear stress may prevent particle aggregation.
3. In oil- or water-dominated systems there are two requirements to prevent hydrate plug formation:
    A. There must be a low concentration of hydrate particles (< 50vol%).
    B. By either applying anti-agglomerants or by particles being oil-wet through oil chemistry, particle aggregation is prevented.
4. Because of the attractive capillary forces that arises when the operating conditions are closer to the hydrate dissociation conditions, stronger interactions between hydrate particles from a quasiliquid layer at the particle interface.
5. Coalescence of water drops in water-in-oil systems can be caused by the formation and dissociation of hydrates. This coalesced free water phase is prone to hydrate blockage formation.
6. Freshly formed hydrates, like other deposits, are more porous and malleable than hydrates that have had time to age and solidify. The aging process (something akin to Ostwald ripening) causes a more dense crystal mass, which make dissociation of the plug increasingly difficult.

Hydrate blockage in condensate , or gas-dominated, systems, especially light condensate, differ from oil- and water-dominated systems in that low viscosity and the lack of surface active components makes it impossible for emulsified water droplets to form without a high shear. A general mode of action of hydrate blockages in condensate systems are given in the following (figure 1.7):[28,47]

- A. In the absence of water-wet walls, hydrates formed in the bulk condensate may not deposit on the wall.
- B. Hydrates will remain on the wall if formed at the pipe surface.
  1. A uniform, dispersed deposit along the flowline is provided by high concentrations of dissolved water.
  2. As the flowline enters the hydrate stability region the free water results in a localized, early deposit.
- C. The main hydrate formation mechanism is deposition on the pipe wall. These deposits can over prolonged periods of time gradually grow to narrow the flow channel and cause significant pressure drops in the system. Because of the fluid shear, these deposits can detach from the wall (sloughing). Loose chunks of hydrate may eventually accumulate in a flow restriction, like a valve, bend or another hydrate deposit, causing the system to jam. However, hydrate deposits can be dissociated with or without chemicals by flowing an undersaturated condensate past the hydrate deposit.

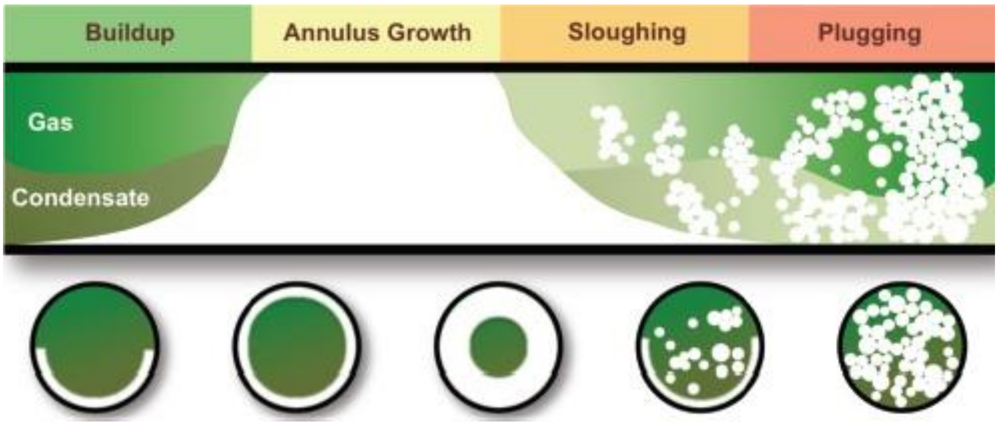


Figure 1.7. Conceptual model for hydrate formation and plugging in a condensate or gas-dominated multiphase flow system.[47]

With hydrate deposition on the flowline walls, the mechanism for hydrate plug formation in condensate system may differ significantly from hydrate plug formation in oil systems. In condensate systems, sloughing and particle jamming will likely occur to form a plug. In oil systems however, particle aggregation will increase the apparent viscosity for effective plugging.[28]

1.5 Gas hydrate coupled with the petroleum industry

Gas hydrate adopts a double-edged role when it comes to the petroleum industry, one being a problem, while the other being a resource. Petroleum engineers focus on three ambiguous sides of gas hydrate, namely: Flow assurance, energy resource and climate change. They are listed in declining importance, with the first and last being a problem, and the second being a resource, respectively. In addition to this as a resource, gas hydrate can also be used as a storage and transport medium for different kinds of gases.[28,48]

In this context only the problem role of the ambivalent gas hydrate will be examined.

The never-ending pursuit for oil and gas compels the petroleum industry into deeper and colder water depths, with the corresponding higher pressures from the additional liquid head. Also, another consequence is that the production fluids cool deep into the hydrate-stability zone, due to longer tiebacks. All these situations surpass the conditions needed for gas hydrate formation, thus increasing the risk of hydrate plugging. Gas hydrate plugs formation can cause problems by forming and possibly blocking subsea pipelines, pipelines in general, transmission lines, wellbores, plug blowout preventers, subsea equipment during both production and drilling operations as well as in other process equipment. In addition to this gas hydrates can jeopardize the foundations of deepwater platforms and pipelines, cause tubing and casing collapse. There is also the possibility for fouling process heat exchangers, valves and expanders by gas hydrate. Therefore such plugs can cause drilling safety problems as well. Flow passages can be reduced or plugged in deepwater pipelines and wellbores, by the potentially forming gas hydrates. Should gas hydrate plugs form in the wellbore, can they impact the ability to open or close downhole safety valves or valves at the seafloor in general. It will also make it difficult to run wireline tools. But the problem is particularly problematic if it happens in a so called umbilical during operations at offshore platforms. Here the economic impact will be severe. One obvious consequence if gas hydrate formation occurs is that flow rates can be reduced significantly or production could completely stop. Conditions that usually arises during well shutdown following a period of flow or during start-up, is that the well gets cold. A cold well have a tremendous risk for gas hydrate formation. But provided the right conditions, of especially temperature and pressure, gas hydrate can form in the well while it is flowing, and in flow lines, carrying hydrocarbon fluids during normal production. Gas hydrates will also occur in all the produced fluids if the required temperature and pressure conditions are reached: Black oil, condensate, gas with condensate, natural gas or crude oil with associated gas, with condensed or formation water and wet gas lines.[14,16,33,46,49,50,51] Gas hydrates may build up at any place in which free water coexists with natural gas at temperatures as high as ~30°C, provided the right pressure and gas composition.[52]

Because producers drill in deeper and cooler waters, gas hydrate is a growing problem. Gas hydrates can form in the wellbore while the fluids go through temperature- and pressure-induced phase changes near the mud line (figure 1.8). In downstream transportation networks once the stream have cooled from reservoir conditions gas hydrates will form often from gas streams, which are produced saturated with water. Also, gas hydrates can form in the flowlines from subsea completions to the separation facilities. The challenges of gas hydrate control in deepwater operations emerge from the harsh environment and the inaccessibility. The well operator have only a limited control over the wellhead pressure. Factors that are deciding if a particular well or flowlines are at gas hydrate forming conditions is the producing formation temperature, heat loss to the environment and Joule-Thomson cooling effect upon gas decompression. Gas hydrates create physical barriers to production and must be inhibited and dissolved if formed in order for gas production to occur. In offshore environments where one have no control over the fluid composition, temperature and bottomhole pressure, the problem of finding an effective gas hydrate control method in a system at hydrate conditions is especially difficult. Deepwater wells must produce large volumes of oil and gas to justify their development costs, and even a short-term interruption in production can cost the operator millions of dollars. The cost of failure can be very high because of the high remediation cost and a significant loss in revenues. Therefore it is crucial that the well and production lines at all time must be maintained free of gas hydrate by the operator.[16,37,52]

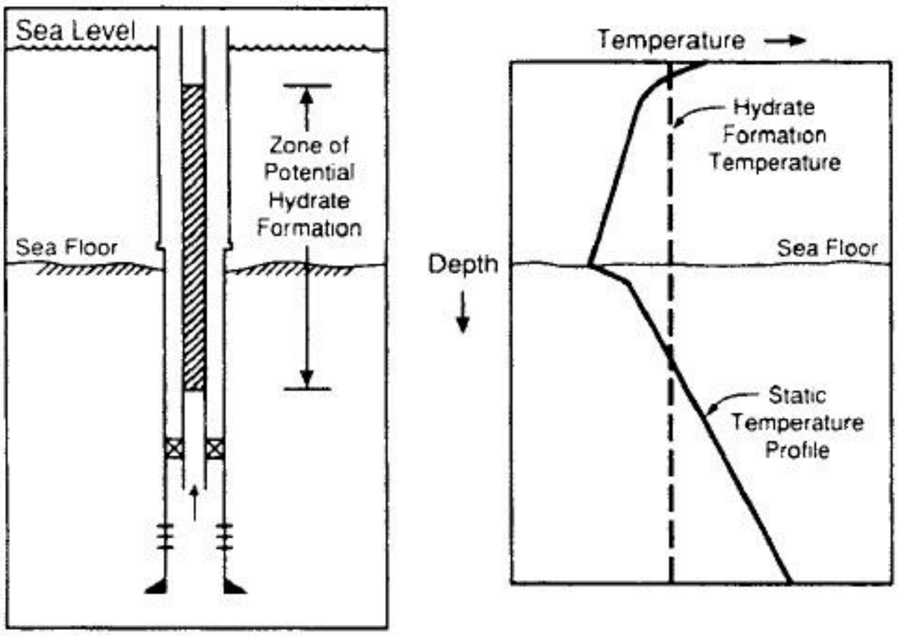


Figure 1.8. Deepwater production well with the potential hydrate formation zone.[51]

One major task when it comes to flow assurance is to develop a plan to manage potential problems of gas hydrate formation, along with dealing with plugs when they occur. The plan includes the ability to predict where and approximately when gas hydrate plugs might form, and of course how to prevent gas hydrate plug formation. Therefore, flow assurance is the one major technical problem for offshore energy development, and gas hydrate plugs are the major concern by an order of magnitude relative to scales, waxes or asphaltenes. This is because of that the plugs form without warning and so rapidly in offshore lines relative to the others. Regardless of whether the fluid is flowing, flow in pipeline, or being substantially stationary, during forced shut-in periods, these hydrates can form and cause problems in both cases. Thus, the resulting solids can form plugs that restrict or block gas and oil flow during production.[4,28,46]

Usually in the free water, just downstream from water accumulations where there is a change in flow geometry, a gas hydrate blockage will occur. This can be for instance a bend or pipeline dip along an ocean-floor depression, or some nucleation site like a weld slag or sand. As mentioned before, these small, individual crystalline cages tend to agglomerate. In doing so they are forming larger gas hydrate structures that can adhere to surfaces, such surfaces as internal pipe walls. These gas hydrate crystals can damage the pipeline or in the worst case lead to blockage of the pipeline to the point of pipe rupture. It is more common to not have more than one gas hydrate plug forming in the pipeline. Both the contents and the geometry of the line determines if the gas hydrate will flow as a slurry or adhere and form a plug. Thus, from this it is clear to see that both the operation procedures and the system design must be improved in order to keep the operation running smoothely.[6,28,38,53,54]

At the phase interfaces where there is an abundance of both water and hydrocarbon, gas hydrates forms most easily. This interfacial phenomenon is a key concept in order for understanding gas hydrate formation and prevention. Specifically, gas hydrates forms at the water/gas interface for water+gas systems. However, gas hydrates forms at the interface between the two liquids, water and oil, from small dissolved gas molecules in the oil, for water+oil+gas systems.[28] Gas hydrates can thus form from a hydrocarbon stream that is a single phase vapor or liquid, or from a two phase steam.[55] Furthermore, there is no requirement for a gas phase as such to form gas hydrates, since it can be formed from gas dissolved in liquid. It is also the dissolved gas that forms the solid gas hydrate, and the gaseous constituents comes from either a gas phase or a liquid phase dissolve in water. Even though the high molecular weight hydrocarbons are too big to fit into the cage-like hydrate structures, reservoir oils usually contain substantial amounts of dissolved gas. As pressure is reduced the dissolved gas in oil can come out of solution in many wells. In a wellbore both the dissolved and free gas can combine with water to form gas hydrates. This water may either be produced water or water condensed from the vapor phase of a gas itself.[51,56]

Consequences can be formidable when hydrate problems occur. It can occur relatively quickly, but difficult to remove and cause serious damage if not removed with care. Therefore pays the petroleum industry particular attention to natural gas hydrates because both the pressure and temperature conditions that are conductive to gas hydrate formation and blockage, are common under normal production scenarios. The crystallization of hydrate particles generally leads to the shutdown of production facilities by the formation of hydrate plugs. These plugs can be the result of deposits growth and/or agglomeration of hydrate crystals. Depressurization (venting) is almost the only available option in order to remove gas hydrate blockages from subsea natural gas or gas condensate pipelines. The industry have developed new tools that can be deployed at short notice to depressurize the wellbore or pipeline. Gas hydrate decomposition by depressurization is a heat and mass transfer dependent process. The line is usually depressurized at each end of the plug. This recommended to do so in order to eliminate the risk for the hydrate plug to suddenly break loose, and thereby becoming dangerous projectiles. Depressurization decreases the gas hydrate formation temperature to below that of the environment, which enables the plug to be dissociated by ambient heat. Depending on the magnitude of the pressure reduction and on the ambient temperature the plug decomposition process follows different modes. A so called pig is used to clean the line after the plug is dissociated. However, depressurization of deepwater pipelines to remove plugs frequently requires days of flow interruption. Also, when flow is haltered because of a plug in a pipeline, it is difficult to place heat at the precise plug site. Thus, this process is normally applied with little or no accurate information about the plug location, size or composition. When depressurization is conducted at small pressure reduction and low temperature, gas hydrate blockage removal is a slow process. Hydrate plug removal is generally difficult task to achieve. Prior to the restarting of the production, a shutdown of several days or weeks may be necessary. During this remediation time the operator cannot produce, which makes the financial impact a very significant event. Up to some years ago, most of the offshore fields were developed with the objective of keeping the effluents outside the hydrate stable zone. This must be done on both flowing and transient (shit-in/restart) conditions. Needless to say, transient operations are particularly problematic because of the temporary extreme subcoolings under these conditions.[16,17,33,50,53,54,57]

Amongst favorable options for reducing field development and operational costs is the application of subsea completions in which the wellheads and production templates are placed at the seabed. An extended subsea gathering networks and transportation of unprocessed wellstreams are used. A cocktail of multiphase fluids, including liquid hydrocarbons (oils and condensate), gaseous hydrocarbons (natural gas) and mixed electrolyte produced water, will convey these lines. Unprocessed fluids produced from these wells may be transported for tens of miles to a main platform using subsea flowlines. Such flowlines are highly susceptible to gas hydrate formation and possibly plugging (figure 1.19). Therefore it is essential for confident and economical operation and design of associated fields, pipelines and processing facilities to obtain a good knowledge of these complex systems.[54,58,59]

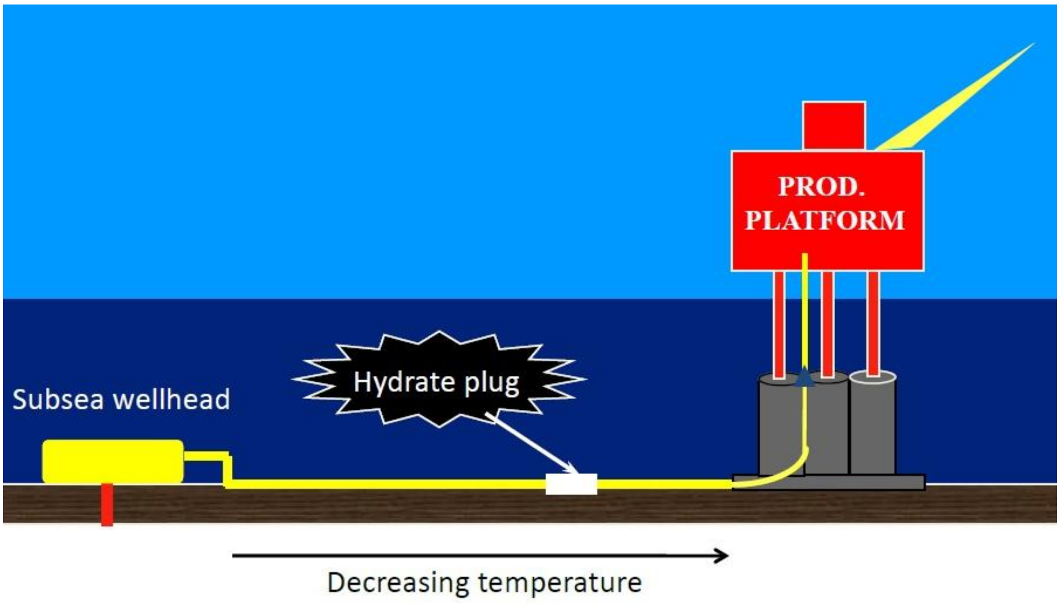


Figure 1.9. Schematic over a subsea wellhead with hydrate plug formed in the flowline to the production platform.[36]

The subsequent increased risk for gas hydrate formation, due to that gas and oil subsea production and transport are moving to deeper developments where the pressure and temperature are well within the hydrate stability region, requires new strategies in flow assurance.[57] There is a gas hydrate plug prevention shift under way when it comes to flow assurance. It shifts from avoidance to management of gas hydrate formation.[28] In deepwater field developments gas hydrate inhibition and control is often the design basis. This particularly holds for low seabed temperatures and high reservoir pressures, which provides a very high driving force for gas hydrate formation. This is encountered in deepwater environments.[60]

In the petroleum industry it is common knowledge that both drilling and productions systems often operate in the gas hydrate region without gas hydrates actually forming. The reason for this is the high order of degree required to arrange the water molecules around the gas molecules in the crystal structure that arises. Because of the kinetics or time factors in the formation of the solid gas hydrate crystals from petroleum liquid or gas and the aqueous phase, this process needs some time even though the gas hydrate is the thermodynamically favored process. However, as the driving force, distance into the gas hydrate region, becomes increased, the time for gas hydrate formation becomes less. Inhibitors can greatly increase this time. Interestingly, there have been demonstrated, both in the laboratory and elsewhere, that there are some oils that can form transportable gas hydrate/water/oil slurries without the need for chemical additives. This favorable property being attributed to the natural surfactants present in the oil.[27,61]

1.6 Gas hydrate formation treatment methods

There are four essential elements necessary for gas hydrate formation. The absence of only one of these elements would make gas hydrate formation impossible, and this is what inhibition methods aim to control or eliminate. These four essential elements are:[62]

- The presence of water.
- The presence of hydrate forming compound in natural gas (for example methane).
- Condition of high pressure.
- Condition of low temperature.

There are a wide selection of methods available for diminish the risk or preventing gas hydrate formation and deposition, which are:[29,33,63]

1. Dehydrating the mixture by separating out the water phase or by removing the hydrocarbon phase. Either way, one of the components must be removed.
2. To keep the pressure low and outside the hydrate equilibrium zone.
3. To add another gas in order to modify the gas phase.
4. To convert the water into transportable hydrate particles without the use of chemicals.
5. To use active heating or passive heat retention at the system pressure in order to keep the temperature above the hydrate stable zone.
6. To treat with chemicals.

The key to the overall success is a full integration of a good front-end design, an effective monitoring program and a comprehensive deployment plan.[37] All these approaches inhibits/dissociates so that higher pressures and lower temperatures will be required for hydrate stability. Method 1 to 5, plus some of the chemicals in method 6 (thermodynamic hydrate inhibitors), are known as thermodynamic inhibition. This is because by changes in composition, pressure or temperature, they remove the system from thermodynamic stability. Hydrates are incapable to form as long as the system is kept outside the thermodynamic equilibrium conditions. A newer method that allows the system to exist in the hydrate thermodynamic stability region, where small hydrate nuclei are hindered from agglomerating to larger masses, is called kinetic inhibition.[33] In addition to this, it also may be important to know which kind of gas hydrate structure one is dealing with in order to prevent hydrates form forming in production.[26]

Though any one of these methods can be effective in preventing gas hydrates, some may not be feasible or desirable for deepwater operations.[37] Therefore, all of these approaches have limitations. This holds particularly in the case of deepwater operations in addition to long tieback systems and/or high water cuts (mature fields).[61]

1.6.1 Dehydration

Water, which is a necessary element in the gas hydrate formation process, can be removed by dehydration of the natural gas.[62] The essential free water phase cannot form when the temperature of the gas in the flowline remains above the dew point. Macroscopic hydrate crystals will not be able to form without this free water. The dehydration process commonly involves the use of molecular sieve, solid desiccants or glycol contractor. Ethylene, diethylene and triethylene glycol can all be used for a glycol contactor or molecular sieve.[15,38,64]

For this method to be effective, it is necessary to significantly reduce the water content. This is done so that the partial pressure of water in the mixture is below the very low equilibrium pressure above the gas hydrate.[65] The use of these approaches is capital-intensive and is not currently applicable in subsea flowlines.[38,64] Dehydration is not even an option because it is not possible to conduct on small platforms with limited space for the processing equipment nor for subsea wells.[34] Also, even after the gas phase is stripped to saturation levels, dehydration is difficult to conduct when supersaturated condensates exist in the flowline. In addition, stripping condensate completely of water is prohibitively expensive. In the end no process can achieve complete dehydration for operative and/or economic reasons.[15]

1.6.2 Pressure alterations

Choking-back the production by lowering the pressure, can reduce the tendency for gas hydrates to form in a production system.[62] The system pressure can be reduced through pressure depletion or flaring.[64]

The pipeline pressure is reduced below the gas hydrate equilibrium pressure at the seabed temperature. Consequently, the gas hydrate blockage starts to dissociate at the boundary subjected to the pressure reduction. A temperature gradient is created with the surrounding environment because of that the dissociation heat is absorbed from the vicinity of the melting front. Under this temperature gradient the heat flows from the surrounding environment to the gas hydrate plug. Therefore, unless the pipeline pressure is allowed to build up to a new equilibrium value that corresponds to the lower temperature, the gas hydrate plug will continue to dissociate.[54]

From an economical point-of-view, keeping the pressure low on a continuous basis is rarely done since the production rates would be too low. During shut-in, depressurization could be carried out. Due to the hydrostatic pressure in very deep water, which keeps the fluids in the hydrate forming region at all time, depressurization cannot be performed.[17]

1.6.3 Modify the gas phase

Although odd and seemingly counterintuitive, a gas such as CO_2 or N_2 can be injected in order to raise the pressure threshold for gas hydrate formation.[66]

1.6.4 Transform water into transportable hydrate particles

In challenging conditions, such as deepwater fields, the industry may need novel and improved techniques to tackle flow assurance problems. Such a novel approach is the cold flow concept, which could represent a major breakthrough in deep water hydrate control. This concept breaks from the tradition of straightforward gas hydrate prevention. Here gas hydrates are not prevented, but managed to prevent their agglomeration and pipeline blockage. In fact, gas hydrate is intentionally induced and managed to form in pipelines. This eliminates the need for expensive thermal or chemical inhibition, while at the same time improving the economics and practicalities of multiphase fluid transport. Thus, the technique is based on gas hydrate management rather than prevention.[17,61,67]

There are several common characteristics in these techniques which are regarded as cold flow:[67]

- Gas hydrates are allowed to form, thus not prevented.
- No heating or insulation is used.
- Gas hydrate agglomeration is avoided by various means.

Several research groups are working on various cold flow concepts. Only the patented HYDRAFLOW concept will be discussed briefly in the following, but the technique holds for most of the cold flow concepts since they basically operates on the same principles.[61,67]

The basics of the technology are to convert most or all of the gas phase into hydrates and transfer them in the form of hydrate slurry in the pipeline. In other words, to convert produced water into transportable hydrate particles without the use of chemicals. These particles are then fed into a shock-chilled water-containing well stream in which the water is emulsified or dispersed in the liquid hydrocarbons by a number of mixers. Here the hydrate particles seed further hydrate growth in the water droplets form the inside out. They grow quickly but in a controlled manner. The hydrate particles become dry, non-agglomerating and non-depositing. In addition to this, they will eliminate free water from the rest of the transport system.[17,61,67]

The objective is to minimize, possibly eliminate the gas phase, by converting it into hydrates through reaction with produced water. In situations where produced water is a limiting factor for hydrate formation, excess water like seawater can be added. In addition, there is also the possibility to adjust the hydrate slurry viscosity by altering the amount of water.[61,67]

By converting the gas phase into hydrates, the density difference between phases (water, hydrates and oil) will be greatly reduced. This should help on alleviate pipeline slugging problems, thus lowering the operational costs. Also, pipeline costs could be further reduced by eliminating the need for heating and/or insulation, while reducing operating pressure or increasing the capacity. Furthermore, it could have the extra benefit of reducing both chemical and disposed water (this includes gas hydrate, scale, corrosion, wax and asphaltene inhibitors) treatment cost through aqueous phase recycling, which also lowers the environmental impact. An additional benefit of the concept is that it could potentially reduce wax deposition problems by maintaining the fluid temperature for a longer time. This is because of the exothermic hydrate formation reaction. The hydrate also provides solid seeds for wax nucleation in the flowing liquid phase rather than on the pipeline walls and abrasion of deposited wax since the hydrate particles are relatively fast moving.[17,61,67]

There are some possible problems with this technique, however. One of them being that in some cases there have to be added a small amount of anti-agglomerant or other chemicals. This have to be done so to control the hydrate crystal size, prevent agglomeration and reduce slurry viscosity. During an unplanned shut-in, free water could agglomerate before it reaches the mixers. For wet gas fields or fields with very high water cuts, the concept does not work. This is due to the impossibility for hydrate particles to flow. Since the free water is removed as gas hydrates, the ions in solution will accumulate leading to possible increased inorganic scale deposit problems.[17,61]

1.6.5 Heating, thermal gas hydrate inhibition

There exist several methods that are used to raise the temperature so as to avoid gas hydrate formation. The point of it all, is to keep the temperature of the fluids in the flowline above the hydrate formation temperature.[38] In this way the crucial low temperature is removed by these heat management techniques. Both external heating and thermal insulation can be used independently or jointly in order to achieve this, such as insulating the tubing and heating the wellbore. Thermal insulating or adding inhibitor is the most used means for dealing with gas hydrate.[37,51,62]

The easiest and simplest method is to insulate the pipe. Insulation will contribute on maintaining the wellbore temperature while the well is producing. This is done by using insulation around the tubing string, thus effectively reducing the heat losses to the environment especially above and near the seafloor. In the case of offshore platforms, the reservoir oil is at a typical temperature of 100°C, and typically the seabed temperature is around 4°C. So there are a huge difference between the hot produced fluids and the cold environment.[34,50,51]

The tubing can be insulated by several methods. Just burying the pipeline can help to some degree, and it is also the simplest method available. The most effective method, however, is to use double-walled pipe with a gas or a vacuum in the annulus. A nitrogen gas blanket can also be used in the annulus of the production tubing string and the production riser or flowline. Potential insulation materials that can be used in the annulus of a double-walled flowline pipe are vacuum, gas or foam.[34,50,51]

External heating can be used jointly with insulation or separately. The pipeline wall can be wrapped with an electrical resistance, heat tracing cable or a heat tracing tube containing a circulating hot fluid. Hot water is injected form the platform into a jacket which is around the production line. This will elevate the temperature of the pipeline wall, thus maintaining the produced fluids outside the hydrate stable region. Electrically heated or bundled flowlines permit heating of a shut-in line.[17,26,38,51]

Considerations when it comes to thermal insulation and external heating, cooperative or individually, includes cost, fabrication method, installation procedure and methods to allow for thermal expansion. The method of thermal insulation is relatively inexpensive than for instance external heating, but it depends on the technology used. There are several advantages of insulating and external heating. The overall volume of gas hydrate inhibitor may be reduced. Inhibitor injection can entirely cease, after the steady state flowing well heats to a sufficiently high temperature. The cool down temperature profile depends on the type of environment, the length of time the well was flowed and the effectiveness of the insulation, during shutdown period following production. The well fluid will remain longer above the hydrate formation temperature, the longer heat is maintained within the tubing or wellbore.[51]

Insulation alone may not be suffice to maintain a gas hydrate channel for long multiphase and gas pipelines in cold and high-pressure conditions.[33] Insulation and heating may not be cost-effective for longer flowlines to carry high GOR (gas/oil) fluids.[37] Therefore, keeping the system free for gas hydrate may only be achieved for short distances through flowline insulation. Although gas hydrates can still form during shut-ins if the ambient temperature is below the hydrate formation temperature at shut-in pressure. A shut-in line can be permitted heated by external heating. However these technologies are capital-intensive and more complex.[38] Because it is an expensive method, it is not used on a continual basis, but only used in extended shutdown situations.[17] Further, in addition to the high capital expenditure (CAPEX) level and the technical challenge faced by both the design and installation of high performance insulation, during a long enough shutdown it will not prevent entering the gas hydrate formation region. Consequently, additional methods have to be anticipated for procedures regarding shutdown and restart operations. Nevertheless, an unsurpassed designed insulation generally prevents gas hydrate formation during normal operation conditions, while at the same time avoids potential wax deposition.[50]

1.6.6 Chemical treatment

In deep sea operations, the ambient operation conditions of high pressure and low temperature are very conductive to the process of gas hydrate formation. Therefore, in such cases the above traditional approaches may be ineffective due to either extreme conditions or high cost.[64] Consequently it appears that the use of inhibitors will be the most effective solution.[15]

As always, there are both advantages and disadvantages combined with these methods.[51] Among operators chemical prevention is considered very effective at gas hydrate prevention and is therefore used extensively.[53] Thus, chemical inhibitors is injected to the unprocessed, wet gas production streams, in order for keeping them hydrate free.[62]

A continuous injection of methanol or glycol during operation is typically done in gas pipelines, since they are normally not insulated. Oil pipelines, however, usually are insulated, and only for transient operations (start-up and shut-in/restart) hydrate inhibition is required.[60] The inhibitors are normally injected at the well head using small diameter umbilicals that extend from the main platform to the well head. Regardless of what type of inhibitor used and the system it is used on, inhibitor injection must be re-established to the required level before restart-up, after either unscheduled shutdowns or failure of the injection system.[55]

Thermodynamic inhibitors and the more recently identified low dosage inhibitors are two chemical classes used for prevention of hydrate formation.[15,17] Low dosage hydrate inhibitors can be a more economical solution for prevention of hydrate formation if they are not too expensive and injected at low concentrations, than using thermodynamic inhibitors or pipeline insulation. There are however another possible method. Here the added chemical reacts exothermically with the produced fluids, resulting in that the produced heat is sufficient enough to keep the system above the hydrate formation temperature.[26] Never the less, it is important for a chemical to be cheap to manufacture, have a high degree of efficiency, be environmental friendly and that it does not corrode the pipes.[8]

All these forgoing methods can either be used individually or jointly for gas hydrate prevention. Although the preferable method will be based on the operating environment and the cost of the control method.[53]

1.7 Gas hydrate chemical treatment for the prevention and/or possible removal

There are two different chemical classes, all of them are now used in the field, which can accomplish the task to prevent gas hydrate plugging:[17]

- Thermodynamic hydrate inhibitors (THIs).
- Low dosage hydrate inhibitors (LDHIs)

If an inhibitor can terminate the growth of the gas hydrate assembly when it is small enough, it is more likely to fall apart then to grow.[6]

THIs have traditionally been used for hydrate formation treatment for many decades. Therefore it is common chemical treatment to use these inhibitors. LDHIs have been used in various application with success worldwide.[39,68]

As it is impossible to both separate out the free water content and to avoid the pressure-temperature-conditions for hydrate formation in multiphase mixtures, the only successful solution will be the selection of effective gas hydrate inhibitors.[19] The amount of inhibitor in the pipeline must be maintained at such a level that hydrate formation will not be encountered at all time. Under-inhibited systems appear to be more likely to cause hydrate problems than systems completely without inhibitor. Both field and laboratory experience indicates this phenomenon.[55] The effective concentration of any hydrate inhibitor chemical depends upon the severity of the condition. This severity is usually measured as the degree of subcooling.[6,37]

1.7.1 Thermodynamic Hydrate Inhibitor (THI)

Chemical inhibition with THIs is by far the most commonly used method used for hydrate control, it have been used for a long time and continues to be the industry standard. This type of inhibitor works as an antifreeze by involving the water in a thermodynamically favorable relationship, so that it is not available for interaction with the gas.[15,37]

These inhibitors have the ability to shift the equilibrium requirements for hydrate formation to higher pressures and lower temperatures.[38,39,53] Thus, the hydrate equilibrium curve is shifted toward lower temperatures and higher pressures by lowering the activity of the water molecules, because the THI outcompetes the water molecules for hydrogen bonds. As a consequence, the operating conditions is forced out of the gas hydrate stable region, and the system operates in the vapor-liquid region.[5,37,64] This works because as ice, gas hydrates consist of stable hydrogen bonded structures. Therefore hydrates, as ice, can be prevented by the same means. In this way the operating conditions falls outside of the hydrate forming region.[6,62]

By the addition of THI the temperature for which hydrates may be formed is decreased. This decrease in thermodynamic temperature for hydrate formation is synonymous to freezing point depression, which is basically what these inhibitors causes. The most powerful THIs are the compounds that is causing the largest freezing point depression for water.[5,59,65]

As mentioned above, gas hydrates can be prevented in the same way as ice. Thus the simplest approach would be to add salts or some other soluble compounds to the water. There are many available means for achieving hydrate prevention, dissolution and inhibition, like alcohols, glycols and salts. Among these are methanol (MeOH, CH_3OH), mono-ethylene glycol (MEG, $HOCH_2CH_2OH$), diethylene glycol, sodium chloride, calcium chloride and potassium formate.[6,15,50,52,53,64,65] Because of their low cost and widespread availability, methanol and ethylene glycol are most common among these.[37,62]

Because methanol easily vaporizes and concentrates in free water, it is preferred over other inhibitors such as glycols or salts. Methanol is injected into the gas phase, which carries it to the site where methanol dissolves in free liquid water and provides hydrate inhibition.[33] On a weight basis, methanol provides the greatest inhibition. Because of methanol being a fluid that possesses both low viscosity and low density, it is better suited for injection through long and narrow diameter chemical injection hoses or tubing. Methanol is also a relatively small molecule. This small size allows it to react at a fast rate with the surface of hydrate solids. Further, hydrate disassociation occurs more rapidly with methanol than with glycol, thus methanol melts hydrates more effectively.[51] Therefore is methanol highly effective at melting hydrates that have already formed.[38] Because of these positive attributes of methanol it is also used for long injection distances.[39,55,65]

Much of the added methanol does not dissolve in the free water but is lost in the hydrocarbon liquid or gas phase. This must also be added to the required amount of THI needed. This loss can make it difficult to calculate how much inhibitor there actually is in the water phase, and for safety operation reasons an excess of the thermodynamic hydrate inhibitor is usually added. The chemical is injected at sufficient quantities to shift the phase equilibrium line outside the anticipated operating temperature and pressure during shut down, re-startup and flow conditions.[33,55] After processing downstream, methanol accumulates in the propane fraction.[26] The refineries tend now to limit the methanol concentration allowed in the oil and condensate which can cause serious problems in water management and desalting operation.[50] Also, in the presence of water, oxygen becomes a corrosion agent, and methanol contains appreciable amounts of dissolved oxygen. Therefore pipeline operators that rely on methanol often treat it with a corrosion inhibitor in order to mitigate the corrosive properties that the methanol possesses.[52]

In order for THIs to be effective they must be added at high concentrations, with effective dosages required in the range 20−50% (20−40%)[59] of the water phase (10−60 wt%, 30−60 wt%, weight %).[26,27,50,52] In severe conditions the needed dosage can be from 20% to over 70% of the total volume of water production. This translates to a daily usage of between 10 and 40 m^3/day of inhibitor, for a typical deepwater offshore system.[53]

Despite the fact that the use of THIs can be very effective, the required dosages can become extremely high, thus raising the cost for the operator. Regeneration systems have been developed to lower the cost on systems where THI is needed on a continuous basis, where the most common regeneration systems being methanol recovery and MEG recovery units (MRU). These expensive reprocessing facilities can normally recover 80−90% of the methanol used as hydrate inhibitor. While these recovery units can lower the cost of a thermodynamic hydrate inhibitor treatment program, for many operators the large volume of THI needed for most operations remains a major problem.[26,39,37,53]

To get the desired large decrease in the formation temperature, huge amounts of THIs must be injected. Especially for offshore locations this will create a logistic nightmare.[6] Shipping of these large volumes of chemicals is difficult and costly and raises safety concerns. It is often the design of offshore systems that limits the maximum amount of inhibitor that can be pumped per day. This subsequently limits the amount of water that can be treated, resulting in an upper limit on oil and gas production and reduced revenue to the operator.[37,53] In order to store and inject these vast amounts of THIs, large tanks and injection equipment is needed. This can affect the overall size, platform space and therefore increase the cost of the production facilities.[26] Hence, the operating costs for these solvent-based inhibitor treatments are expensive, in addition to that the offshore facilities for these treatments can be both complex and logistically intensive. It is also becoming increasingly unacceptable to storage these large inventories of solvent on offshore platforms form a safety perspective.[69]

Much more methanol will be needed as exploration & production (E&P) operations move into regions of lower temperatures and/or deeper water. As a consequence, the issue of economics will receive more attention. Typical capital costs to prevent hydrates in a processing plant are 5−8% of the total plant cost.[33] Methanol injection leads to a high operational expenditure (OPEX) level in addition to that it also needs large size storage facilities. All this results, in addition to the erratic pressure, in potentially high concerns about health, safety and environment (HSE) risks.[50] Therefore, replacement of the traditional THIs are highly desirable from both health, safety and environmental in addition to commercial considerations.[69] These new hydrate inhibitors can lead to very substantial cost savings, not only for the reduced cost of the new inhibitor, but also in the size of the pumping, injection and storage facilities. This makes it possible to redesign production facilities on a smaller scale. It is however a technological challenge for the oil and gas production industry to develop these alternative, cost effective and environmental acceptable hydrate inhibitors.[26,37,39,53] Oil companies have switched from an absolute avoidance heuristic to one of acceptable risk.[70] For this reason, LDHIs have been developed.[39]

1.7.2 Low dosage hydrate inhibitor (LDHI)

A never-ending demand for oil and gas have forced the oil companies to develop an increasingly number of fields that are susceptible to hydrate formation. Such fields are found not only in colder areas like the Arctic and the North Sea, but also in deepwater developments in tropical areas. Also some smaller, thus economically marginal, fields could not be economic exploited with the use of traditional hydrate prevention techniques. This development have led to that the total cost related to conventional hydrate prevention, such as the use of methanol, glycol, thermally insulated pipelines and gas dehydration to increase rapidly. All this initiated a search for chemicals that could prevent hydrate or hydrate plug formation, when dosed in sufficient small quantities. Many different chemicals were developed, but only kinetic hydrate inhibitors and anti-agglomerants made it to development and, eventually implementation.[71] The hydrate management landscape is therefore on a never ending evolution with the proliferation of deepwater operations and a subsequent rise in the usage of conventional hydrate inhibitors. In both academia and in the petroleum industry LDHIs have been actively investigated for more than a decade. The promise of LDHIs was to fulfilling their initial promise as a technically sound, economically viable and operational robust alternative to conventional inhibitors as THIs.[60]

Both kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) goes collectively under the name LDHIs. The reason for this is because compared to the THIs the sufficient quantity used are normally numerous times lower.[17] The adequate concentration of these LDHIs is currently expected in the range 0,5−4 wt% versus the water rate. With LDHIs the unprocessed effluents are produced inside the hydrate stability zone.[50]

KHIs and AAs have two different modes of action. Although the mechanisms of these LDHIs are not fully out understood, there is a huge difference in the inhibition behavior of KHIs and AAs.[6,72]

By the replacement of THI by LDHI the operator can expect the following benefits:[52]

- Reduced cost of treatment.
- Reduced shipping costs.
- Reduced product storage footprint requirement on the platform.
- Reduced product crane lifts on the platform.
- Reduced product volume to handle.
- Reduced line differential pressure.
- Reduced corrosion rates, as measured with flow line coupons.
- Reduced replacement and maintenance cost for pneumatic methanol pumps.

Compared with THIs, LDHIs effective dosage rates are orders of magnitudes lower, with a volume reduction greater than 25 times. These inhibitors can thus provide significant capital expenses (CAPEX) savings by eliminating bulky topsides equipment. This is because less topside storage space is needed, in addition to smaller umbilicals and easier transportation. Further, potential operating expenses (OPEX) savings in treatment costs can be obtained.[60] These potential OPEX savings are associated with that on a per unit basis LDHIs are more expensive than THIs, but only a small quantities are required to inhibit hydrate formation. Because of the relatively small dosage requirements one could expect that the biggest cost savings would have been on the reduction of OPEX, but surprisingly this is not the case as their price are high. In fact, the main economic incentive of using LDHIs is the large reduction of CAPEX via the reduction of the size of storage, piping, processing facilities and pumping. In addition, they present the benefit of significant reducing the HSE risks by being far less flammable, volatile and relatively more environmental friendly than THIs.[50] Another reduction on CAPEX as well as OPEX and environmental expenses, occurs when there is no longer the need for separation and recycling systems. Because LDHIs does not need to be removed from the product stream before entering the market, like methanol and glycol must, by the implementation of LDHIs these costs are eliminated. They are normally nontoxic and/or biodegradable, thus they provide an environmental friendly technology.[15]

1.7.2.1 Kinetic hydrate inhibitor (KHI)

All known KHIs consists of active matter formulated in a solvent, with the active matter being water soluble polymers. The solvent is composed of MEG and heavy alcohols. Often other smaller organic molecules are added as performance enhancers, so called synergists.[17] KHIs are added at relatively low concentrations, < 1wt%.[26] Rather than shifting the thermodynamic equilibrium of hydrate formation, like the THIs does, the KHIs kinetically interacts with the hydrate formation (figure 1.10). They are believed to interfere with the hydrate nucleation step and/or the crystal growth process. Hench, these inhibitor polymers retards the rate of hydrate formation rather than affecting the thermodynamics of the system. The induction time is extended because of the interference which slows down the kinetics. Increasing the KHI concentration will increase the time it takes for hydrate crystals to form, increase the induction time.[62,68] Since these inhibitors act by both delaying the hydrate nucleation step and slowing down the initial crystal growth during a finite period in case of high subcoolings, their efficiency and thus their applicability depend upon two main factors: The subcooling at the pressure to which the produced effluents are exposed and the residence time of these effluents inside the stability zone of hydrate.[50]

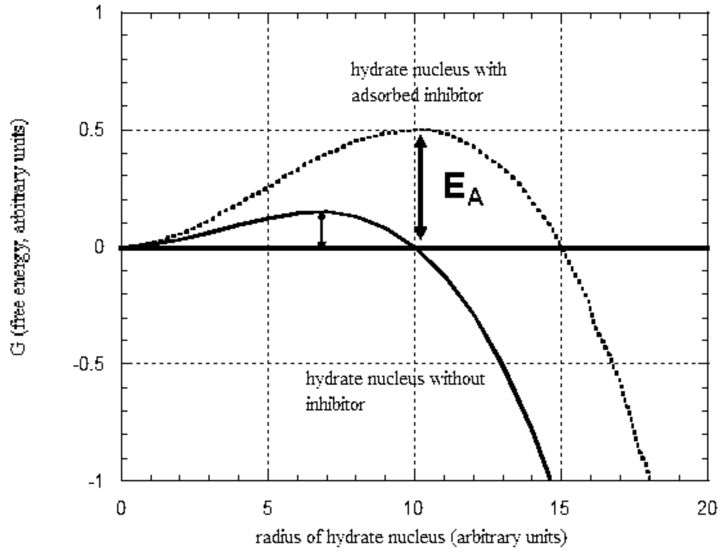


Figure 1.10. The KHIs increase both the activation energy for nuclei formation as well as the critical nuclear size.[36]

In the inhibitor polymers there exist two essential structural features. Firstly, the polymer needs functional groups that can hydrogen bond to water molecules, both in the liquid water and/or to the surface of hydrate particles, a hydrophilic group.[2] This is usually amide groups that does this task. Secondly, directly or adjacent to each of the amide groups a hydrophobic group must be bounded. It is a highly necessary condition that hydrophobicity is present for a polymer to have good performance. Further, the role of hydrophobicity and the phenomenon of hydrophobic hydration appears to be critical factors in the control of the polymer activity in water.[73] There are many factors that can affect the inhibition of these KHIs. These factors being the number of pendant groups present, the spacing between them, their structures and the way they are attached to the chain (carbon backbone) in addition to the length of this very chain itself. The pendant groups may selectively key into the cavities, instead of hydrocarbon gas, to prevent hydrate formation. In addition, these pendant groups on the chain can act as AAs, terminating any hydrate particles from joining together by taking up so much space around them.[5]

Proposed mechanisms in which KHIs work are steric stabilization and surface adsorption on the face of the growing crystals. By adsorbing at the crystal-liquid interface it is possible for these KHIs to control the growth and the agglomeration of the hydrate crystals.[2] They are assumed to bind to the surface of hydrate particles in the early stages of nucleation and growth. This will effectively prevent the hydrate particles from reaching the needed critical size or slowing down the growth of hydrate particles that have reached this critical size. At this size the particle growth becomes thermodynamically favorable.[26]

The water soluble polymers, which make up the active part of the KHIs, coordinate the water molecules in a way similar to hydrate structures. In this way the hydrated polymers interrupt the guest molecules and water cages from forming hydrate crystal nuclei, hence they disturb the water structure. By the action of these inhibitors the rate of hydrate nucleation is reduced many orders of magnitude.[38] In theory these KHIs have anchor points that work by distorting the hydrate structure. In fact, one of the main features of them is their availability to fit into the growing hydrate structure (figure 1.11). The KHI locks into the growing crystals which deforms, effectively increasing the crystallization energy so that the crystallization process terminates. By absorption onto the hydrate crystal the polymer block the gas diffusion to the hydrate surface, hence forcing crystals to grow between and around the polymer strands. Consequently, increasing the amount of energy needed to form hydrates and thus slowing down the reaction kinetics.[5,72]

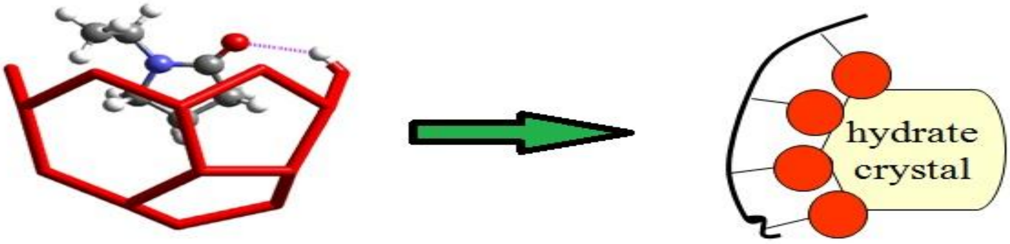


Figure 1.11. KHI prevents guest molecules to occupy the water cages in the gas hydrate, represented in red in this schematic. The dotted purple line shows van der Waals bonding between the gas hydrate and the KHI.[36]

Low molecular weight KHIs are best to inhibit the nucleation process, while those with high molecular weight is best to inhibit crystal growth. This is because the KHIs with low molecular weight possesses relatively short chains which are excellent to alter the water structure. The KHIs with high molecular weight fail at this point, and they can also curl up. When a inhibitor loses its hydrogen bonds, hydrophobic interactions will make the molecule to aggregate and eventually precipitate. This effect is linked to the cloud point of the KHIs.[5,26]

Since hydrate is most likely to form first at the water-gas or water-oil interface it seems reasonable to design them to exist in this interfacial region. In this region the hydrate forming gas diffuses into the water. Therefore are the KHI polymers water soluble or dispersible, thus they inhibit only in the water phase. They appear to be independent on the water cut but being affected by interactions either in the bulk water phase or water interfaces. The dosage of KHI must be increased according to the water cut to maintain the same inhibitor effect if all the other conditions remains constant (temperature, pressure and production water composition). This have to do with that the water cut usually increases as a field is produced.[26]

Although all KHIs are water soluble polymers and therefore have negligible solubility in hydrocarbon liquids, the presence of liquid hydrocarbons can have either positive or negative impact on their performance. Consequently, if a liquid hydrocarbon phase is expected in the system and the degree of subcooling is close to the maximum of what the inhibitor can handle without hydrate deposition and plugging, then the hydrocarbon effect on the performance of the inhibitor must be addressed before field trail is conducted.[37]

A line which is treated KHI operates under thermodynamically favorable conditions for forming hydrates, causes the formation of hydrate crystals to be delayed much longer than the residence time of fluids in the flowline, especially water. If the line treated with KHI is shut-in and held at conditions favorable for hydrate formation, depending on the subcooling and the inhibitor concentration in the flowline, it remains hydrate free for hours, days or even weeks.[38] The higher the subcooling, the lower is the efficiency regarding its hold time (time before initiation of rapid hydrate formation)[60] of the KHI. Thus, the subcooling is indeed the driving force of the kinetics of hydrate formation. As a consequence, the KHI dose rate is to be designed so that it enables the effluent to go through the production system without hydrates forming. This must also be maintained even when the system is operating inside the hydrate stability zone. The concentration of KHI is directly linked to its efficiency for given conditions. Undoubtedly, under dosing will result in increased and faster risk for hydrate formation. On the other hand, over dosing is not wished as it will lead to rapidly unnecessary high OPEX as the efficiency of the inhibitor is rapidly plateauing when the concentration is increased.[50] Non the less, a safety factor is added in addition to cover planned or unplanned shut-ins.[37]

KHIs can be a relatively cost-effective solution. At low concentrations, and if the inhibitor are not too expensive, they can be a more economical solution compared to THIs for preventing hydrate formation. Per volume unit, the KHIs are much more expensive than the THIs, but the used volume is considerably smaller, roughly 1−5% of the volume of THI. This can lead to considerably savings.[26,53,59]

Polymers with lactam rings are often employed as KHIs. All KHIs have a higher tolerance towards subcooling in the laboratory than in the field. This is because the clean laboratory set-up gives additional subcooling.[26,37] All KHIs have a maximum subcooling limit, beyond which they are ineffective.[60]

By their very definition, KHIs are indeed time-bound. The delayed growth effects are substantial and represent a clear kinetic influence by the inhibitors on the hydrate formation process. They can successfully prevent hydrate formation for a finite time only. As mentioned, KHIs prevent any hydrates from forming for a given period of time. Once this period have elapsed, a certain gas uptake eventually leads to hydrate plugging by a often very rapid conversion of the remaining water into large hydrate accumulations. So when they fail, they may fail catastrofically.[6,59,60]

If the subcooling or induction time is exceeded, there are no doubt that hydrates can form even in the presence of KHIs. They are not crystal modifiers, have no effect in changing the hydrate structures nor are they expected to alter the physical properties or surface morphology. After KHI failure, hydrate formation is attributed to the displacement, the desorption, of inhibitors from the hydrate lattice because hydrates are eventually more thermodynamically stable. The hydrate formation rate is often decreased in the presence of KHIs.[37]

1.7.2.2 Anti-agglomerant (AA)

As with the KHIs, AAs are also added at relatively low concentrations, < 1wt%.[26] AAs may not completely prevent hydrate formation, but they inhibit them from forming solid plugs. It is likely that AAs disrupt further growth of the crystals by being incorporated into the hydrate crystal lattice. Hydrophobic moieties then function to keep individual hydrate particles separated and dispersed in the liquid hydrocarbon phase. Thus, AAs permit hydrates to form but by dispersion remediate their agglomeration, deposition and plugging.[6,74] By doing this a transportable slurry of hydrate crystals are maintained and all the hydrate crystals do not build up to a plug in the pipe.[59]

There exist two essential structural features that the AAs must possess in order to function properly. They need a "hydratephilic" (hydrophilic) head (seeks hydrate crystal surfaces) that can incorporate itself within the hydrate crystals. Further, they need a "hydratephobic", or "oleophilic" (hydrophobic), tail that serve to disperse the hydrate crystals into the liquid hydrocarbon phase. The most powerful among these are certain organic, quaternary ammonium and phosphonium salts with one or two long "hydrate-phobic" tails (figure 1.12).[60] Hence, onium compounds with at least four carbon substituents are used as AAs.[75]

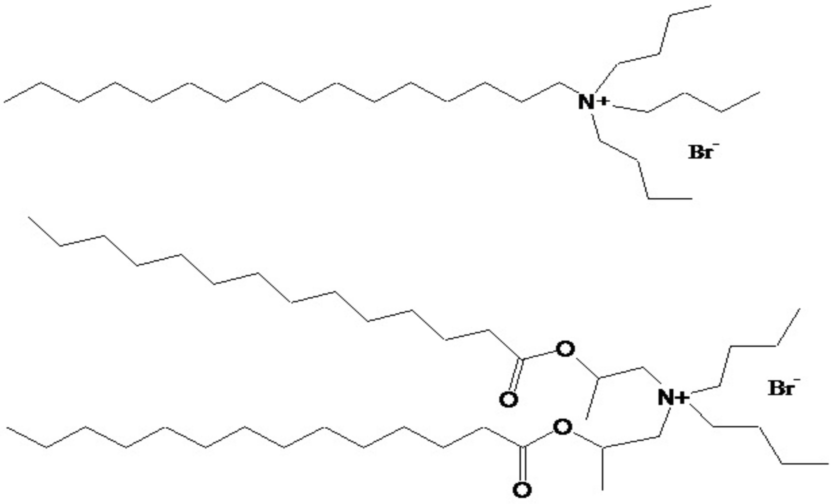


Figure 1.12. Quaternary butylammonium surfactants (AAs). Top: Mono-tail and water soluble. Bottom: Twin-tail and oil soluble.[36]

AAs are surfactant molecules, which operates in the gas-water interface, and are able to surround the hydrate crystals and thus prevent massive crystal growth. The resulting wettability of the hydrate particles will depend on the molecular structure of the surfactant, thus different surfactants induce different emulsion behavior. They can make oil-in-water emulsions that interfere with the hydrate crystallization process. As mentioned, AAs allow hydrate crystals to form but manage their size so that they can be dispersed in a hydrocarbon fluid.[72,76] It can be seen from the structural features which they posses that they are believed to have a dual mechanism of action that makes this possible:[39,46,59,74]

- ✓ The first mode of hydrate inhibition arises from the very fact that AAs are thought to exhibit the ability to change the crystal size of hydrates and the morphology of their agglomerates. They affect the structure of the growing hydrate, by applying growth inhibition as a result of AAs binding to the surface of the initially formed hydrate. In doing so, they alter the structure of the gas cage. The polar head incorporate itself into the growing hydrate crystal. This interaction disrupts the growth process resulting in smaller hydrate crystals. As a consequence, the resulting hydrates are slushy-like and more transportable, thus minimizing the risk of pipeline plugging.[6,62]
- ✓ The second mode of hydrate inhibition is achieved by AAs dispersive behavior. The hydrophobic tail functions to disperse the hydrate particles into the hydrocarbon phase preventing further agglomeration. These molecules allow the previously formed hydrates to disperse in the oil phase, thereby making it possible for the gas-water mixtures to be transported through the pipelines as a slurry (figure 1.13).

AAs have physical and chemical properties that both work together to prevent hydrate particles from agglomerating and plugging pipelines.[59] Despite that AAs inhibition mechanisms are considerably different from those of KHIs, some of them are also known to provide some KHI inhibition.[6,39] Since the mechanisms which AAs exhibits does not depend on termination of hydrate formation but rather preventing accumulation into a plug, quite a paradox in his respect arises as they can actually promote hydrate formation.[60]

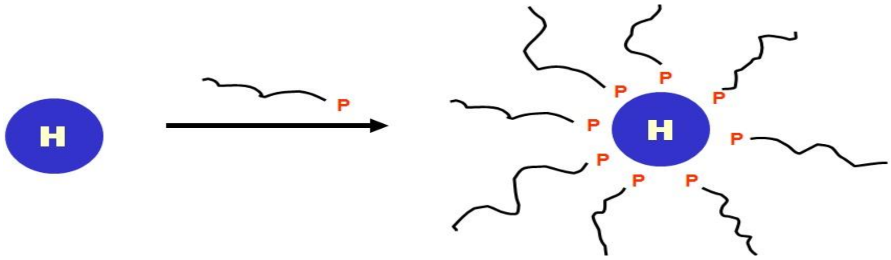


Figure 1.13. AAs second mode of action where they binds to the hydrate surface and forms a hydrophobic layer around the hydrate particle. This prevents further growth and makes the particle transportable as a slurry.[36]

AA components are surface active components that absorb to the hydrate surface, resulting in a lyophilic or oil-wet surface. This results in flocculation and dispersions rather than agglomeration and hydrate plugs by the reduction of the possibility of strong attractive hydrogen bonding between hydrate particles. Hydrate crystals can only agglomerate if they are "water-wetting" , while "oil-wetting" hydrates do not accumulate into plugs. This suggests that the bulky hydrophobic tails prevent the hydrate crystals from becoming covered by a water-layer, in addition to keeping hydrate crystals dispersed in the oil phase and keeping them physically separated. It can be envisaged that the former plays a crucial role in the agglomeration process when the water surrounding individual hydrate crystals coalesce and thereafter build up.[71,76]

There exist two subclasses of AAs, both of which are in commercial use:[17]

- Production or pipeline AAs.
- Gas well AAs.

Both subclasses allow hydrates to form but they prevent them from agglomerating and subsequently accumulating into larger masses. Pipeline AAs enables the hydrates to form as a transportable non-sticky hydrate particle slurry dispersed in the liquid hydrocarbon phase. Gas well AAs disperse hydrate particles in an excess of water.[17]

For AAs ability to permit hydrate growth but remediate by dispersion they are often preferred for well production shut-ins and cold start-ups. Further, their performance is relatively unaffected by the degree of subcooling, they are compatible with most production chemicals and are able to tolerate high brine systems, and therefore find many applications.[74] Regarding their performance in different hydrocarbon fluids, they perform excellent in systems containing condensates and black oils (the oils including asphaltic, non-asphaltic, paraffinic and non-paraffinic types).[6]

For some AAs it appears probable that emulsification of the oil and water phases prior to hydrate formation may be a critical part of the process. The AAs effect may be dependent on the mixing process at the injection point and the turbulence in the pipe, in these cases. Also, it can be expected that a water-in-oil emulsion to be required as an oil-in-water emulsion had a water-continuous phase which seems more liable to hydrate agglomeration. Separation of the water as droplets in an oil phase seems a likely way to avoid agglomeration.[26]

The effectiveness of a given AA have been shown to be dependent on the salinity level, composition of the hydrocarbon fluid and the amount of water (water cut) in the formation.[39] One fundamental limitation when it comes to AAs, is that they require a liquid hydrocarbon phase to be present in order to transport and suspend hydrates that may form.[6,60]

1.7.2.3 Kinetic hydrate inhibitors and anti-agglomerants compared

The only characteristic that is positive for both KHI and AA is the low concentration needed for adequate inhibition of a system. Other attributes are either positive for one of them, while being negative for the other. Therefore to discuss advantages and limitations they have to be compared.[26]

As with most chemicals, there are advantages and disadvantages associated with the use of KHIs and AAs. In general, AAs can handle a higher degree of subcooling and sustain a longer shut-in period than what the present KHI technology can achieve. Thus KHI have less subcooling potential and a shorter shut-in period compared to the AA technology.[37,62] The subcooling can be as high as 25°C in some deep sea environments.[77] Therefore are KHIs less desirable for situations with long shut-in periods.[39] This limited activity is the single most biggest limitation of KHIs, meaning that they can only be used in applications down to approximately 6−7°C subcooling in long distance pipeline transport for many miles. Still, the KHIs are far from structurally optimized, and probably there are classes of them that remain to be discovered that give much higher degree of subcooling. Although KHIs with longer growth delays may be discovered, there is still the possibility that some pipeline conditions are unsuitable for their use. The type of overpressure or the produced water in the pipe may render them less effective. Therefore there is a chance that the autocatalytic stage for hydrate growth is reached and the pipeline is blocked. Newer the less research is done to prolong the growth delay so that the system never reaches the autocatalytic hydrate formation.[59] Even so, for some applications of extremely high pipeline pressures or low temperatures this may still be a bridge too far. AAs on the other hand appears to be independent of the degree of subcooling, because AAs allow hydrates to form as very fine crystals dispersed in the hydrocarbon phase. These type of applications generally do not depend on subcooling. AAs are therefore often preferred for well production shut-ins, cold start-ups and/or deepwater applications, thus they can be applied for a wide range of temperature and pressure applications. This is maybe not the case of very high subcoolings. Here the driving force for hydrate formation may be so high that the rate of hydrate formation surpass the AAs from being effective at separating hydrate particles (figure 1.14).[17,26,74]

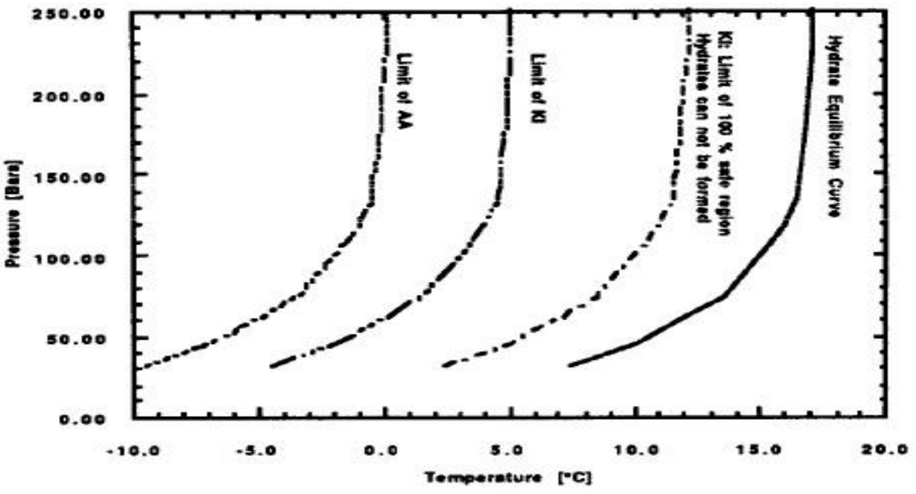


Figure 1.14. Theoretical pressure and temperature operating regions for KHIs and AAs. Relative to the equilibrium curve there is a curve for safe operating region for KHIs of today. Also a hypothetical subcooling limit for AAs are also added.[26]

The fluids are not moving and will cool down to the seabed temperature during a shutdown. The lack of turbulence during shutdown will minimize the gas diffusion into the aqueous phase, thus greatly reduce the rate of both hydrate nucleation and formation. The fluids become turbulent and consequently the gas diffusion and hydrate formation become rapid during start-up. It is in this condition problems may occur. Regardless whether the fluids are flowing or stationary, the subcooling in itself may be too much of a task for the KHIs to handle. To overcome this, some operators, that rely on these inhibitors, envisage pumping methanol into the line before start-up. They then switch back during normal production to KHI injection. The best way to avoid methanol completely is to use AAs. The preformed slurry of hydrate crystals must not agglomerate during shutdown so that the slurry transportation can begin again at start-up. This must be ensured by the AAs.[26]

A minimum of 50‒70% oil cut is needed in order for AAs to function properly so that they can transport and suspend hydrate crystals.[6,60] The requirement of a liquid hydrocarbon phase is the major limitation when it comes to AAs. Hence, the water cut should be below approximately 50%, otherwise the hydrate slurry gets too viscous to transport.[18] The KHIs requires no liquid hydrocarbon phase in order to function properly, they work at any water/oil ratio (WOR).[6,37,62]

Beside these major limitations, KHIs are more environmental friendly than AAs and KHIs provide an environment free of hydrate. Further, AAs may cause production problems, such as emulsions and bad water quality. Also, pumping the resulting hydrate slurries can become an issue for the operation due to concerns of increased energy consumption, erosion, overpressure, oversize pump availability/operability and lack of experience.[37,62] AAs are compatible with most production chemicals, KHIs are not and the effect of which can be altered.[74]

1.8 Production chemicals

When it comes to the choice of production chemicals the operator must consider the following factors:[17]

- Health and safety regarding storage and handling.
- Compatibility.
- Efficiency.
- Cost.
- Stability.
- Environmental impact.

The oil and gas industry is relying more and more on chemical solutions for flow assurance. These production chemicals are becoming more prevalent and they not only interact with each other, they can interact with the environment as well.[72]

To diminish the health and safety aspect associated with some solvents that some production chemicals are made up by, both the chemical manufacturers and service companies have made an effort to replace them with less toxic and safer solvents. Hench, these solvents must have a higher flash point and/or lower volatility than the solvents they replace.[17]

The most frequently used production chemicals are corrosion, scale and paraffin inhibitors, especially in subsea pipelines. Material and chemical compatibility with the system treated is a key factor to determine whether the specific chemical can be deployed. Material compatibility involves both metallic and nonmetallic compounds. The chemical compatibility between production chemical can be influenced by each other. Therefore it is of utmost importance to carry out compatibility studies to investigate its effect on performance of existing chemicals.[37]

Some chemical suppliers have made combinations of different production chemicals, each of which have its specific properties (such as gas hydrate inhibitor mixed with a corrosion inhibitor). This makes it possible to only use one storage tank, pump and injection line. Some multipurpose component products are available, but for the most mixtures of individual compounds that are compatible with each other are on the market. It is beneficial that the production chemicals possesses a low viscosity, so that their blends can be pumped along an umbilical cord with ease. This will however set a concentration limit for certain components in these production chemicals and their solvents, especially in cold waters. In a mixing situation, which usually occurs by accident, incompatibility can arise between different production chemicals. Hence, as a rule, subsea injection points are placed at least three pipe diameters apart. This is done to ensure that immediate blend of different production chemicals do not occur. In addition, some production chemicals are oil soluble (hydrophobic) while some are water soluble (hydrophilic). This makes it impossible to inject them through the same transport line.[17]

Injection of production chemicals to a subsea wellhead is done using one or more umbilical flow lines (supply cable) which goes from the platform down to the wellhead. These umbilical cables have typically a diameter of 0.6‒2.5cm and can reach lengths of up to 50km.[17] This makes the physical properties like viscosity, flash point and pour point, important issues not to be overlooked. Among them, viscosity is the most critical property, and because of hardware limitations it is difficult to be compromised. Viscosity directly affects the overall pressure drop rating across the chemical line. A higher pressure rating would be required for the injection line, because of a more powerful pump would be needed as the viscosity increases.[37]

The production chemical that provides the best performance and works adequately at an affordable price is the one chosen. Through the entire life cycle of the production chemical, which involves transport, storage and injection, the chemical must remain stable. At field locations, where the temperature can be very high, the effectiveness of the production chemical may change of it degrades too rapidly or undergo phase change. In order for the avoidance of injection problems in cold weather the chemical should neither freeze nor be too viscous.[17]

In areas where a high degree of degradation ability of production chemicals are required, a quandary arises. Because the operator would like to have chemicals that does not deteriorate during storage, but is degraded quickly in seawater. This proves to be a technological challenge for the petroleum industry to develop chemicals that are both effective, does not decompose during storage and have an diminished impact on the environment by being easily degraded.[17]

1.9 Environmental issues

Extensive petroleum hydrocarbon exploration activities often result in the pollution of the environment, if not restored which could lead to disastrous consequences for both the biotic and abiotic components of the ecosystem (figure 1.15).[78] The environment have come more into focus. Thus, the environmental impact that different chemicals can cause is investigated. Further, the risk that deploying and managing oilfield chemicals are attempted minimized. The discharge of environmentally harmful oil field chemicals, normally through produced water, is also tried diminished.[17]

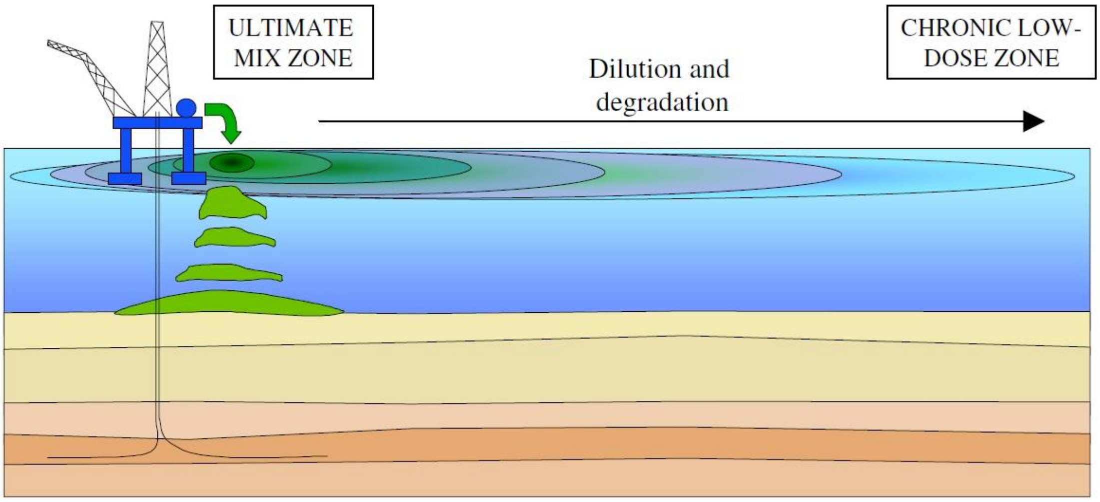


Figure 1.15. E & P operational discharges to the marine recipient will either settle on the adjacent ocean floor or spread, dilute and eventually degrade in the water column downcurrent the operation area. Hence, ecologically relevant impact phenomena may rather occur in waters where contaminants are highly diluted (chronic low dose), and less in the ultimate mixing zone of the effluent stream.[79]

Produced water contains oil residues, which in itself are an environmental threat. The environmental threat reaches a whole new level if the production chemicals follows the produced water and gets discharged to the sea. This represents the biggest environmental risk during normal production. Different government regulations in different countries resolve in different production water discharge regulations. New water treatment technology have also entered the marked. Reinjection of produced water into the well is a good way to prevent discharge to the sea. In offshore applications this can help to maintain the reservoir pressure high enough so more oil can be recovered. Reinjection is a good alternative onshore as well. The production chemicals in the liquid hydrocarbon phase will however during normal production not be released into the sea. A discharge will thus be unintentional, caused by a leak or some other type of accident.[17]

Since these production chemicals are added to the well stream, they may end up in the water, liquid hydrocarbon or gas phase, but they are most prone to follow either the water or liquid hydrocarbon phase, or even an intermediate state of them.[17]

Oilfield chemicals products are incorporated into a fluid design to solve a specific technical wellbore or matrix problem in a well. These products may have primary active ingredients that can possess harmful effects if discharged to the environment.[80]

The persistence of petroleum pollutants released in the marine environment depends not only on the toxicity of the chemical, quality, concentration and the actual quantity discharged of the hydrocarbon mixture in the discharge stream, but also on the properties of the affected ecosystem. Hence, petroleum hydrocarbons can persist almost indefinitely in some environment, whereas under another set of conditions, the same hydrocarbons can be biodegraded completely within a few hours or days. In the marine environment, bacteria are the dominant hydrocarbon degraders. [79,81] Either physicochemical or biological methods can be used for remediation of petroleum contaminated system. Chemical agents, that are a part of the physicochemical methods, can be used for remediation of oil pollutant. These chemicals, however, are sometimes just as toxic as the ones they are suppose to remediate. Therefore, the attendant negative consequences of the physicochemical approach are currently directing greater attention to the exploration of the biological alternatives. Hence, the physical (weathering) and biological action of nature is the best approach.[78]

Bioremediation is an acceleration of the natural fate of oil pollutants and hence a "green solution" to the problem of oil pollutants that cause minimal ecological effects.[82] The complete biodegradation, or mineralization, of hydrocarbons produce the nontoxic end products water and carbon dioxide, as well as cell mass (largely protein) which can be safely assimilated into the food webs.[81]

A sequential row of disorders going from the molecular level and up to the higher hierarchical levels of biological organization can be addressed to an adverse effect of a pollutant chemical. This means that toxicant impacts at higher hierarchical levels are always preceded by changes in more fundamental biological processes. Pollutant induced alterations early in the effect sequence may therefore be used as early warning signals of potential pollutant impact at higher levels of organization.[79]

New links between environmental pollutant exposures and the occurrence of putative adverse effects in aquatic organisms have been discovered over the past decade. This have lead to more strictly regulations or even part of a phase-out process of commonly used chemicals. In addition, a range of new biological monitoring tools have been developed. These tools enables the detection of effects in laboratory exposed organisms at more environmentally realistic contaminant concentrations. They also makes it possible to perform more relevant ecotox effect studies in field recipients. It is obvious that new kinds of environmental pollutant effects will be discovered as the understanding of biological and biochemical processes increases.[79]

Therefore all proposed production chemicals to be used in the North Sea must go through ecotoxicology test to determine if they are environmentally acceptable to be used. OSPAR Convention (Oslo and Paris convention, the Convention for the Protection of the marine Environment of the North-East Atlantic) have developed guidelines that each component in a production chemical must undergo. In connection with offshore exploration & production activities in the OSPAR maritime areas, the Harmonised Offshore Chemical Notification Format (HOCNF) is applied to all chemicals used. The toxicity data on exploration & production products are normally provided on the basis of the OSPAR HOCNF.[17, 79,83]

Three main factors are normally considered in the hazard ranking:[79]

1. Octanol-water partitioning parameters. Indicates the bioaccumulation potential of the pollutant.
2. Biodegradation rates. A measure of persistence of the pollutant.
3. Toxicity. Measures acute aquatic toxicity parameters.

Bioaccumulation potential and persistence are important elements since hydrophobic (lipophilic) xenobiotics that also are resistant to degradation generally are considered as potentially environmental hazardous. These compounds often accumulate in organisms and biomagnify along the food webs.[79] For instance, the Norwegian sector normally demands 28 day biodegradation > 60% biodegradability on new chemicals, in addition to one of the three requirements: Molecular weight > 700, bioaccumulation Log $P_{OW} < 3$ or low toxicity EC50 > 10mg/L. This rules out all LDHIs commercialized to date.[18,84]

The lack of harmonization of the regulations makes meeting all these environmental requirements more tricky for companies that operate in offshore waters around the world, that are attempting the difficult task of developing products that:[80]

- Meet environmental requirements in various parts of the world.
- Perform the job that they are design to do.
- Have the lowest possible risk to human health and safety.

Developing new and more environmentally acceptable products requires working in close companionship with regulatory agencies, chemical suppliers and clients to achieve compliance with relevant international statues. The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which they have made test guidelines that is standardized for many countries around the world. This is important in that test results from one laboratory can unambiguously be compared to results from another laboratory, since they both are using the same test guidelines. Therefore, for instance testing chemicals biodegradability in seawater can be done in the same manner across the world, leading to comparable results.[83,85]

Technical achievements are only realized by continued commitment and product improvements to meet or exceed health, safety and environmental (HSE) objectives. Therefore is there a requirement that production chemicals should be more environmentally friendly (green chemicals). The efficiency of these chemicals must be quite high, especially since many new fields are found in areas with harsh conditions. Improving the characteristics of these chemicals in order to reduce the risk or damage to marine life requires changes in previously acceptable products. These changes can be elimination of restricted materials and incorporating components with improved ecotoxicity. But it have been proved to be difficult to design environmentally friendly chemicals with the same efficiency as the less environmentally friendly ones.[17,80]

1.10 Experimental methods

Although most major oil companies applies LDHIs, many fundamental questions that directly relate to unimpeded pipeline operation remain unanswered. For instance, inhibitor ranking that are measured in the lab for seemingly identical systems are not only highly variable but depend also on the type of equipment used. Nevertheless, oil companies use these measurements to predict LDHI performance in the field, and the way they interpret these measurements are not less variable.[71]

The first issue when it comes to designing a hydrate induction rate experiment is to establish how hydrates will be detected. Gas hydrate detection can be done in multiple ways:[86]

- Detection of an exotherm due to hydrate heat of formation (exothermic process).
- Detection of an increased differential pressure drop in a flowing system.
- Detection of a gas volume decrease in excess of vapor liquid equilibration in a closed, constant pressure system.
- Detection of a pressure drop in excess of vapor liquid equilibration in a closed, constant volume system.

By any of the above mentioned events, hydrate induction rates and onset temperatures are based on hydrate detection. When the system drops below the hydrate equilibrium temperature the induction rate experiments initializes, and terminates when gas hydrates are first detected. The temperature of a system where gas hydrates are first detected is defined as the onset temperature. In some experiments the system temperature is ramped down below the gas hydrate equilibrium temperature and held at constant temperature for an induction period. The time required to observe gas hydrate formation onset at the hold temperature is defines as the induction time. It is suggested that the induction time consists of two parts: An intrinsic induction time that the system needs for reaching a precursor state and during which the first hydrates cannot form, as well as an additional period that the length of which is purely determined by chance. The intrinsic induction time should be virtually independent of the system volume if the intrinsic induction time is indeed at time needed to bring the system in a precursor state that allows for macroscopic hydrate formation. In addition to if reaching this precursor state entails the completion of a large number of steps.[86]

In practice this would mean that the LDHI induction time of a large system, like a pipeline, becomes equal to the intrinsic induction time that is measured in the laboratory. But still the intrinsic induction time measured in the laboratory can depend on variables such as rate of mass and heat transfer, which in turn may depend on the flow regime.[71,86] Important parameters such as the water history and impurities on the nucleation of gas hydrates can be masked by the stochastic nature of the induction time.[2]

Not unexpectedly, the observed induction times depend on the pressure, the temperature, the LDHI used and the detailed composition (includes any other oil field chemical used) of the system in which hydrate formation is to be prevented. Even if these parameters are as far as experimentally possible held constant in a large number of replicate experiments, a wide spread in the measured induction time is usually observed.[71]

Hydrate nucleation events actually take place before a system reaches the onset temperature or a time shorter than the experimental induction time. Hench, hydrate detection rates by purely experimental means set a lower bound to the actual induction rates. In order to achieve repeatability in measured hydrate detection rates the randomness of nucleation must be reduced in the experiments. This is best done by using well mixed and large systems to minimize statistical fluctuations in the test.[86]

Although not always successfully, LDHIs are now used in many field, and most of the currently used LDHIs were declared ready for use in the field based on results from laboratory tests. It remains a challenging process to implement LDHIs based solely on these results, as long as it is not totally clear to what extent these results are produced by statistical fluctuations rather than by more deterministically proceeding molecular processes. Therefore, the best option is to measure LDHI induction time distributions by carrying out many replicate experiments whilst using different types of equipment. Conservatively it must then be assumed that the LDHI resident time in a pipeline will not be longer than the shortest induction time measured in the laboratory. Thus, validating a LDHI for use in the field is much more tedious than most expert had expected at the time when these chemicals were developed.[71]

The second issue is linked to how to accurately measure hydrate dissociation temperatures. Commonly used methods follows:[86]

- Observance of an endotherm.
- Differential pressure drop across an element in the flowing system.
- Gas volume changes at constant pressure.
- Gas pressure changes at constant volume.

Hydrate dissociation temperature is commonly regarded as the closest observable temperature to the hydrate equilibrium temperature. Measuring this temperature is generally simpler than measuring the induction rate. The temperature at which a system of fixed composition and pressure is at the hydrate equilibrium is defined as the equilibrium temperature.[86]

Experimentally endotherms are temporally not well defined and not used. Therefore measurement of the temperature at which either a differential pressure returns to its nonhydrated value, a gas volume returns to its nonhydrated equilibrium value (in a constant pressure apparatus) or a pressure returns to its nonhydrated equilibrium value (in a constant volume apparatus) are used methods for experimentally measure the equilibrium temperature. In multicomponent experiments caution must be exercised when measuring the equilibrium temperature, in order to ensure that the observed hydrate decomposition occurs at constant hydrate, water and gas phase compositions. If the hydrate type, salinity or gas phase composition, after the onset of hydrate formation, where to change the measured value of the equilibrium temperature would be shifted relative to the actual value for the initial compositions. The compositions of the bulk water and gas phases will be constant during the experimentally measurement of the equilibrium temperature, only if the water and gas fractions in hydrates are small. It is recommended to measure the equilibrium temperature before adding any inhibitor or other chemical to the system. The presence of LDHI for instance, will cause the system to equilibrate slowly and makes the measurement of the equilibrium temperature difficult.[86]

Experimentalist are allowed to rank LDHIs by the maximum subcooling achievable in comparable systems, by the coupling of reliable measurement of hydrate dissociation temperatures with reliable detection of the onset of hydrate formation. In addition, LDHIs may be ranked by comparison of the induction time as a function of subcooling and inhibitor concentration.[86]

Then it is the issue of choosing a composition to rank LDHIs. The establishment of screening/testing capabilities in many laboratories have come from the desire to rank inhibitors in the compositions found in a particular field application. Part of the composition issue is verification that the inhibitor is chemically and biologically stable. If used properly, the composition used to compare inhibitors is more important than the choice of apparatus.[86]

In order for interpreting, modeling kinetic experiments and for predicting when hydrates will form in pipelines, a quantitative description of the driving force for hydrate formation is needed. Faulty interpretations and predictions are likely without a satisfactory description of driving force. Both the hydrate nucleation and growth rates should correlate with driving force. Experimental determination is crucial for finding the relationship between formation rate and driving force. The measure of driving force can be conducted in multiple ways, among them are the measure the extent of overpressure above equilibrium pressure, extent of subcooling below equilibrium temperature and the change in Gibbs free energy when hydrates form.[29]

Thus, the last issue in the design of kinetics experiments is the method of applying the driving force for hydrate formation. It is convenient to use a method that applies, via a reproducible path, a variable driving force to the system. All initial phases, being either liquid water, liquid hydrocarbon and gas, should be maintained constant and as nearly equilibrated as possible. The following conditions should be met insofar as possible in order to satisfy these requirements for onset and induction time experiments:[86]

- ✓ Surface area is large and constantly renewed by either stirring, pumping or sparging.
- ✓ Pressure is constant.
- ✓ Water structure is initialized by heating the system above the temperature at which residual hydrate structure melts.
- ✓ Temperature is maintained uniform and temperature changes are gradual before the onset of hydrate formation.
- ✓ There is a large excess of water and/or each of the hydrate forming component after initial hydrate formation, such that water and gas compositions are not altered before hydrate detection occurs.

These conditions make the thermodynamic path experimentally reproducible form not only test to test, but from laboratory to laboratory as well.[86]

There are obvious advantages of segmenting the different phenomena into separate studies in the laboratory. Here experiments can be done in a controlled manner, and the effects of important variables in that phenomenon can be isolated. But when doing so, a decoupling of the interaction of the phenomena is done and perhaps therefore not completely capturing what may happen in actual flowlines. Because of this, flowloop test should be executed to consider all of the phenomena together to mimic as close as possible the scenario in the field of flowlines.[47]

Therefore there exist neither laboratory experiments nor procedures where the result of which can be unambiguously translated into the performance of a LDHI in the field. Further, the ways that these LDHIs act at the molecular level are not totally well understood. In addition, the influence of auxiliary variables such as the possible interference of LDHI with corrosion processes and the flow regime have not been systematically studied. Consequently it remains a challenge to predict the performance of a LDHI in the field based on the results of even an extensive laboratory testing exercise.[71]

Operators will not usually risk operating the production line right at the performance limit of a LDHI, but maybe at 1−2°C less subcooling or higher LDHI dosage than was qualified in the laboratory or pilot tests.[55,87,88] Because of all this, LDHIs would be much more used if these uncertainties were removed and laboratory performance can be unambiguously related to field performance. Before field trials or field implementation of the LDHI, the last and best step is to run tests in large pipe wheels or loops. The reason for this is because that test results from small "clean" laboratory equipment is most influenced by the stochastic nature which hydrate formation possesses.[71]

1.11 Hydrate inhibition test equipments

LDHIs are relatively expensive materials, and thus it is always advantageous to determine means to decrease the dosage levels of these hydrate inhibitors while maintaining effective inhibition.[75] Although there exist a variety of computer models of gas hydrate, the modern theory have no answers on a number of fundamental questions about gas hydrates. Thus engineering solutions of the majority of these problems rely today on the results of direct experimental research.[43]

Test equipment and methods for identification and evaluation of potential LDHIs and appropriate concentrations are numerous. The most used apparatuses are, here listed in their increasing level of complexity: THF rigs, rocker rigs, autoclaves, pipe wheels and flow loops, all with their own benefits and drawbacks, which will be discussed in the following.[6,18,60,75,86,89,90]

1.11.1 Atmospheric hydrate inhibition test equipments

THF (tetrahydrofuran) rigs are among the most simple test equipments out there (figure 1.16). Although simple, it is a very effective technique for studying growth inhibition. It measures the growth rate for a single THF hydrate crystal. This apparatus is typically used in situations where fast screening of LDHIs are essential. It is also beneficial that THF forms Structure II hydrate, which is the same structure frequently formed by natural gas hydrates. The equipment operates under atmospheric pressure, without any flammable gas. It is therefore relatively safe to operate.[18] However, THF tests are not reliable indicators of hydrate formation kinetics for natural gas systems, this because the THF system have different mechanisms of hydrate formation and inhibition relative to natural gas systems.[86]

Figure 1.16. A THF rig.

In addition to THF, cyclopentane (CP) can also make Structure II hydrate under atmospheric pressure. Therefore have there also been made equipment where CP is used to make hydrates (figure 1.17).[91]

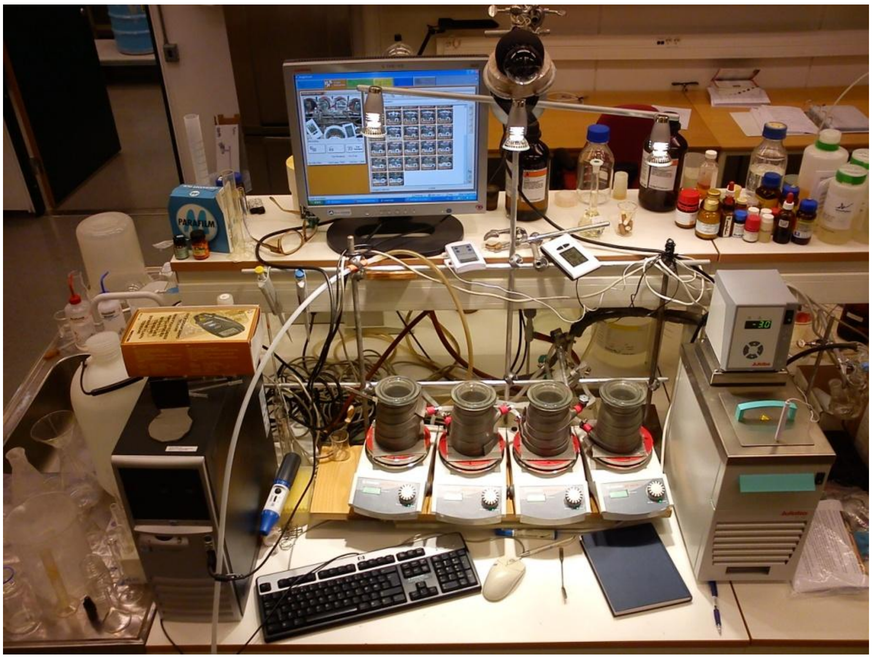


Figure 1.17. Equipment for making CP hydrate.

1.11.2 Rocker rigs

The next apparatus on the list is the rocker rig or the ball stop rig (figure 1.18).[18]

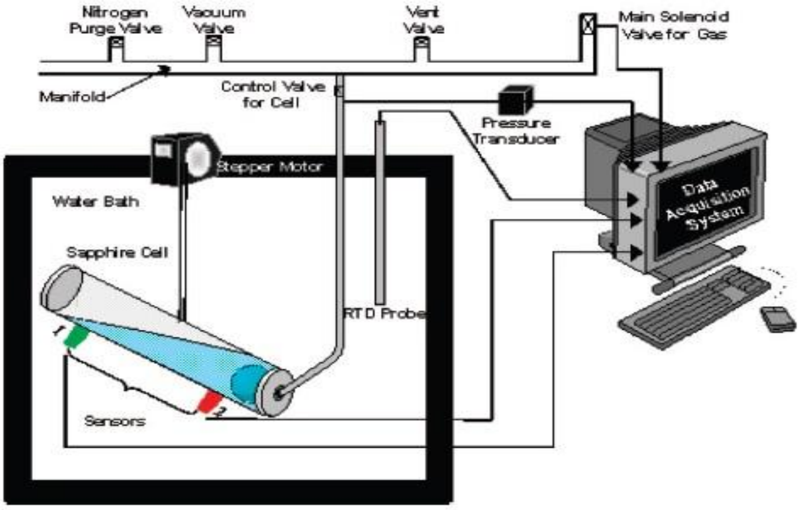


Figure 1.18. Schematic over a rocker rig.[92]

In this test equipment a bank of small pressurized cells often with a metal ball inside, are placed in a cooling bath. Here they are rocked back and forth. Some cells are made with a sight glass or made entirely of sapphire, and they can contain two stainless steel balls in addition to a pressure transducer or sometimes a temperature probe and two run time sensors at both ends for run time measurement as well (figure 1.19). The stainless steel ball in the cylindrical fluid chamber provides agitation during rocking. A typical experiment proceeds as, each cell is rocked back and forth to simulate flow conditions. This rocking motion causes the stainless steel balls within to transverse the longitudinal axis of each cell, thereby creating additional agitation. The cells are plugged up with hydrate when the balls stop moving. The cells can also be held static to simulate a shut-in condition. During the static condition, the cells are placed at a horizontal stagnant position. Data logging includes the pressure in each cell, the water bath temperature and periodically visual observations. As the temperature is decreased the pressure decreases as well, as with all isochoric experiments. At room temperature the maximum working pressure in a cell may be about 10.3MPa, and typical maximum test pressure at 4.4°C may be 7.6–9.3MPa. Rocking cells have the advantage of high throughput and can test several different inhibitor formulations, concentrations, water cuts, fluid and gas compositions in a single test run. In addition it require only small amounts of test fluids. In general rocking cells are considered a conservative test. Further, experience has shown that when properly conducted, it adequately predicts both AAs and KHIs performance in the field. The apparatus is a simple but excellent test equipment.[18,75]

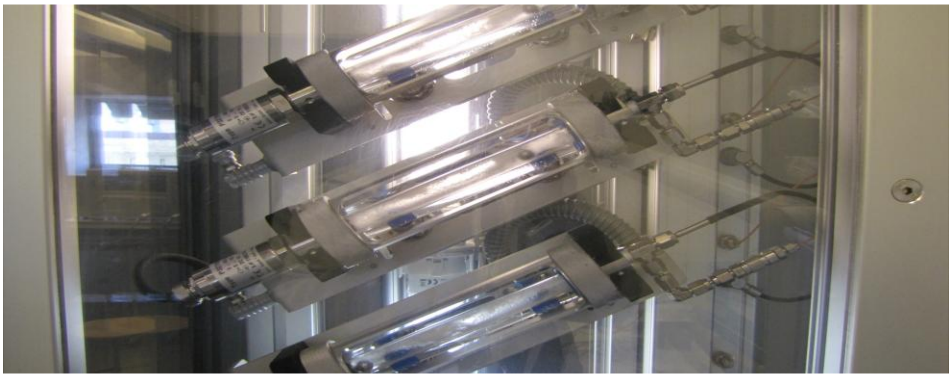


Figure 1.19. Sapphire multi-cell rocker rig.

1.11.3 Autoclaves

Then it is the autoclave or high-pressure stirred cell (figure 1.20).[18]

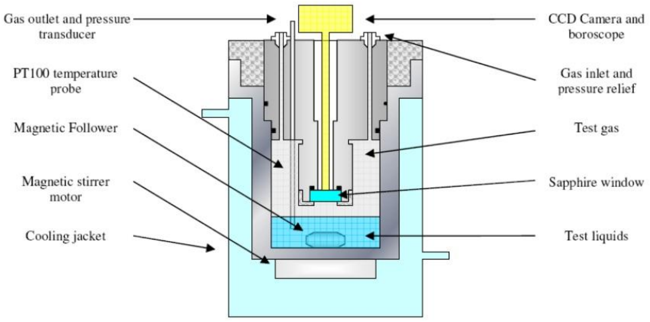


Figure 1.20. Schematic of an autoclave.[15]

These autoclaves can have a window for visual observations or they can be entirely made of sapphire (figure 1.21). The cell is either placed in a jacket or immersed in a temperature controlled cooling bath. The cell is slowly cooled or quench cooled and held at either constant pressure or volume, and are filled with gas, brine and oil or condensate. The agitation is normally provided by either a magnetic stir bar or a blade type agitator-mixer. They usually requires only a few hundred milliliters of fluids per test. Here parameters like the inner temperature, pressure, and sometimes the torque exerted on the stirrer are measured. A pressure decline owning to the gas consumption as well as the exothermal hydrate formation event are measured. The contents and viscosity are visually monitored, such as by image monitoring.[75] A range of pressures can be applied, and it can be as high as 35MPa. These apparatuses are well suited for KHI testing with very long hold times of seven days or more. These autoclaves can be effective in reproducing the relative ranking of inhibitors determined in other types of pressurized test apparatus, thus like the THF rig it can be used for screening tests. [86,93]

Figure 1.21. An autoclave seen from above.

1.11.4 The wheel apparatuses

The wheel apparatus, pipe wheel or loop wheel are the next apparatus to be described (figure 1.22).[18]

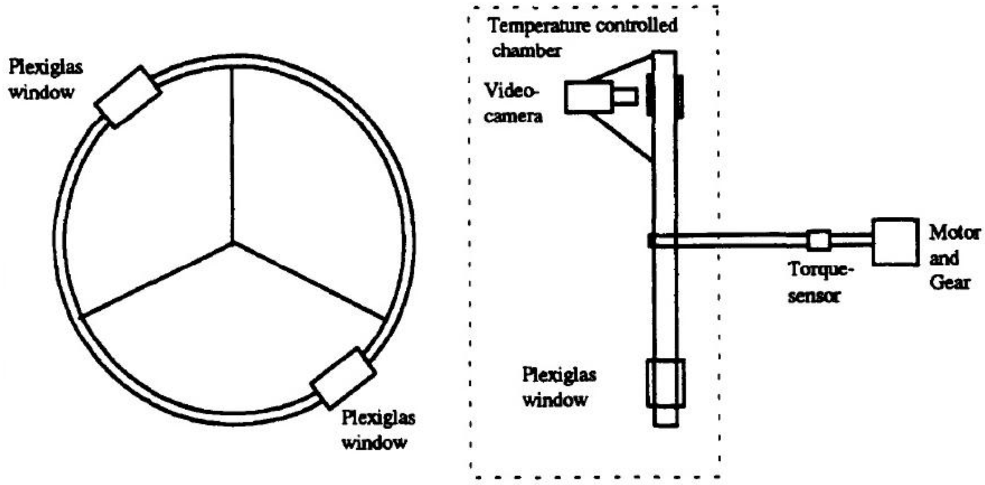


Figure 1.22. Schematic of a wheel apparatus.[94]

These apparatuses can be a wheel-shaped pipe flow loops, and may consist of 2−5inches (5.1−12.7 cm) pipe shaped as a circular loop or wheel of 2 meters in diameter. It rotates about a horizontal axis. Other are normally placed vertically, with a diameter of usually 1−3inches (2.54−7.62 cm). They can have a high pressure capable window, often two, for visual inspection typically with a video camera (figure 1.23). The rotation velocity of the wheel determines the flow regime, laminar or turbulent. Peripheral velocities may range from 0.3−5m/s. Conceptually, the wheel is spun past the gas and liquid rather than the reverse. Hence, the flow wheel apparatus have no requirement for circulating devices such as compressors or pumps. Pressures up to 25MPa may be applied. Either pumps nor compressors are used in this apparatus which makes the apparatus easier to operate and maintain. The wheel is placed in a temperature controlled chamber, and the temperature may range from −10°C and up to 90°C. Also here, the wheel is filled with gas, brine and oil or condensate, less than 50% liquid. The parameters to be controlled and measured here are torque exerted on the wheel, pressure, temperature and visual appearance.[40,75]

This apparatus have a more realistically simulation of pipe flow conditions than the autoclave apparatus, however it is far more expensive. The rotating wheel can model slug flow in the pip and is useful for examining shout-in and restart conditions, especially in situations where hydrate particles can potentially settle out to form plugs.[93]

Figure 1.23. Wheel apparatus.

1.11.5 Flow loops

Last, but not least, it is the flow loops. Conventional flow loops often comprise a stainless steel loop, usually with a high pressure capable sight glass for image recording (figure 1.24).[18,75]

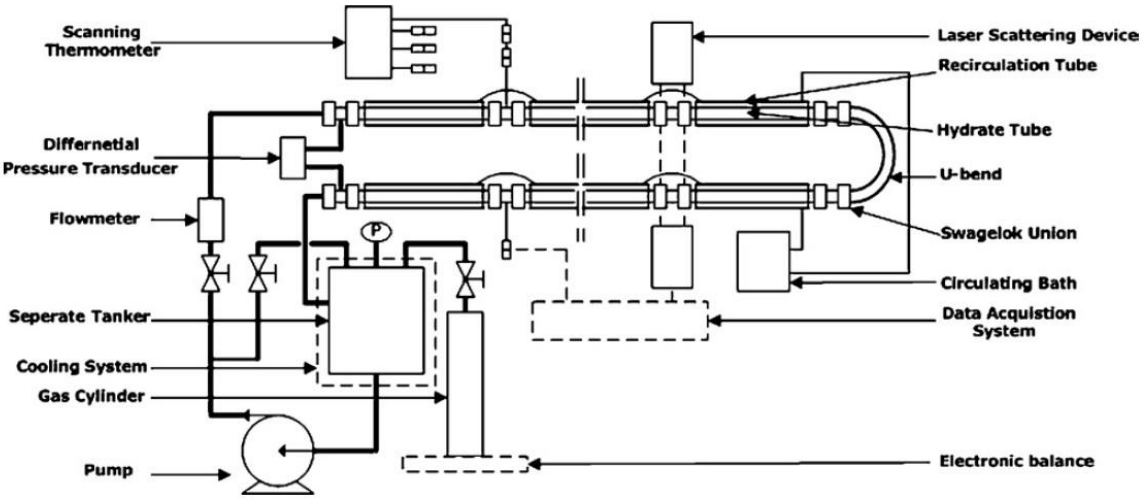


Figure 1.24. Schematic of a flow loop.[95]

This test equipment is usually placed horizontally, and normally operated under high pressure using gas, brine and oil or condensate. They may be closed systems or at constant pressure. Circulation and the velocity, which controls the flow regime, is provided by a pump. The loop is typically placed in a temperature controlled chamber or bath. Flow loops range in size from the mini-loop of ¼inch (0.635cm) in diameter, bench scales of 0.5inch (1.3cm) in diameter to 3m long and up to the full scale pilot loops of 4inches (10.16cm) or more in diameter and 84m long (figure 1.25). A number of these large temperature controlled pilot flow loops have been constructed to study hydrate formation under simulated field conditions. The pressure, pressure drop, temperature and/or water conversion are measured. Visual appearance is monitored by visual monitoring. The loop is divided into numerous parts, each of which has a differential pressure gauge and a temperature probe. The pressure applied can be in the range of 12MPa. Tests in these apparatuses focus on flow regime, shut-ins, restart conditions, water cuts and fluid compatibility. This type of equipment are quite expensive, which also hold for the bench scale experimental apparatus. The most realistic simulation of pipeline conditions available is provided by these apparatuses, thus they provide the closest mach to field system conditions. Flow loop reactor testing results are very repeatable. They are recommended for ranking LDHIs according to subcooling and induction times as a function of concentration, based on the preferred conditions of reproducible driving force and reliable hydrate detection. A disadvantage, that can be detrimental for the result, is that in some cases the pump can crush hydrates. This can make especially AA experiments difficult to interpret. Each experiment run is typically very time consuming, requires a long lead time and considerable amounts of fluid. Such apparatus are at a disadvantage in situations where evaluation of an approach or method to inhibit gas hydrates must occur quickly with limited field fluids. In addition flow loop testing can be impractical in applications where multiple formulation testing and concentration optimization are necessary and therefore requires several sets of tests. Hence, these apparatuses are most often used for fundamental studies and for final test before field implementation.[18,40,75,86,93]

Figure 1.25. Flow loop 4inches (10,16cm) in diameter and 100m long.

Studies have shown that results from flowloops as small as 0.5inch (1.27cm) agree with results from 4inches (10.16cm) flowloops, also they agree with results in 8inches (20.32cm) field pipes. Therefore is it reasonable that all sizes in between will also agree. All this hold for turbulent flowing systems. Stratified flow, shut-in conditions and wavy flow did not however agree with turbulent flow results. A conclusion was drawn from this that a broad range of laboratory test apparatuses can predict field performance, provided that the flow characteristics (fluid compositions, temperature and pressure) can be simulated. By the use of flowloops of 0.5inch (1.27cm) and 4inches (10.16cm) in diameter, as well as high-pressure autoclaves, LDHI behavior in field pipelines can be reproducibly and accurately predicted. However, high-pressure rocking cells appear to give unacceptably high data scatter in addition to that they give a different subcooling than the flow loops. Precise temperature control and appropriate shear conditions (turbulent flowing systems) are required for accurate prediction of LDHI performance. Laboratory test results under stratified, shut-in and wavy flow regimes results in large scatter in data and thus generally does not agree with turbulent flow results. It have also been postulated that rocker rig and autoclave flow is not an adequate representation of the flow in pipes, like wheels and flow loops are.[40,45,75]

Thus there exist several types of testing equipment and methods designed to mimic field conditions for hydrate formation and inhibitor testing. These equipments fall into three types of apparatuses: Rocking cells, autoclaves, wheels and flow loops. By charging the system with a gas phase, hydrocarbon phase and aqueous phase under conditions of high pressure and low temperature such as those of the field, and then measure the performance and concentrations of various inhibitors under these conditions each apparatus attempts to recreate the field conditions. To accurately reproduce the field conditions it is important to use the actual gas and fluid compositions from the field. That the apparatuses can simulate both steady state and shut-in/restart conditions are important.[40,75]

All this adds up to an never-ending demand for better and more reliable test equipment, hence there are always room for new apparatus which can fill the gap between the existing ones. Further, it is desirable that new methods and apparatus of forming gas hydrate and its inhibition be found which yield reliable and predictable test results, in addition to provide a consistent method for hydrate formation and inhibitor testing. Ideally such methods and apparatus may require minimum amounts of fluids, be conducted in a relatively short time, be easy to set up and be of relatively low cost.[75]

CHAPTER 2: EXPERIMENTAL

As mentioned in chapter 1 (1.2, 1.4, 1.5, 1.6, 1.7 and 1.11) gas hydrates are nonstoichiometric crystalline solids where gases of certain-molecular-weight stabilize the hydrogen-bonded water molecule cages. The agglomeration of these solids can form plugs that can cause severe problems for the oil and gas industry. There exist many methods for inhibiting hydrate formation, one of them being the usage of LDHIs. Because LDHIs are relatively expensive, it is therefore advantageous to determine means to decrease the concentration for adequate inhibition. Further, these inhibitors are normally declared ready for use in the field based on results from laboratory test apparatuses.[4,12,16,37,50,71]

In the laboratory scientists aspire to make test equipment which mimic what happens under field conditions. The test equipment is tried to be made less labourious, more accurate, safer to operate, more reliable, more realistic and generally simpler. In the laboratory the parameters that go into the system may be controlled. The parameters can be adjusted one at the time, in a controlled manner. In this way the influence of the parameters on the system can be determined. This, however, cannot be done in the field.

It has been found that prior methods of studying the intentional formation of gas hydrates and methods for inhibiting their formation, tend to suffer from inconsistencies and not being repeatable. There have been discovered a method for hydrate inhibition testing by using a laboratory table top wheel. It involves contracting a fluid including a mixture of an aqueous phase and hydrate forming gas with an amount of LDHI, under hydrate forming conditions. The table top wheel apparatus has been designed for determining the formation of hydrates in gas-liquid mixtures in a simulated flowing environment.

The purpose of this thesis was to test to see if a newly designed tabletop wheel could work as the normal big wheels do, if it could be used to rank inhibitors. In the new wheel a swirling motion causes the liquid to be moved around. The principle is based on the so called "Euler Disk" mechanical movement. Thus, in the apparatus used in this experiment only external influence causes the movement of the liquid.

2.1 Description of the apparatus

A prototype bench top wheel was designed by Malcolm A. Kelland (Professor at UiS) and Anders Grinrød (M-I Swaco). The concept, initial mechanical design and the custom made electronics was provided by Anders Grinrød. The rest, including but not limited to mechanics, was made by Einar Tostensen (IRIS). Most of the founding was supplied by the University of Stavanger (UiS), and a small percentage was paid by M-I Swaco.

A prototype bench top wheel was designed, figure 2.1. It consists of two disks, one acrylic disk on top and one stainless steel disk at the bottom, joined together by two circles of screws. On the acrylic disk there were five connection points, one gas intake which also worked as an outlet, one inlet hose, one outlet hose, a temperature probe and a pressure gauge. In addition, the linkage to the step motor that makes the wheel swirl was also connected here. On the stainless steel disk there is a track, shaped like a half pipe, were the liquid and gas reside, as well as two o-rings on either side of the track. On the sides of the half pipe there were placed small cylindrical plastic stoppers with regular gaps to create turbulence. On the base of the disk there was a connection for the ball joint. This ball joint was a part of the rack which held the engine and supported the wheel. This assembly was submerged in an insulated aluminum water bath, which again was connected to a water heater/cooler. Two boxes contained the electronics, one designated for motor control and one designated for data acquisition. All data was transmitted and received by a computer via USB, where a software program was used to control the rotation velocity and to read off the temperatures and pressure. The software recorded both the temperature form the water heater/cooler and the wheel in addition to the pressure in the wheel. From these recordings graphs could be made.

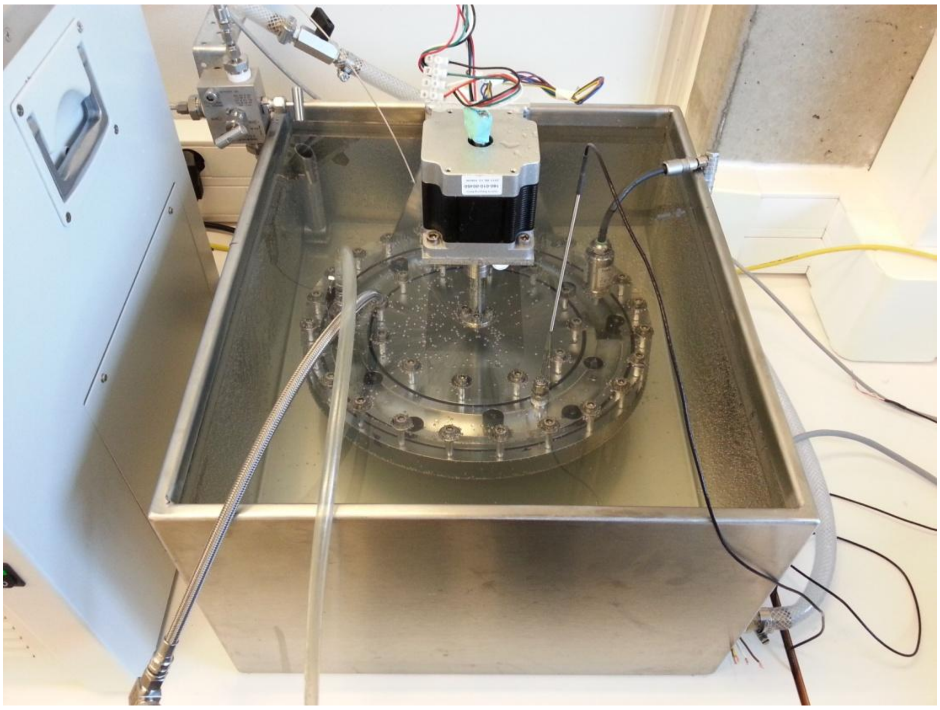


Figure 2.1. The table top wheel in its early phase, submerged in the water bath.

2.1.1 Detailed description of the apparatus

There is provided a test apparatus for the formation of gas hydrates that includes two disks, joined by screws to form a bench top wheel. The wheel had a total diameter of 325.00mm, with 275.40mm and 224.60mm for the exterior and interior diameter of the half pipe track in the bottom disk, respectively, figure 2.2.

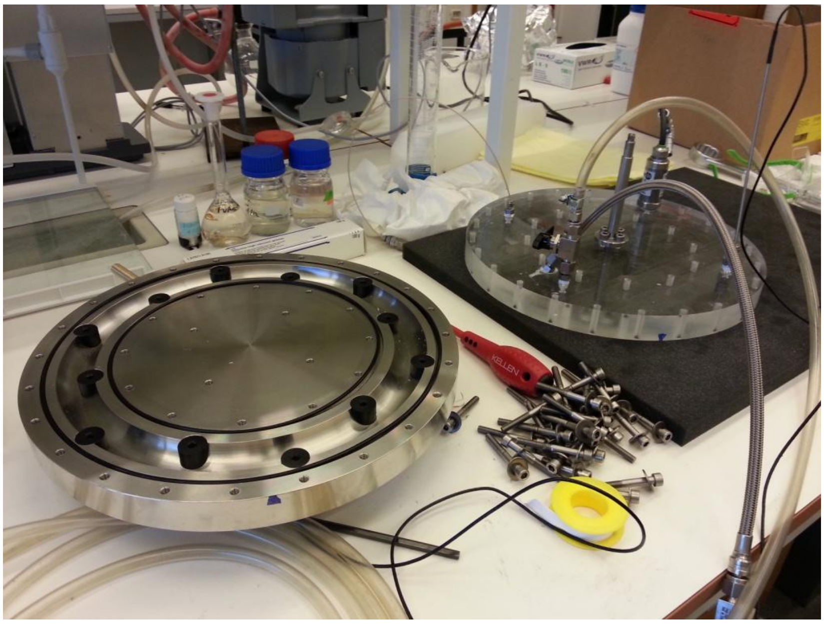


Figure 2.2. The two disks that make up the wheel. Bottom disk and top disk to the left and right respectively.

Furthermore, the half pipe, or semicircle, in the bottom stainless steel disk had a radius of 12.70mm and could contain approximately 200ml liquid. The two o-rings that were disposed on either side of the half pipe were 3.50mm wide. There were 12 plastic stoppers in the half pipe track, each with a diameter of 12,00mm and from the bottom of the disk there were 5.80mm to the bottom of the stoppers. The bottom disk had a height of 20.00mm. On the side of the disk there was a rod, which went into gap in the rack. This rod was necessary for preventing rotation and maintaining the Euler disk movement, figure 2.3.

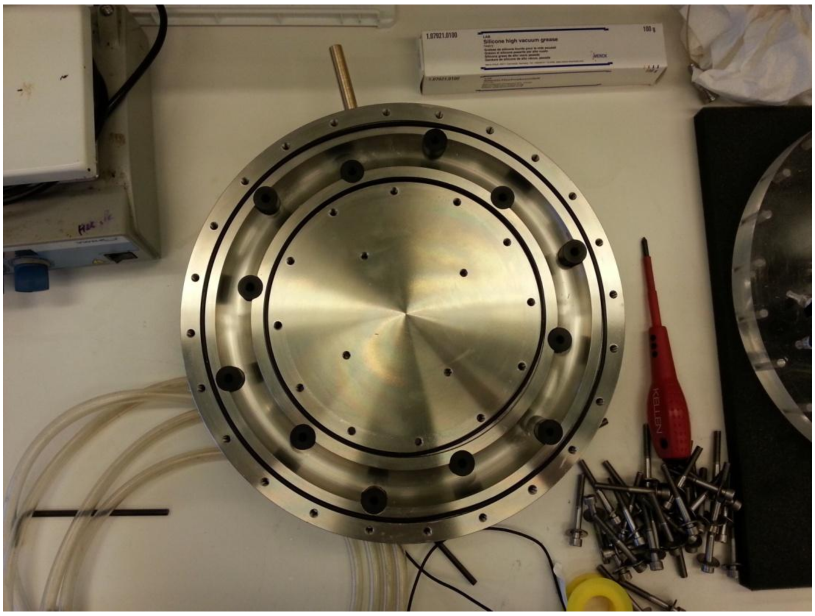


Figure 2.3. The bottom disk with all its attributes as seen from above.

On the base of the disk there was a female part of a ball joint, figure 2.4. This joint had a diameter of 70.00mm and had a concave curvature, which fit snugly with the male part of the ball joint.

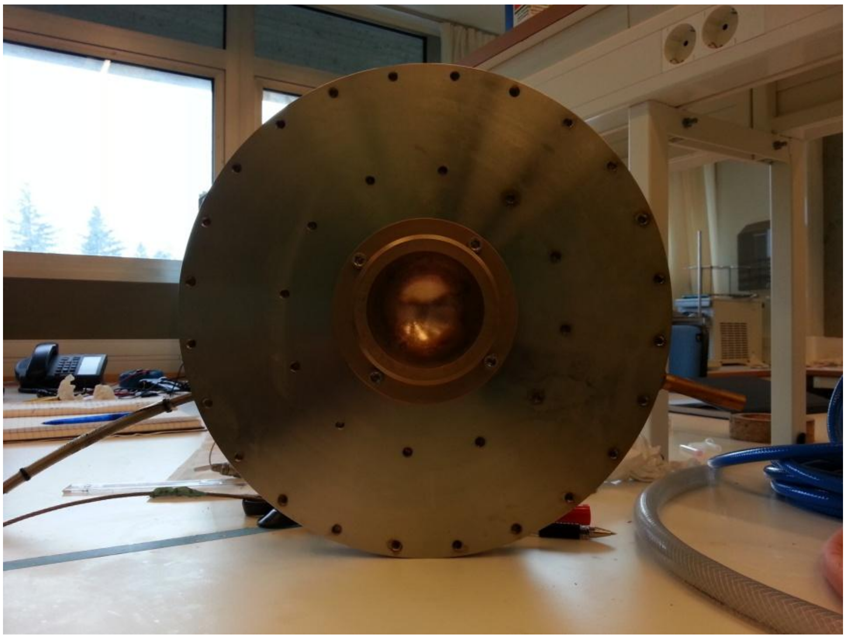


Figure 2.4. The base of the bottom disk showing female part of the ball joint.

The male part of the ball joint was composed of a hemisphere affixed to the bottom of the support rack, figure 2.5.

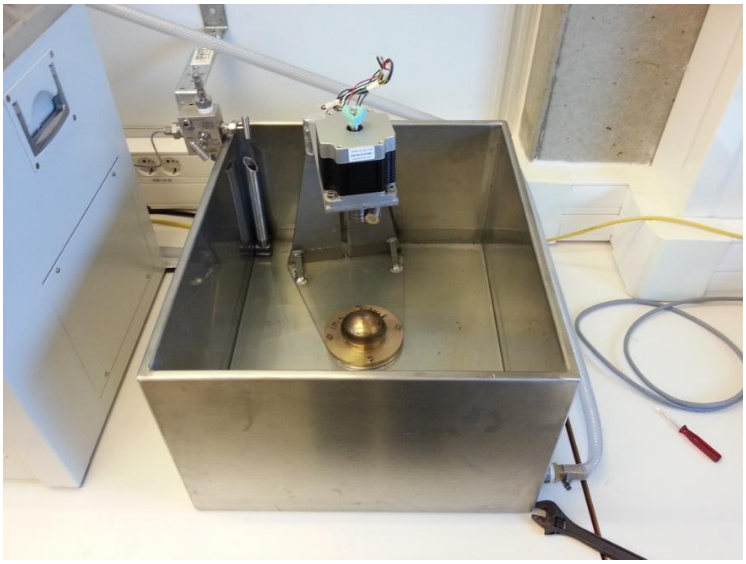


Figure 2.5. The support rack in the water bath, with the step motor on top and the male part of the ball joint at the bottom.

On top of this stainless steel disk, there was another disk made up entirely of acrylic. This polyacrylate disk was 25.00mm high, and with the same diameter as the stainless steel bottom disk. Five connection points served as gas inlet in addition to being outlet, inlet hose, outlet hose, temperature probe and a pressure gauge was on top of the acrylic disk, figure 2.6.

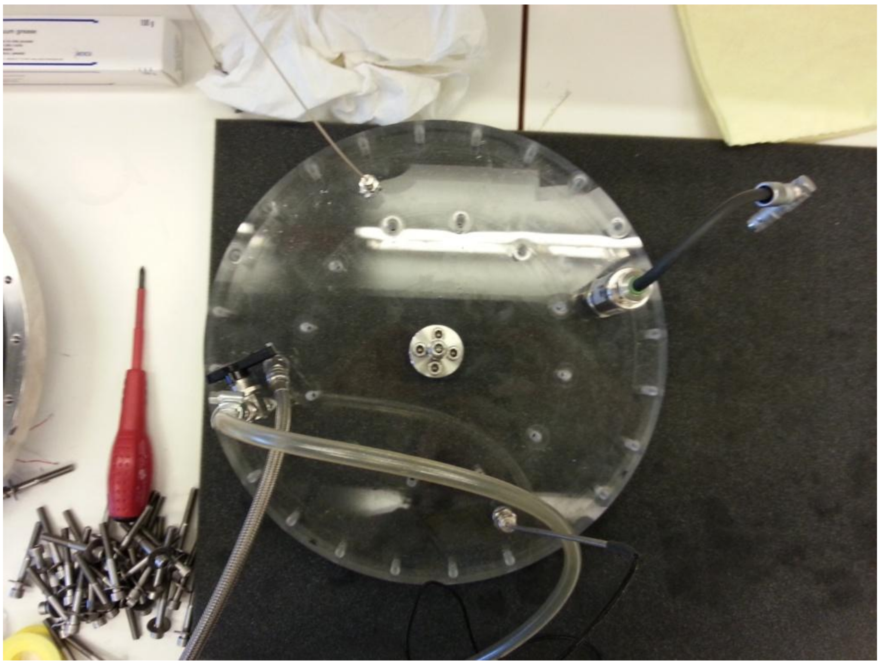


Figure 2.6. The acrylic top disk as seen from above, clockwise with pressure inlet/outlet, pressure gauge, temperature probe and inlet as well as outlet hose respectively. In the middle of the disk the connection to the step motor resided.

These two disks were sandwiched together by a set of two circles of screws. The inner circle consisted of 12 screws, while the outer circle consisted of 24 screws, all with the length of 14.20mm. The total height of the wheel, excluding the female part of the ball joint at the base of the bottom disk, was 45.00mm, figure 2.7.

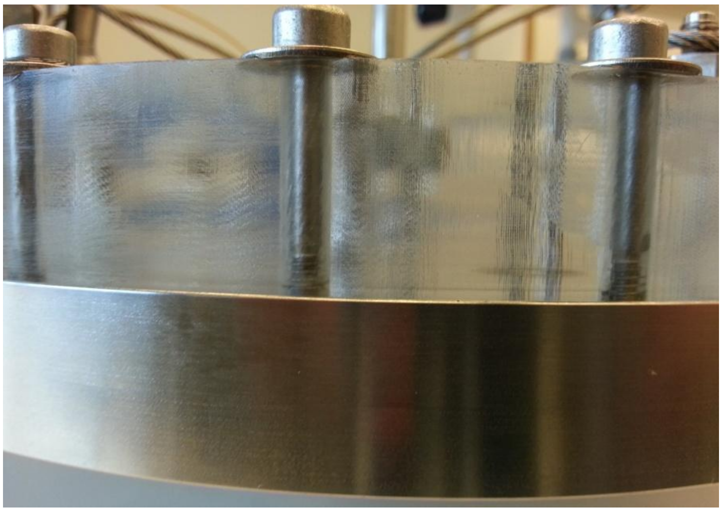


Figure 2.7. The wheel made up of the acrylic top disk and the stainless steel disk at the bottom, with the screws holding them together, as seen from the side. Here it is clear to see the height difference between the disks.

In the middle of the top disk, there were four screws which connected the bar to the disk, figure 2.8. This bar was placed normal to the disk, then inserted into a ball joint which came at an approximately 90° angle from the step motor. The motor was placed on top of the support rack, and swirled the wheel in a circular motion with a tilt. In being a so called step motor implies that the motion that the engine provides can be terminated at any desired angle, because signals was transmitted sequentially to electromagnets in the motor.

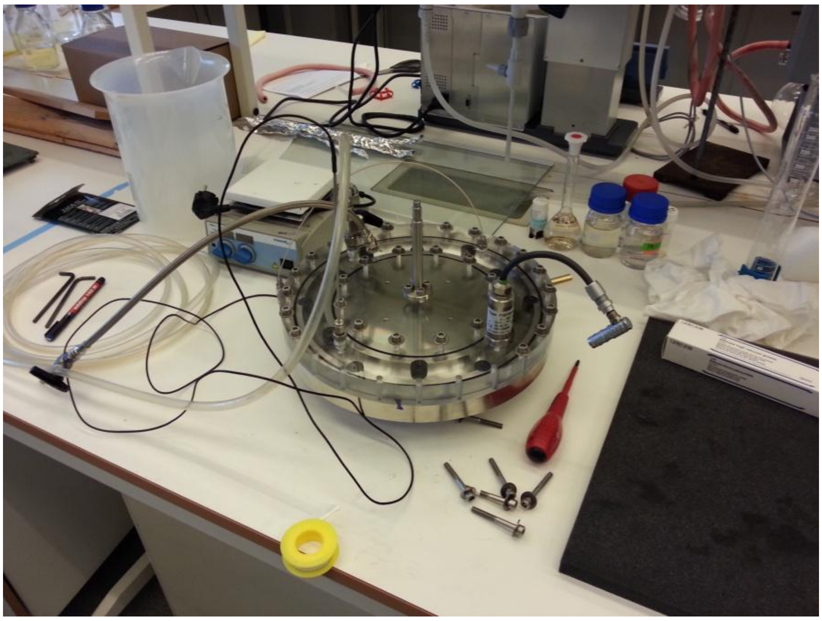


Figure 2.8. The wheel under assemble.

This assembly was submerged in a water bath. Only the top of the support rack, which include the step motor, was above the liquid. The water bath was made of aluminum, with insulation in between. It could contain approximately 40L of liquid. The water bath was rectangularly shaped, with external dimensions of 500.00mm in length, 425.00mm in width and 270.00mm in height. Internal dimensions being 475.00mm in length, 400.00mm in width and with the same height of 270.00mm, thus the water bath was 25.00mm thick. Each long side had a 1/2inch (1.27cm) pipe connections. Hoses that went to a water heater/cooler was connected too these pipe connections, figure 2.9. The water heater/cooler was of the type Julabo FP40-HL with temperature stability ±0.01°C. In addition it could contain 16L cooling fluid, had a pumping capacity flow rate 22−26L/min, a heating capacity of 2kW and a working temperature range form −40°C to 200°C. The heating/cooling fluid used was a mixture of mono ethylene glycol (MEG) and distilled water.

Figure 2.9. The whole assembly with the water heater/cooler to the left and the wheel submerged in the water bath to the right.

Both the temperature of the water heater/cooler, the temperature inside the wheel as well as the pressure in the wheel, in addition to controlling the rotation velocity, was recorded by electronics contained within two boxes. One box contained the high current needed to power the step engine in order to control the rotation velocity of the wheel, while the other contained the low current to sample the temperatures and the pressure, figure 2.10. The need for two boxes was based on the fact that low current are highly susceptible for interference by the high current, which could affect the data quality possibly render the delicate data sampling useless. Both boxes were connected to a computer.

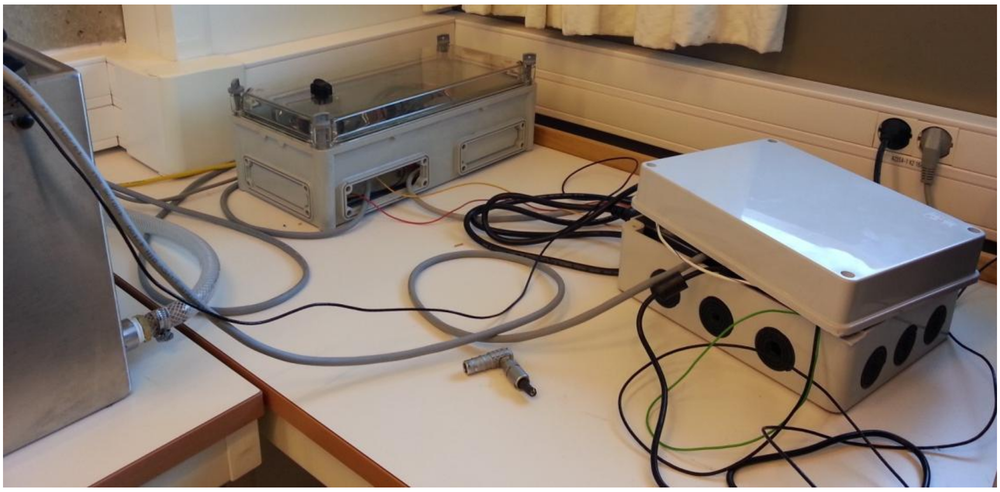
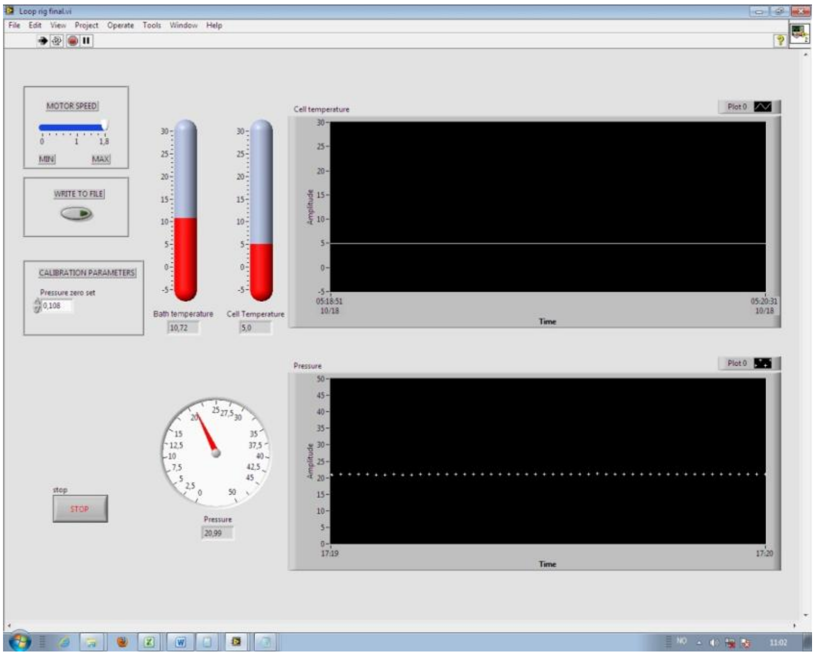


Figure 2.10. The two electronic boxes. The farthest away contains the electronic to control the rotation velocity of the disk, with a start/stop switch on top of the lid. The closest one contains electronic to interpret the pressure and temperature signals. They are connected to each other and the closest one is connected to a computer by an USB cable.

Here a software package made it possible to adjust the rotation velocity in addition to monitor the pressure and temperatures. The software was made by using LabVIEW (version 12.0f3) by National Instruments. Both temperatures and the pressure was sampled about every 10 second, figure 2.11. The data acquisition was done by LabVIEW with National Instruments USB6008. Two analog channels, temperature and pressure, set up in differential mode. The temperature measurement from the wheel was done by a PT100 element with LKMelectronic 224/1, 0−10V transmitter connected to the USB6008 in differential mode. It had a linear fault < 0.1%. The pressure measurement was done by TecSis pressure transducers P3276B086101 and P3325B086101 (used one at a time). Both of which with 0−5V transmitter connected to the USB6008 in differential mode, 3-wire and an accuracy 0.5% of full scale. An analog output to control the stepper motor velocity was also set up using the USB6008. Motor control card was Grinrød Laboratorier SMC3500V3, 3.5A, 16 microstep stepper motor driver interfaced to one analog output of USB6008 with Grinrød Laboratorier VTFV2 voltage to frequency converter. The stepper motor specifications were 200step/rev, 350Ncm holding torque, 4.2A/Phase hybrid stepper motor.



Pressure zero set 0,108

Bath temperature 10,72

Cell Temperature 5,0

Pressure 20,99

Figure 2.11. The final software interface. Top left is the bar to control the step motor velocity, underneath is the record button for data sampling, then there is a calibration parameter for the pressure and at the bottom a stop button. To the right of this there are two bars, the one to the left is the water heater/cooler temperature and the one to the right is the wheel temperature. Below is the pressure depicted by the pressure meter and by numbers. To the top right is a graphical representation of the wheel temperature, and below is a graphical representation of the pressure.

The whole experimental apparatus assembly consisted of many parts, figure 2.12.

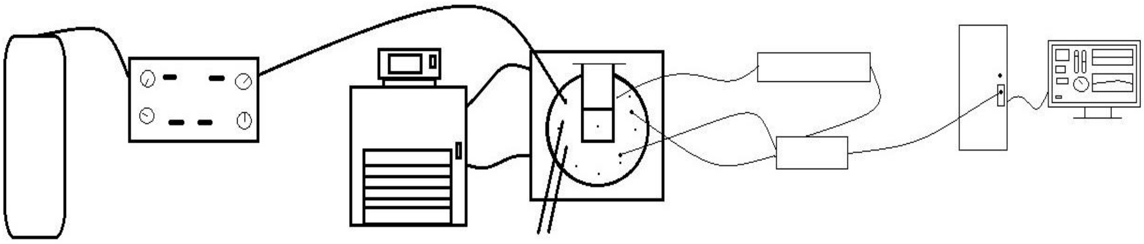


Figure 2.12. Schematic of the whole apparatus setup, from left to right: Gas, gas booster/distributer, water heater/cooler, the table top wheel in the water bath as seen from above, the two electronic boxes, computer and monitor with the software interface.

In being a prototype, some of these measurements on the wheel and the water bath may have changed some from blueprints to manufacture.

2.2 Experimental method

This experimental method description is described as conducted after several adjustments had been done to both the equipment and method:

- Each experiment was initialized by adding the required amount of liquid to the wheel. In this experiment this liquid consist of inhibitor solution as well as hydrocarbon liquid.
- The wheel was then pressurized with gas to 40bar (4000kPa).
- The swirling motion was initialized.
- Both the temperature of the water heater/cooler and the internal temperature in the wheel, in addition to the pressure in the wheel was recorded using the software.
- The water heater/cooler was set to the desired test temperature.
- Normally the test was run overnight.
- By visual inspection, it was observed for any hydrate formation.
- Ranged the inhibitor performance by visual inspection from A to E (A being best and E being worst).
- Terminated the data recording.
- Melted the potentially formed hydrates by ramping up the temperature.
- Terminated the rotation and depressurized the wheel.
- Emptied the wheel of all fluids.
- Washed the wheel three times with distilled water. If a new hydrocarbon liquid was to be used, an additional washing procedure was carried out: After first washing one time with distilled water, the new hydrocarbon liquid was added and finally the wheel was washed three times with distilled water. All by applying circular swirling motion.
- Conducted a new experiment.

In this particular experiment only anti-agglomerants were used as inhibitors. The anti-agglomerants used were a series of n-alkyl-tri(n-butyl)ammonium bromides. As mentioned in the theory, anti-agglomerants need a hydrocarbon liquid to function properly.[6,60] The hydrocarbon liquids, which represented the oil phase, were two different "white spirits", in addition to n-decane and o-xylene. They represented the light hydrocarbons, mimicking condensate.

At a temperature of 20°C in the table top wheel, through the inlet hose a total volume of 60mL was added. Of these 60mL, 40mL was the hydrocarbon liquid and 20mL was the aqueous solution, with or without anti-agglomerants or electrolytes. This gave a water cut of 33%. The wheel was then in a careful and controlled manner pressurized with synthetic natural gas (SNG) provided form Yara Praxair. The gas composition is given in table 2.1. This makes Structure II hydrate. Because of safety reasons, the wheel was not pressurized any higher than 40bar. The software was used to read off the pressure inside the wheel. Once on 40bar, the pressure decreased rapidly if a hydrocarbon liquid had been added in the wheel, especially if rotation was applied. The pressure quickly drops, because the gas dissolves more in the hydrocarbon phase than in water alone.

Thus, the gas diffuse into the hydrocarbon phase. Therefore the wheel was set in motion, and when the pressure had stabilized, it was pressurized again. This was done until the pressure was constant at the needed pressure. Hence, after pressurizing to 40bar, the wheel was rotated until the pressure drop halted. Then it was pressurized up to 40bar again, and this was done until the pressure stabilized on 40bar under continuous rotation. The measured pressure was gauge pressure. The rotation speed was 18rpm. The pressure shown by the software had a tendency to fluctuate, which made the pinpointing of exactly 40bar impossible. But ±1−2bar have no impact on the measurement, but ±1−2°C would have had. Thus it was more important to ensure that the temperature does not fluctuate too much.

Table 2.1. Synthetic natural gas (class 2).

Component	mole%
Methane	80.40
Ethane	10.30
Propane	5.00
CO_2	1.82
Iso-butane	1.65
n-butane	0.72
N_2	0.11

The same software was no used to record data, from both temperatures and the pressure. The water heater/cooler was then set to 0°C (onset, T_o= 0°C) , down from the experiment initiation temperature of 20°C. It was left like this overnight. The water bath reaches 0°C, and this translates to a temperature in the wheel of approximately 0.05°C. Thus, the table top wheel operates by applying an isochoric process. The next day the data recording was terminated. At the same time the wheel was visually inspected for gas hydrate formation.

The ranking procedure was adopted from other research groups,[75,96] but since this being a unique and new equipment, alterations to this ranking was done. Visual observations include documenting a rating assessment of the content of the wheel. A determination if hydrates was visible, an evaluation of any visible hydrate surface adhesion properties and an estimate of liquid levels. The performance of the anti-agglomerants was ranked from A to E according to the visual observations as follows:

A. Fine dispersed hydrates without any deposits.
B. Dispersed hydrates with minor deposits, coarser hydrate particles.
C. Significant deposits and/or slushy plug, but most of the free liquid was moving.
D. Slushy hydrate plug, with very viscous free water.
E. Hard hydrate plug.

A pass was usually rated as an A or B, and judged upon if no hydrates form. If hydrates did form the crystals must remain small, neither agglomerate, nor adhere to any surface in any significant manner and/or the liquid viscosities remain low. Thus forming a hydrate slurry, figure 2.13. Ranking C was given when the hydrate formation surpass the conditions described above. Here the deposits were significant and could result in a slushy plug. However, most of the liquid remained free with low viscosity. This ranking was on the threshold of failing, thus a marginal pass.

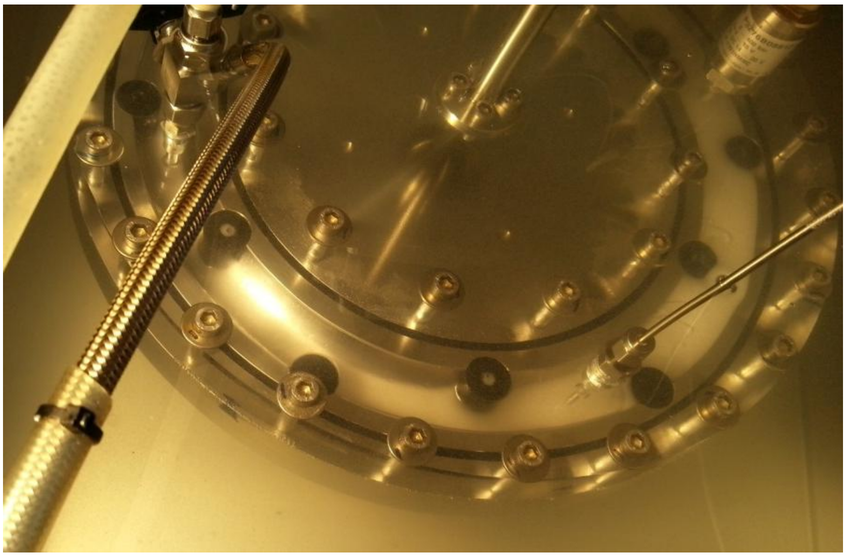


Figure 2.13. A section of the wheel showing the hydrate slurry formed, which gave rank A.

A fail was usually rated as either D or E, both of which formed plugs but an E plug was much worse than an D plug. Further criteria being if the hydrates form plugs, or deposits leading up to a plug and/or the viscosities increase significantly, figure 2.14. None the less, a D ranking gave a slushy plug with very viscous liquid. While an E ranking gave a hard, totally solid plug, with no free liquid.

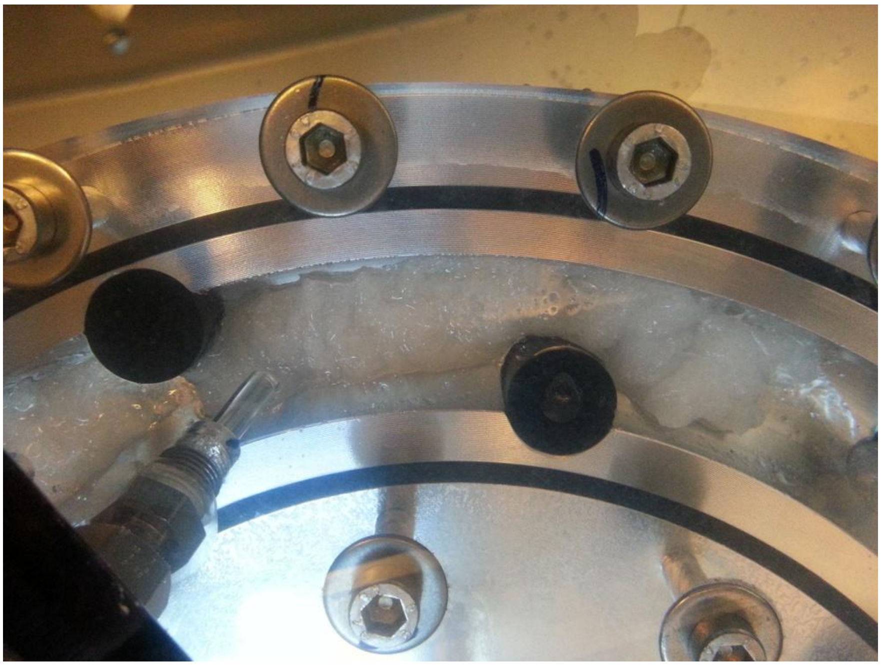


Figure 2.14. A section of the wheel with massive hydrate formation, resulting in a plug of rank E.

The water heater/cooler was then set to 20.1°C, this gave 20°C in the wheel, to melt potentially formed hydrates and to reach the initiation temperature for conduction of an experiment. The motion was halted and the wheel was depressurized. All liquid was emptied from the equipment. It was then washed three times with distilled water, by rotation of the wheel. If a new hydrocarbon liquid was to be used in the following experiment, some alterations were done to this washing procedure. After it had been washed one time with distilled water, the hydrocarbon fluid was added and finally washed three times with distilled water. It was important to get rid of as much as possible of the remaining liquid in the wheel, before conducting a new experiment.

The memory effect of water was not considered in this experiment, only fresh water without any direct hydrate history was used. This was because it can be very time consuming to conduct experiments that involve this effect, especially for apparatus that heats up and/or cools down slowly. This was done despite the fact that the memory effect can produce reliable and repeatable hydrate formation, and that hydrate formation may not even occur at all without it.[97]

2.2.1 Anti-agglomerants used in the experimental work

All the anti-agglomerants used in this experiment had been previously synthesized in the laboratory.[96] They all were n-alkyl-tri(n-butyl)ammonium bromides with varying chain lengths. The chain varied in length from octyl (C8) to octadecyl (C18), in addition to coco (a mixture of chain lengths, mostly C12−C16 range).

The synthesized anti-agglomerants were n-octyl-tri(n-butyl)ammonium bromide (OBAB, C8), n-decyl-tri(n-butyl)ammonium bromide (DBAB, C10), n-dodecyl-tri(n-butyl)ammonium bromide (DDBAB, C12), n-tetradecyl-tri(n-butyl)ammonium bromide (TDBAB, C14), n-hexadecyl-tri(n-butyl)ammonium bromide (HDBAB, C16), n-octadecyl-tri(n-butyl)ammonium bromide (ODBAB, C18) and coco-tri(n-butyl)ammonium bromide (CBAB). All of which, with the exception of ODBAB, which were partially soluble in both aqueous and hydrocarbon phases and formed oil-in-water emulsions, were water soluble at the test concentrations and did not form emulsions.

All anti-agglomerant concentrations were based on the aqueous phase, thus weight percentages (wt%) of anti-agglomerant used was based on the water phase. They were weighed out and dissolved in distilled water with or without NaCl (assay > 99.5% from VWR international).

2.2.2 Constant cooling test procedure

At 20°C the pressure in the wheel was set to about 40bar. In motion the wheel was cooled down from 20°C to 0°C, with a cooling rate of 7.2°C/h. Since the wheel was a closed system, it implies that a pressure drop was observed during the constant cooling. A deviation from the constant pressure drop, however, indicated gas consumption from hydrate formation. Sometimes, if very rapid hydrate nucleation occurred, an exothermic spike for the temperature in the wheel was observable on the graphs. However, hydrate nucleation might have been initiated earlier but was undetected.

The driving force for hydrate formation in these experiments was subcooling, which was given by the difference between the hydrate equilibrium temperature (hydrate dissociation temperature) at the experimental pressure in addition to composition and the onset temperature of the respective constant cooling experiment.[6,37]

Dissociation temperature was determined to be 11.50°C for 33% water cut. Thus, the subcooling used in this experiment was about 11.50°C, since the onset temperature was approximately 0°C in the table top wheel.

2.3 Adjustments to both the apparatus and method

As it can be with all brand new equipment, and more so with prototypes, there may be many things that must be sorted out before and under tests.

During the initial test phase of the table top wheel, several gas leaks emerged. This led to dismantling the table top wheel, which was taken apart and cleaned. Some silicone grease was disposed on the steel disk and on the two o-rings inside to help in making a better gas proof seal. The disk was subsequently assembled by tightening the screws in an orderly fashion. As far as it was possible the same amount of force was used on each of the screws. It was then placed back in the water tank. A pressure test confirmed that the newly made seal did not leak. The first experiments were only done with water, before anti-agglomerants in addition to a hydrocarbon fluid was added. Also, all the electronics that made it possible to control the rotor speed of the engine, interpret pressure gauge and temperature signals was all placed in one box, figure 2.15. This gave some fairly big interference on the pressure and temperature signals. Thus the electronics had to be separated, one box with low current circuits (pressure gauge and temperature) and another box with high current circuit (control of the engine rotor speed). Line filters were also installed in each of the boxes to reduce EMI (Electromagnetic Interference).

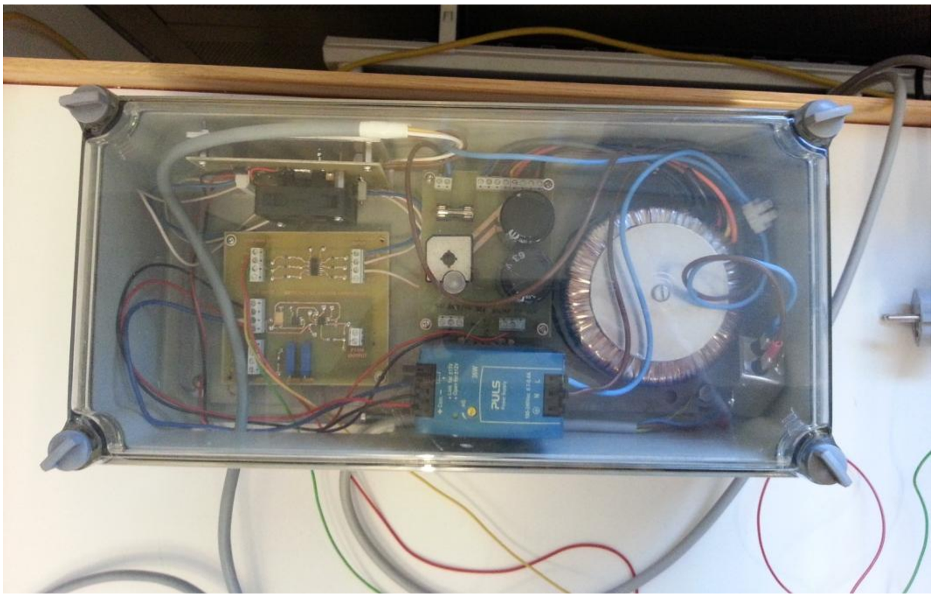


Figure 2.15. The electronic before it was divided into two boxes.

In the first initial tests, neither the temperature in the water heater/cooler, the temperature in the wheel nor the pressure could be measured due to ongoing development of the software, figure 2.16.

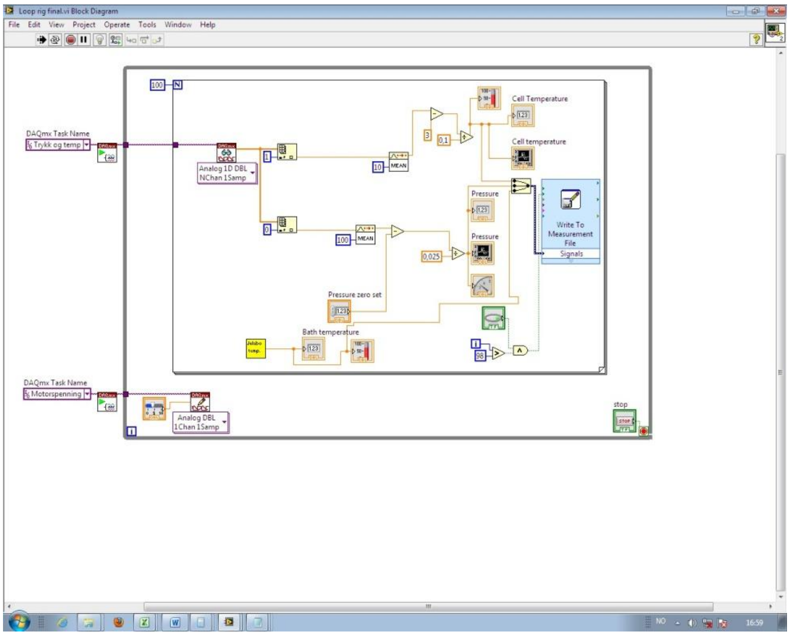
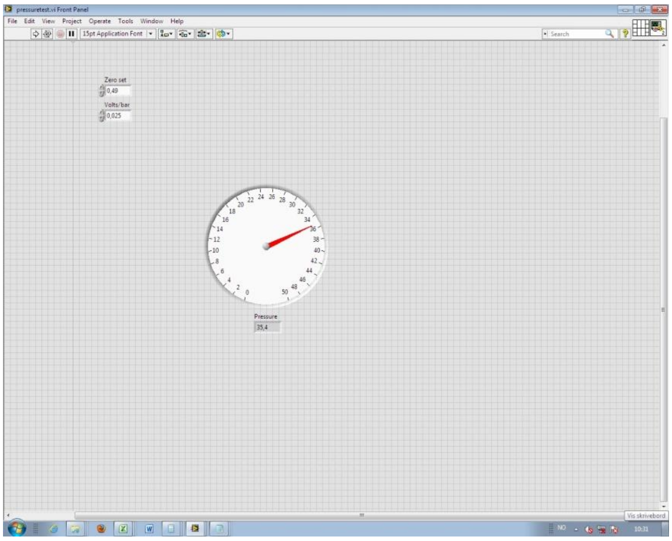


Figure 2.16. The LabView block diagram.

The wheel was pressurized by the aid of a pressure meter on the control panel of a gas booster/distributer, while the pressure gauge on the wheel was calibrated. This pressure meter showed only an approximate pressure, figure 2.17. Afterwards the gas booster/distributer was only used to distribute the gas to the wheel.

Figure 2.17. The pressure gauge used before the pressure gauge on the wheel had been calibrated. The bottom left pressure gauge was used.

When the pressure gauge was calibrated, an early version of the software was used, figure 2.18. This could be used to read off a more accurate pressure. Later the final software interface made it obsolete, but the old version still had its place. This because the more sophisticated final version had more program loops which made the pressure meter lag. Therefore, when the wheel was to be pressurized the old version vas used.



Zero set 0,49

Volts/bar 0,025

Pressure 35,4

Figure 2.18. This was the original software interface. In the upper left corner the zeroing and bar/volts parameters could be adjusted. The pressure was read by the pressure gauge and the corresponding number underneath.

In order to try to increase the hydrate formation temperature, both Ocma clay and five small stainless steel balls were tried, figure 2.19. The flow regime in the table top wheel was laminar, and they were added in an effort to try to increase the turbulence of the flow. The stainless steel balls was added by unscrewing the pressure gauge and inserting them in through the opening. They had a tendency of hitting the temperature probe, and thus hydrate formation initiated very often at this place in the table top wheel.

Figure 2.19. A section of the wheel showing the five stainless steel balls added in an effort to increase the turbulence in the system.

Because the pressure and suction pump on the water heater/cooler could not be separately adjusted, it caused the water heater/cooler to empty itself. A couple of valves on the hoses that went to and from the water heater/cooler made the situation much better. However, another problem arose, air bubbles impaired the view to the wheel. This made it extremely hard to observe for any hydrate formation without switching off the water heater/cooler, figure 2.20. Adjusting the valves made it somewhat better, but moving the water heater/cooler had very little effect.

Figure 2.20. The air bubbles severely obstructed the visibility to the wheel making it difficult to observe for hydrate formation.

The best effect was achieved by applying a hose to make the water outlet in the water bath to be underneath the waterline, figure 2.21.

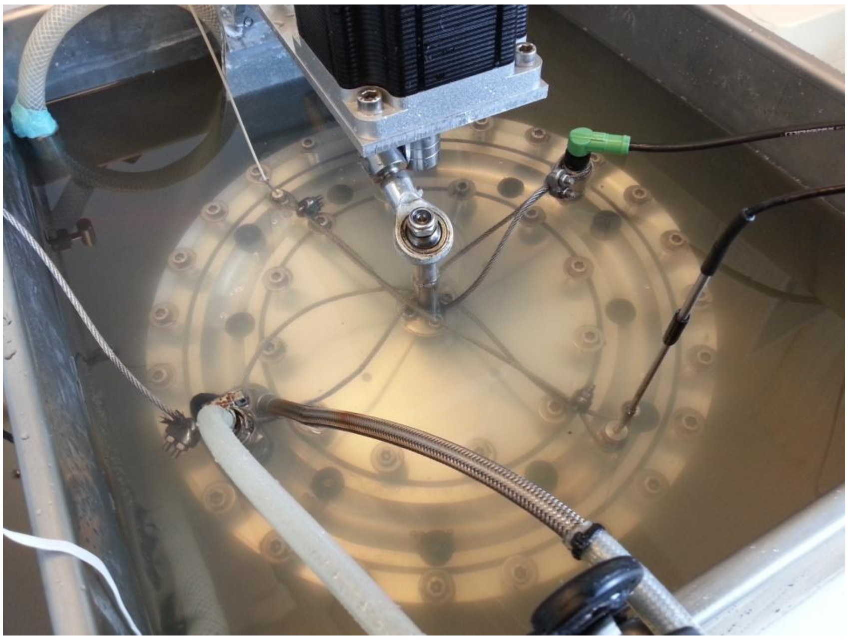


Figure. 2.21. The hose aided in the clarification of the view.

The liquid in the water bath was a mixture of distilled water and MEG. If the concentration of MEG in the mixture was too high, the pH of the liquid would drop. This is because MEG in contact with the oxygen in the air makes an acid, which could then possess a corrosive effect on the metals.

It was desirable to have video recording of the experiments. Several means were thought of in order to approach the problem. Since there were so many air bubbles in the water bath, one of them were to make a waterproof housing for the camera and mount it to the wheel. But when the air bubble problem was diminished, a conventional camera placed above the wheel was the approach that could be used.

To make the apparatus safer to operate, a wire was used to secure all the connections to the top disk, figure 2.22.

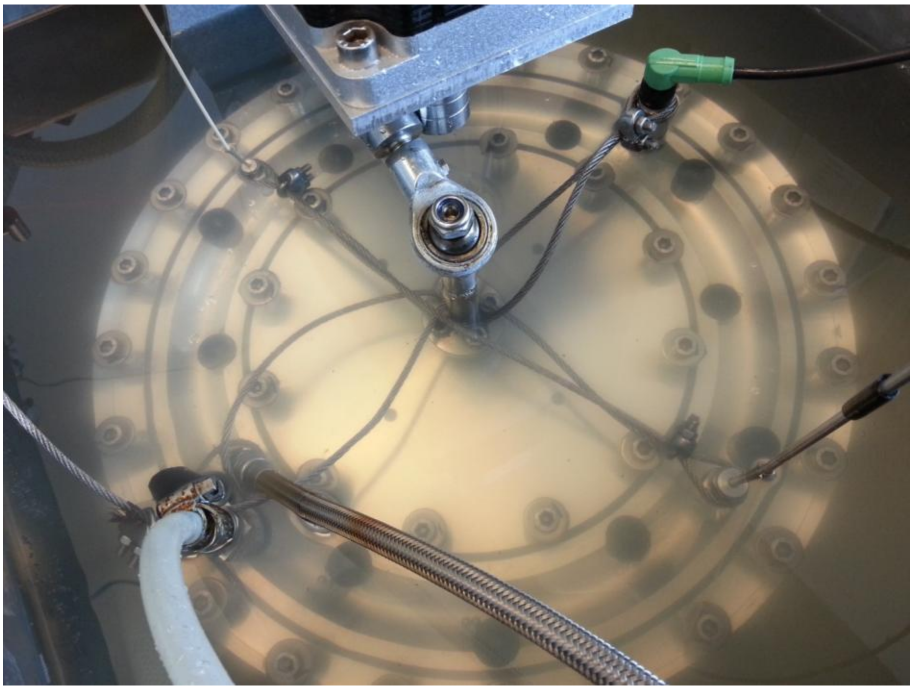


Figure 2.22. The wheel in the water bath with the wire strapped around all the connections to the acrylic disk.

The wheel was pressurized without any liquid to make sure there were no leaks.

A full list of all experiments in addition to all the adjustments, as well as blueprints from the apparatus can be found in the appendix.

2.3.1 Issues associated to the apparatus

During the experiments, issues can arise despite if the apparatus used is a well proven laboratory device or a prototype. Even more so, several issues occurred with this prototype table top wheel.

After 42 experiments, the original pressure gauge was broken, and not reparable. It was replaced with a new sensor. Also, after 58 experiments the quick gas release broke. It was also replaced with a new one.

It was always a question of if and for how long the acrylic disk would withstand the pressure used during the course of the experiments, since this being the single most vulnerable part of the entire apparatus, figure 2.23.

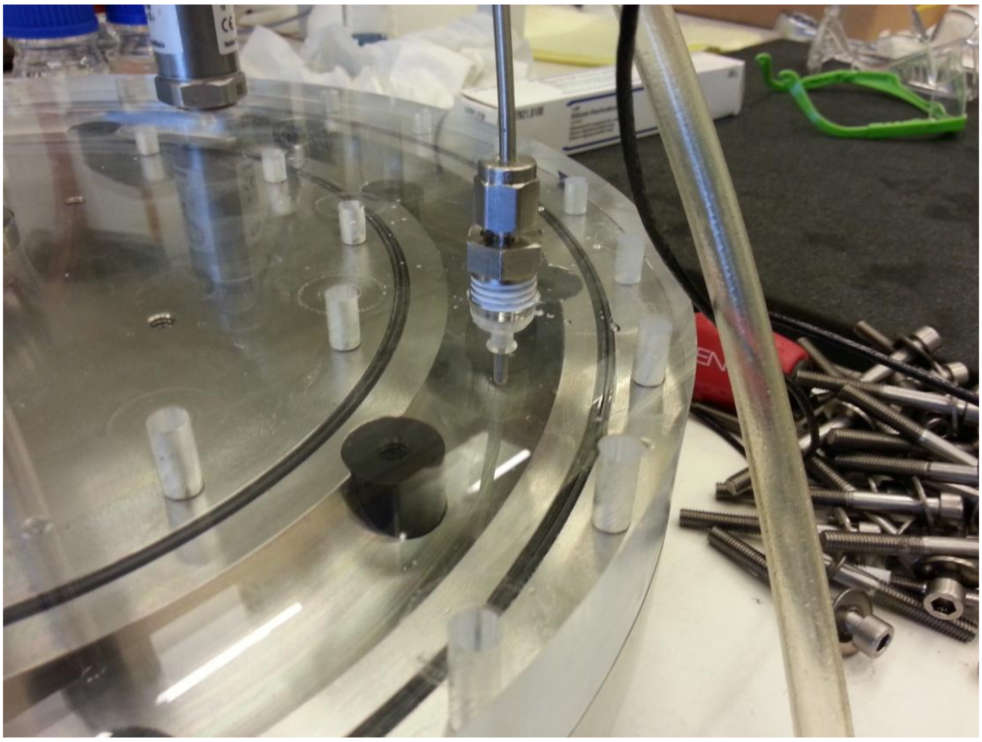


Figure 2.23. The wheel in its early stages, showing the temperature probe with no cracks in the acrylic disk.

After several experiments small cracks emerged at the connection points to the acrylic disk. They were superficial and possessed no risk at that point. All connections were then secured with steel wire in order to prevent the connectors from acting as projectiles in the case of catastrophic failure. Over several more experiments they had evolved and become somewhat bigger, still no risk. Then after 59 pressurized experiments the cracks suddenly expanded severely, figure 2.24. Further experiments were terminated at this stage.

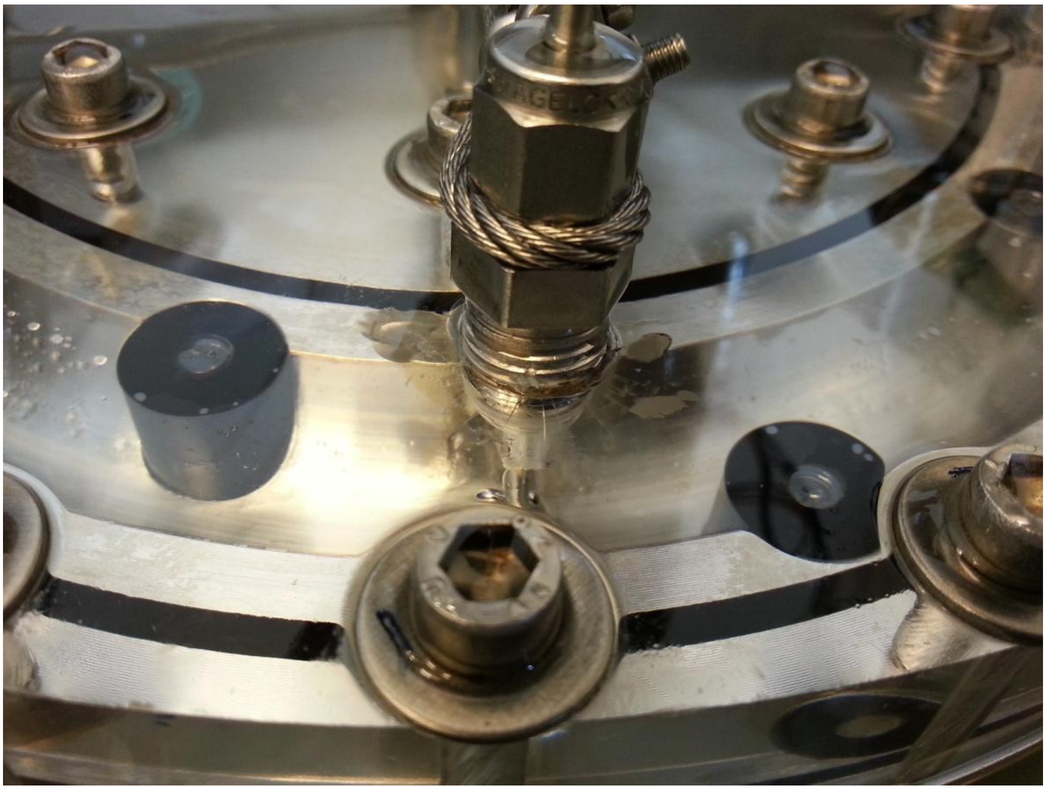


Figure 2.24. The wheel after 59 experiments, showing the severe cracks around the temperature probe.

2.4 Experimental results

In this experiment, all tests were conducted with constant cooling. Some preliminary experiments were done so to validate the operation of the apparatus and determine the experimental method to follow. Then purely ranking experiments of the different anti-agglomerant chain lengths were done, in both distilled water and 1.5wt% NaCl solution. These were compared to the ranking given on earlier experiments over the same anti-agglomerant range in a rocking cell apparatus. Some anti-agglomerants were tried out in 7wt% NaCl as well as different hydrocarbon fluids.

The anti-agglomerants were a range of single-tail quaternary tributylammonium bromide surfactants, with varying alkyl chain length from 8−18 carbon atoms, in addition to a mixture of chain lengths manly in the range of 12−16 carbon atoms. This was done in order to determine the influence of the length of the hydrophobic tail on the performance of the anti-agglomerants. Further experiments on the effect of salinity on the performance were conducted. The salinity was varied from 1.5wt% to 7wt%. The influence on anti-agglomerants performance by the usage of different hydrocarbon fluids were also tried out. The different hydrocarbon liquids were two different white spirits from Effekt by Europris AS and from Kemetyl Norway AS.

They both contained the same substances as well as the same ratio between aliphatic and aromatic hydrocarbons, hence they contained naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons and 15−30% aromatic hydrocarbons. The two other fluids were n-decane ($C_{10}H_{22}$, 1L= 0.73kg, M= 142.29g/mol, assay (GC, area%)≥ 94%, density (d 20°C/4°C)= 0.728−0.732) and o-xylene (C_8H_{10}, 1L= 0.88kg, M= 106.16g/mol, assay (GC, area%)≥ 98%, density (d 20°C/4°C)= 0.878−0.881) both from Merck Schuchardt OHG.

A typical graph from the experiment contained both temperatures from the water heater/cooler and the wheel, in addition to the pressure in the wheel, figure 2.25 and 2.26.

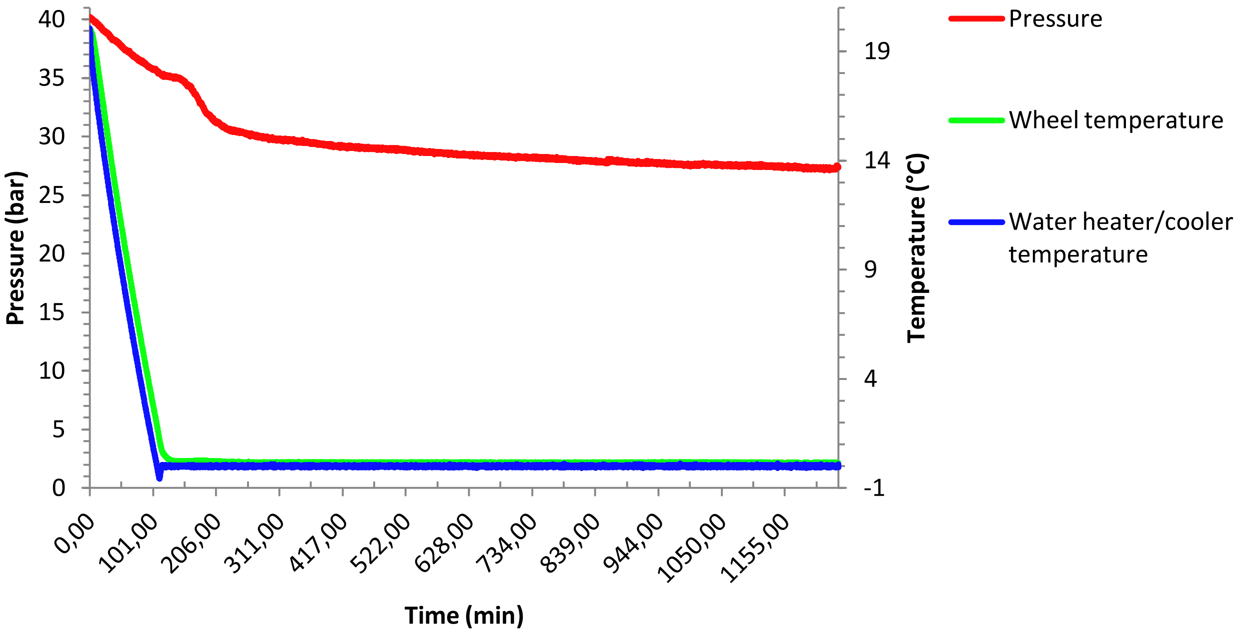


Figure 2.25. A typical graph of an entire experimental run. 2000ppm TDBAB in n-decane which gave a rank B.

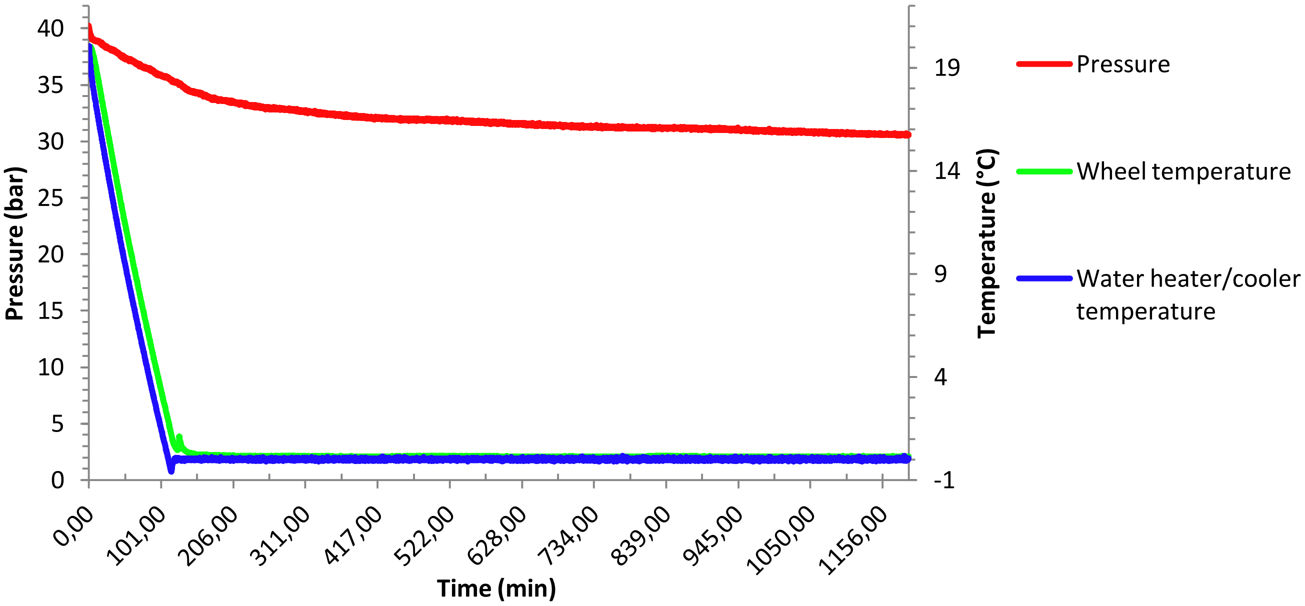


Figure 2.26. A typical graph of an entire experimental run. 1000ppm TDBAB in n-decane which gave a rank E.

2.4.1 Preliminary experiments

These experiments were conducted in order to validate if there indeed could form gas hydrate in the apparatus, in addition to come up with the experimental method in which the experiments should follow. In these experiments only distilled water with or without white spirit were conducted. Neither the temperatures nor the pressure could be logged in these experiments.

The temperature in the water bath was measured by a digital thermometer every 5 minutes for 45 minutes during a cool down. At the same time the temperature in the water heater/cooler was shown on a display and written down. They were compared and a deviation of 1.26°C was calculated in temperature difference from the water heater/cooler to the water bath.

A pressure test was conducted to make sure that there were no leaks in the table top wheel, which it confirmed that there were no significant leaks.

The wheel was filled with approximately 50ml when only distilled water was used. In the very first experiment 30bar was used, then 40bar was chosen for the rest. The hydrate formation temperature was lower than. Therefore different means were tried to enhance the hydrate formation temperature, table 2.2.

Table 2.2. Experiments with only distilled water and the effect of additives to assess in hydrate formation, the stainless steel balls temperature was an average of three experiments.

Additive	Hydrate formation temperature (°C)
No additive	1.40
Ocma clay	2.30
Stainless steel balls	10.26

In addition to distilled water, different water cuts were tried, both 20% and 33% (12ml distilled water and 48ml white spirit, 20ml distilled water and 40ml white spirit respectively). Both the formation and dissociation temperature was determined. Dissociation temperature measurement experiments are extremely time consuming, because the temperature are increased minutely and held for a given time at each step. Here four such experiments were done in order to determine the dissociation temperature both with and without white spirit. They were conducted by after hydrate had formed, the temperature was set to 10°C and held there for 15 minutes. It was then increased to 11°C for 15 minutes. From 11.1°C and up to the dissociation temperature, the interval was increased by 0.1°C and held for 10−15 minutes. The formation and dissociation temperature was tried measured for distilled water, 20% and 33% water cut as well, table 2.3.

Table 2.3. The formation and Dissociation temperatures for distilled water, 20% and 33% water cut. For the two latter an average of two experiment on each was calculated.

Temperature (°C)	Distilled water	20% water cut	33% water cut
Formation	10.26	4.87	4.20
Dissociation	16	11.35	11.50

Different rotation velocities were also tried out. Here the rotation was increased from 18rpm to 36−38rpm. Here no difference was observed between the different velocities, so 18rpm was the rotation speed used.

2.4.2 Effect of varying anti-agglomerants chain length in both 1.5wt% NaCl solution and distilled water

This was the main effort in this experimental work. In all 29 experiments on the effect of varying chain length as well as the effect of 1.5wt% NaCl solution were conducted. These experiments were the same as the ones carried out in the rocking cell apparatus, with the same parameters as far as anti-agglomerant range, gas and liquids. Thus, the same gas composition and liquid composition was used.

The main objective was to determine the minimum anti-agglomerant concentration required to get a pass. Then these results from this equipment were compared with the results from the rocking cells, in order to validate this new equipment. If the same trend could be found between these two apparatuses, it means that the table top wheel is approved at least for this types of anti-agglomerants.

Comparison of adequate concentrations of anti-agglomerants and their chain length for a pass, from both equipments is summarized in table 2.4 as well as shown graphically in figure 2.27. Adequate anti-agglomerant concentration in both distilled water and 1.5wt% NaCl solution in the table top wheel represented graphically in figure 2.28.

Table 2.4. Concentrations (ppm) needed of the various chain length anti-agglomerants in both 1.5wt% NaCl solution and distilled water, for both the wheel apparatus and the rocking cells to achieve a pass. Neither OBAB nor DBAB in addition to ODBAB were there carried out any experiments in distilled water. This is because a concentration of 15000ppm in 1.5wt% NaCl either gave no pass or barely passed.

AA type	**Wheel**		**Rocking cells**	
AA chain length	**Distilled water**	**1.5wt% NaCl**	**Distilled water**	**1.5wt% NaCl**
OBAB	-	No pass	-	No pass
DBAB	-	No pass	-	No pass
DDBAB	4000	3000	3000	250
TDBAB	5000	2000	5000	1000
HDBAB	15000	2000	10000	1000
ODBAB	-	15000	-	10000
CBAB	5000	4000	4000	500

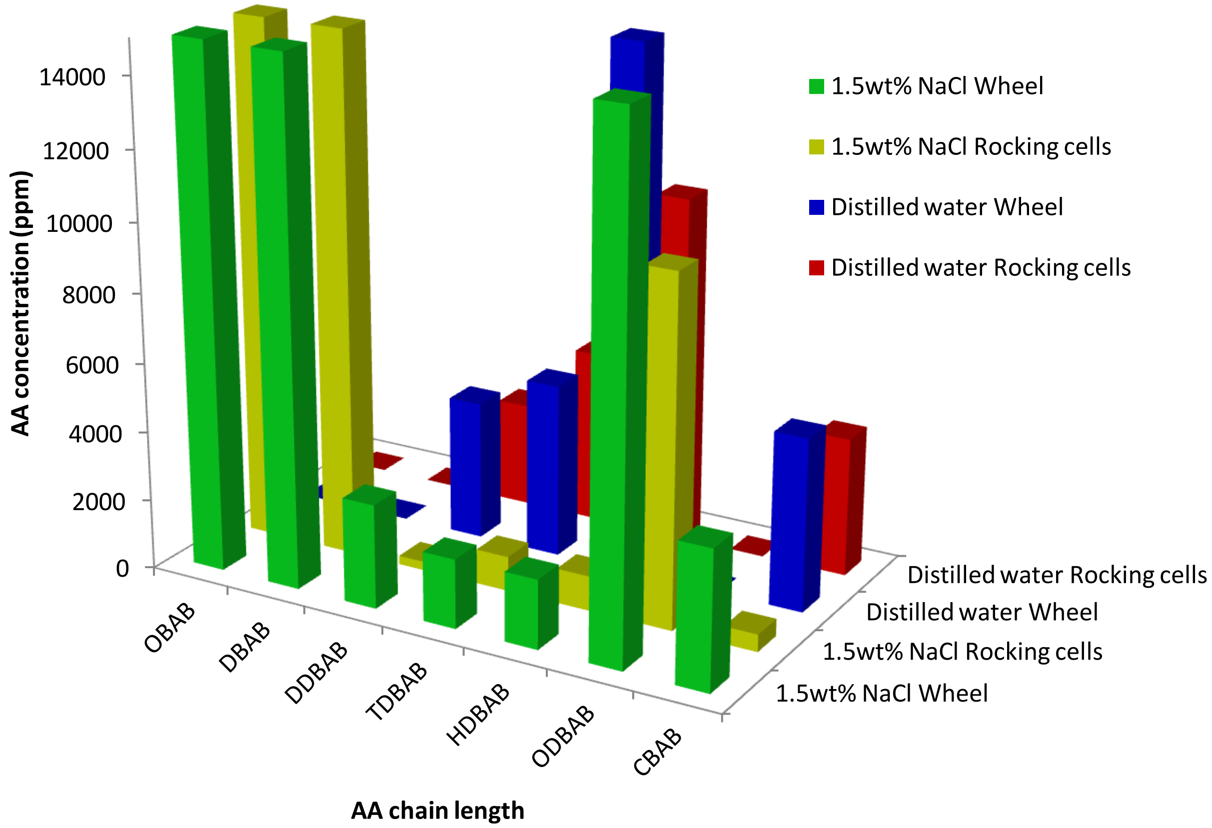


Figure 2.27. Both the results from the table top wheel and the rocking cells compared.

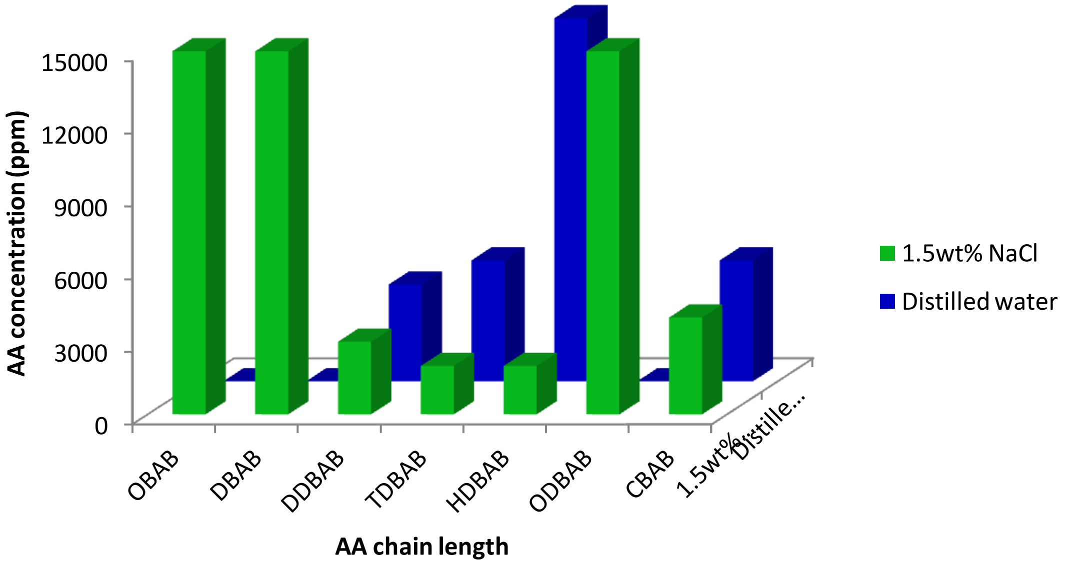


Figure 2.28. Performance in the table top wheel of the anti-agglomerants in 1.5wt% NaCl solution and distilled water respectively.

2.4.3 Effect of varying anti-agglomerants chain length in distilled water, 1.5wt% and 7wt% NaCl solution

Different electrolytes concentrations effect on DDBAB and TDBAB were tied.

Some experiments on DDBAB and TDBAB were conducted with 7wt% NaCl solution. The results of which, in addition to 1.5wt% NaCl solution and distilled water, can be found in table 2.5 and in figure 2.29.

Table 2.5. The influence on the efficiency concentration (ppm) of both DDBAB and TDBAB in distilled water, 1.5wt% NaCl solution as well as and in 7wt% NaCl solution.

AA chain length	**Distilled water**	**1.5wt% NaCl**	**7wt% NaCl**
DDBAB	4000	3000	1000
TDBAB	5000	2000	500

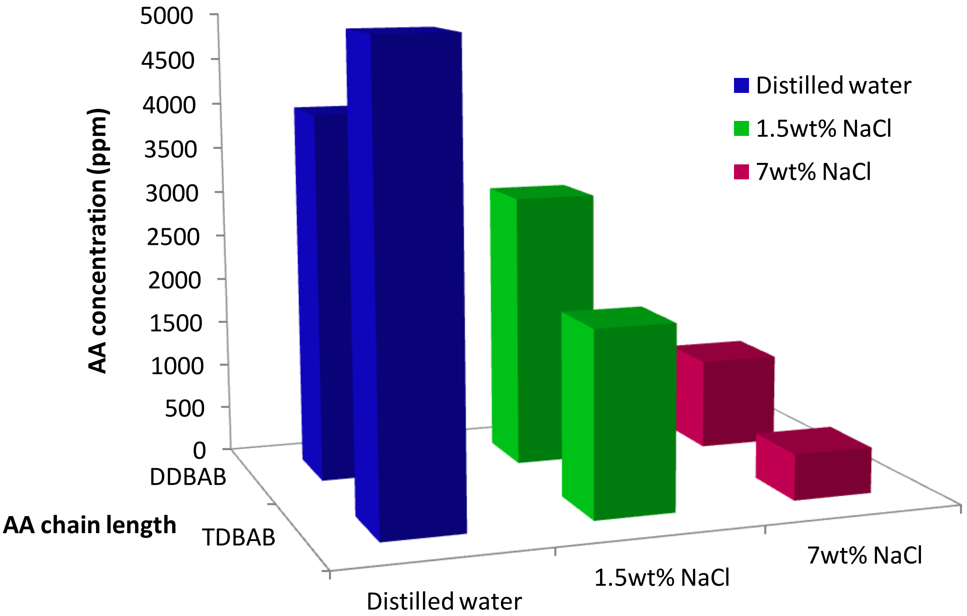


Figure 2.29. The effect on DDBAB and TDBAB in distilled water, 1.5wt% NaCl solution and 7wt% NaCl solution.

2.4.4 Effect on anti-agglomerants chain length efficiency by hydrocarbon fluids

Different hydrocarbon liquids were tried out to determine the effect they had on anti-agglomerant performance.

Two different white spirits were tried out on DDBAB, TDBAB and HDBAB, table 2.6 and figure 2.30.

Table 2.6. The different anti-agglomerants and the effect the different white spirits had on the concentrations (ppm) of the anti-agglomerants to get approved.

AA chain length	**White spirit Effekt, Europris**	**White spirit Kemetyl**
DDBAB	4000	5000
TDBAB	5000	5000
HDBAB	15000	No pass

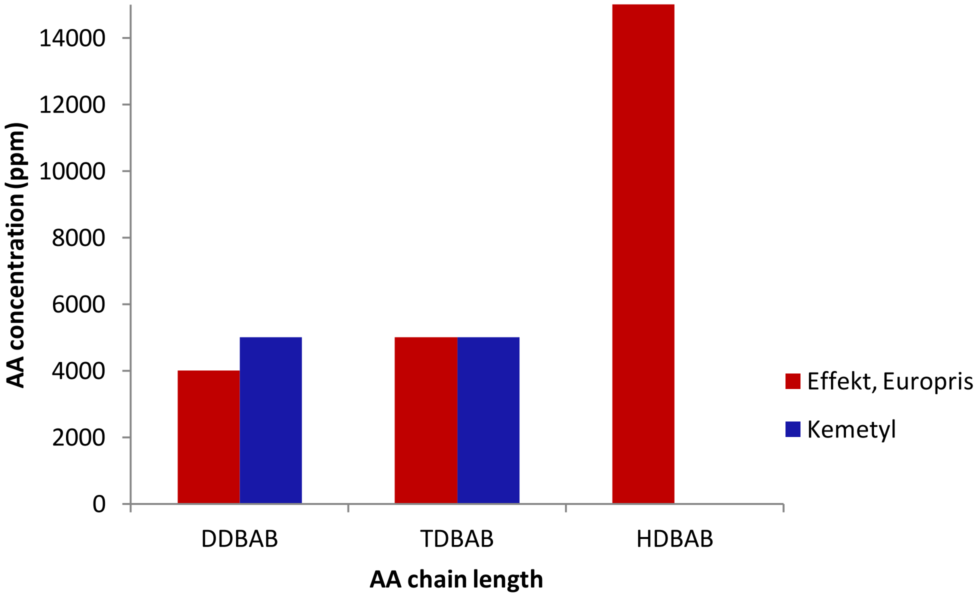


Figure 2.30. The effect the seemingly chemically identical white spirit possesses on the anti-agglomerants.

A total of four different hydrocarbon fluids were tried out on TDBAB to assess the effect they possessed on this particular anti-agglomerant, table 2.7 and figure 2.31. The pass concentration for o-xylene was not determined, for reasons to be clear in the following.

Table 2.7. The effect on anti-agglomerants by the different hydrocarbon fluids and the needed concentration (ppm) of the anti-agglomerant to get an adequate result which gave a pass.

AA chain length	White spirit Effekt, Europris	White spirit Kemetyl	n-decane
TDBAB	5000	5000	2000

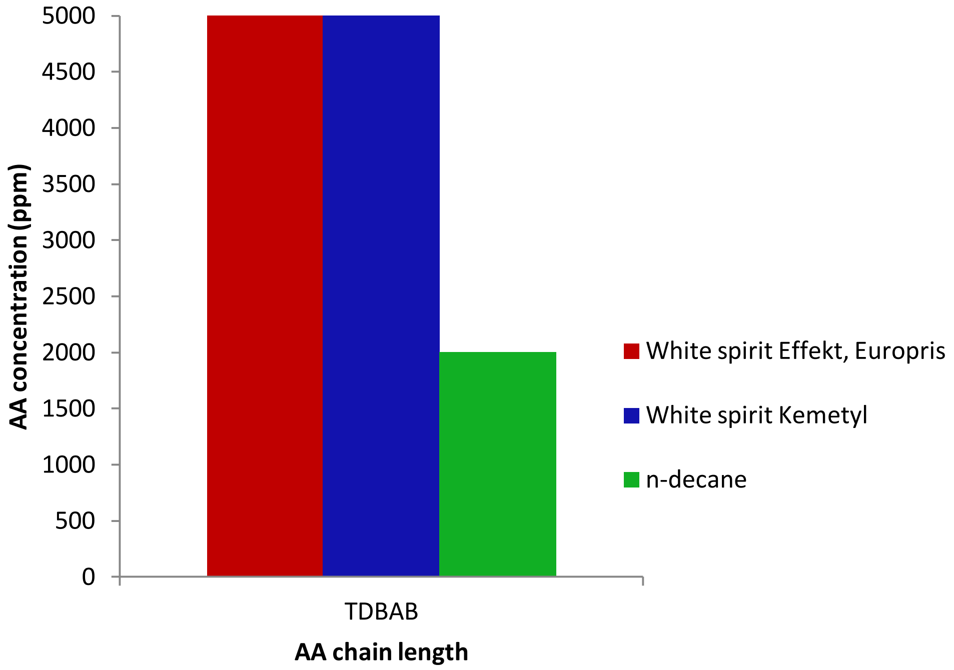


Figure 2.31. The effect on TDBAB by the different hydrocarbon liquids.

2.5 Discussion

All experiments were conducted by applying constant cooling. The pressure drop was used to confirm hydrate formation and if there were to be any gas leaks in the table top wheel, but visual inspection was the most reliable method for determining hydrate formation. Pressure and temperature against time graphs from the data acquisition were made. They contained the temperatures from both the table top wheel and the water heater/cooler in addition to the pressure from the wheel (figure 2.25 and 2.26).

From these graphs distinct differences can be observed as well as some resemblance. In both graphs the water heater/cooler line behaves similar, with the same cooling rate. The line for the wheel temperature also behaves sort of similar, but with one important difference. In figure 2.25 the line decreases and then flattens out, while in figure 2.26 it decreases and then before it flattens out have a little spike. This spike is caused by the exothermal hydrate formation process. It is typically associated with catastrophic and rapid hydrate formation, which was the case for this particular experiment. This catastrophic hydrate formation can also be observed on the pressure line. In the figure 2.26 the pressure almost immediately start to decrease. This indicates a catastrophic hydrate formation by forming a hydrate plug. If the formation rate is far greater than the dispersion rate facilitated by the anti-agglomerant, gas hydrate agglomeration and plugging tend to occur. In figure 2.25 the pressure decreases before it shortly flattens out, then it quickly drops and then flattens out. This is typical for slow and scarce hydrate formation by forming a hydrate slurry. In both cases the hydrate formation initiated approximately at 0°C, after 100 minutes. These two graphs, one for a fine hydrate slurry and one for catastrophic hydrate formation, shows the general trend for these experiments.

2.5.1 Preliminary tests

Before it was finally decided on a test method, a range of different approaches were tried out, to determine the parameters to be used.

The initial tests with distilled water and gas showed hydrate formation at a much lower temperature then expected out from some graphs with pressure against temperature. Hydrate was formed at 1.40°C with no additive. In order for making more turbulence inside the wheel, different approaches were tried out in order to get the formation temperature for hydrate formation higher. The equipment was filled with 50ml distilled water and a quarter spatula of Ocma clay, and pressurized to 40 bar. At a temperature of 2.30°C hydrates was formed. Afterwards, five stainless steel balls (4mm in diameter) were placed inside the table top wheel. The tests afterwards confirmed that this had some influence on the hydrate formation temperature, by increasing it to 10.30°C by taking the average of three experiments (table 2.2). They did this although they were partially hindered from movement by some sort of grease, possibly some silicone grease from the effort in making the wheel gas proof.

After some experiments, partly by washing the wheel with white spirit, the grease disappeared. The stainless steel balls had a tremendous impact on the formation temperature for hydrate formation. They also made the formation more reliable. These balls coupled with the plastic stoppers in the half pipe of the wheel, helped on making the flow regime, which was laminar, more turbulent. This turbulent aid hydrate formation by mixing more gas into the liquid phase, thus enhancing the hydrate formation.[41] The Ocma clay had very little to no impact on the hydrate formation temperature. The hydrate formation is a stochastic process, so the formation temperature will fluctuate.[2] Although the Ocma clay did increase the onset temperature, it maybe only be due to the stochastic process.

Both the formation temperature and the dissociation temperature was tried measured for distilled water, 20% and 33% water cut (table 2.3). Both temperatures were determined after the five stainless steel balls had been added. As expected there were some scattering in the formation temperature, since this being a stochastic process. The temperature was highest for distilled water, then 20% followed by 33% water cut, 10.26°C, 4.87°C and 4.20°C respectively. Distilled water had the highest dissociation temperature of 16°C. The difference between 20% and 33% water cut was minimal, with 11.35°C and 11.50°C respectively. Hence, not surprisingly there was a huge difference in the formation and dissociation temperature between distilled water and the two water cuts, and that the difference between the two water cuts were minimal. More gas will dissolve into the liquid phase when a hydrocarbon phase is present. This could be a possible reasons for this observed effect. To really determine these temperatures, multiple experiments should be conducted. These dissociation experiments are far from as accurate as how they possibly can be. As mentioned, those experiments are extremely time consuming, and each temperature increase are small and held for a considerable amount of time. Here in this isochoric process, the temperature increase was small and the time at each temperature was relatively long, but considerably shorter than what is required to get it exactly.[98,99] Still, they are good enough to get a dissociation temperature around where it should be. From a computer program (PVTsim by Calsep), theoretical pressure and temperature graphs over the hydrate equilibrium curves for the SNG used in distilled water had previously been made. For 40bar, this curve gave an equilibrium temperature of 15.7°C, which correspond fairly well with the equilibrium temperature for distilled water at 40bar in the table top wheel, 16°C.

The rotation velocity was altered to find out if it induced hydrate formation faster. No effect was observed by doubling the rotation velocity, from 18rpm to 36−38rpm. Higher rotation speed corresponded to higher flow rates of liquid in the wheel. Higher velocities were not tried out since these could induce resonance waves and sloshing in the water bath. Had the turbulence significantly increased, the hydrate formation would probably have started earlier.

2.5.2 Effect of varying anti-agglomerants chain length in both 1.5wt% NaCl solution and distilled water

There were a dual objective in these experiments. Firstly, the minimum anti-agglomerant concentration were to be determined in both distilled water and 1.5wt% NaCl solution. The 1.5wt% NaCl solution was recommended because it represents the salinity level in many reservoirs. Secondly, these results were to be compared to the results for the same anti-agglomerant range in both distilled water and 1.5wt% NaCl solution, obtained in the RCS 20 rocker rig from PSL Systemtechnik. The maximum concentration was set to 15000ppm for this experimental work, because usage of more than 20000ppm anti-agglomerant in oilfield application is generally economically unfavorable.[96]

When the 1.5wt% NaCl solution was used as the aqueous phase, both OBAB and DBAB failed even at the highest test concentration of 15000ppm. A further increase in the alkyl chain length to DDBAB, TDBAB and HDBAB in addition to CBAB gave a fine hydrate slurry at reasonable concentrations, 3000ppm, 2000ppm, 2000ppm and 4000ppm respectively. The performance diminished significantly once the chain length was increased to ODBAB. Here a concentration of 15000ppm, which was the maximum concentration used, was needed to achieve a pass (table 2.4 and figure 2.28). Thus, the anti-agglomerant with the best efficiency in 1.5wt% NaCl was TDBAB, despite that it had the same pass concentration as HDBAB, it had a better rank (A/B). The ranking of the anti-agglomerants that passed was, from best to worst: TDBAB-HDBAB-DDBAB-CBAB-ODBAB, with an average pass concentration of 5200ppm. By increasing the alkyl chain length, the hydrophobicity increases as well. Hence, an increase in the chain should enhance the performance, as the results confirmed, with DDBAB, TDBAB and HDBAB in addition to CBAB. But making the chain length to long will make the performance decline, as they tend to portion strongly to the hydrocarbon phase relatively to what the shorter chains do. Further, ODBAB was the only anti-agglomerant tested that was difficult to dissolve in the aqueous phase. Emulsifications were formed, therefore the inhibitor was less available in the interface between hydrocarbon and water in addition to the bulk water, compared with the shorter chain anti-agglomerants. For some anti-agglomerants the emulsification of the hydrocarbon and water phase prior to hydrate formation may be critical part of the process.[26] This may be possible reasons for the observable performances.

When distilled water was used as the aqueous phase, neither OBAB nor DBAB as well as ODBAB was conducted in these experiments. This because they either gave no pass, OBAB and DBAB, or the pass concentration was the maximum concentration for this experiment, ODBAB in 1.5wt% NaCl. For the other anti-agglomerants, the same trend as for 1.5wt% NaCl could be observed. Both DDBAB, TDBAB in addition to CBAB gave reasonable concentrations for adequately performance, 4000ppm, 5000ppm and 5000ppm respectively. But increasing the chain length to HDBAB, the performance diminished, giving it a pass concentration of 15000ppm, which again was the maximum concentration used in this experiment (table 2.4 and figure 2.28). This was a much higher concentration than expected form the observed effect in 1.5wt% NaCl.

Hence, the best performing anti-agglomerant in distilled water was DDBAB. The ranking of the anti-agglomerants tested was, form best to worst: DDBAB-TDBAB-CBAB-HDBAB, with an average pass concentration of 7250ppm. The same reasons as described above possibly holds here as well.

By comparing the results obtained in 1.5wt% NaCl and distilled water, it was clear to see a significant enhancement in the anti-agglomerant performance (table 2.4 and figure 2.28). The most outstanding performance enhancement was for HDBAB. To get the same performance in distilled water as in 1.5wt% NaCl solution the concentration need to be 7.5 times as high. On the average the concentration needed to be 4500ppm higher in distilled water compared to 1.5wt% NaCl, thus 2.63 times higher representing an increase of 163.63%. For the other anti-agglomerants the performance enhancement was not that huge, but none the less clear. TDBAB had the best performance in 1.5wt% NaCl solution, while DDBAB had the best performance in distilled water. Salts are used as thermodynamic hydrate inhibitors. They have the ability to shift the equilibrium requirements for hydrate formation to lower temperatures and higher pressures, by outcompete the water molecules for hydrogen bonds.[38,53] The salinity concentration effect on anti-agglomerant performance had been reported previously.[39,67] This could be possible mechanisms responsible for the observed effects.

The results from the table top wheel were compared to the results obtained in the rocking cells (table 2.4 and figure 2.27). In both these experiments, the same gas composition, white spirit (Effekt from Europris AS), anti-agglomerants, NaCl concentration of 1.5wt%, distilled water and water cut of 33% was used. In addition constant cooling procedure was applied in both apparatuses. Therefore the results from each of these apparatuses should be fairly comparable. The biggest differences lie in the apparatuses itself. The table top wheel had utilized a pressure of 40bar in its tests, while the rocker cells used a pressure of 79bar. Further, the volume in the table top wheel was 200ml, filled with 20ml aqueous phase and 40ml hydrocarbon phase, a total of 60ml liquid. A volume of 20ml, filled with 3ml aqueous phase and 6ml hydrocarbon phase, to a total of 9ml was in the rocker cells. The flow regime between the two apparatuses differed considerably. Here the table top wheel had a circular swirling motion, while the rocker cells was rocked back and forth.

The first notable difference between the results from the apparatuses are the needed concentration of ati-agglomerants to achieve an adequate result, in both 1.5wt% NaCl and distilled water. Only TDBAB in distilled water had the same concentration in both apparatuses, of 5000ppm. For all the other anti-agglomerants tested, they needed a higher concentration in the wheel apparatus than in the rocking cells. Both DDBAB and CBAB in distilled water needed 1000ppm more in the table top wheel, compared with the rocker cells. HDBAB on the other hand required 5000ppm more in order to get a pass in the table top wheel than in the rocker cells. As in the rocker cells, the anti-agglomerant concentration could be decreased to get a pass in 1.5wt% NaCl in the table top wheel. But still all the anti-agglomerants required a higher pass concentration here than in the rocker cells. DDBAB needed 12 times the concentration in the rocker cells to get a pass in the table top wheel.

Both TDBAB and HDBAB needed 1000ppm more in the table top wheel compared with the pass concentration in the rocker cells, while ODBAB needed 5000ppm more and CBAB required 8 times the pass concentration in the rocker cells. Thus, in both apparatuses TDBAB and HDBAB had equal concentrations within each apparatus of 2000ppm and 1000ppm in 1.5wt% NaCl, for the table top wheel and rocker cells respectively. Within each apparatus the difference between 1.5wt% NaCl solution and distilled water was highest for the rocking cells, with an average of 4812.5ppm, 8 times higher resulting in an 700% increase in pass concentration. This means that the rocking cells had the biggest difference between anti-agglomerant pass concentration in 1.5wt% NaCl solution and distilled water than what the table top wheel had. On average the anti-agglomerant pass concentration in distilled water was 1750ppm, 1.32 times higher, representing an increase of 31.82% and in 1.5wt% NaCl solution 2650ppm, 2.04 times higher, representing an increase of 103.92% in the table top wheel compared to the rocker cells. One peculiarity with the results, however was that in the table top wheel the best performing anti-agglomerant was TDBAB in 1.5wt% NaCl solution and DDBAB in distilled water. For the rocker cells the best performing anti-agglomerant was DDBAB in both 1.5wt% NaCl and distilled water. In the table top wheel both DDBAB, TDBAB in addition to CBAB only differed by ±1000ppm, much less than the difference in the rocker cells.

Possible reasons for the increased anti-agglomerant pass concentration in the table top wheel could be because of the different flow regimes which the apparatuses represent, with the circulate swirling motion of the table top wheel and the rocking motion of the cells. In the rocking cells, far more test gave a rank C than what was achieved in the table top wheel. All this could be from the fact that the balls within the rocker cells have a diameter barely smaller than the diameter of the cells, coupled with that these cells are rocked back and forth, will make for a much harsher flow regime than what was achieved in the table top wheel. This could perhaps hinder and destroy the slushy plugs, thus making this apparatus more anti-agglomerant concentration sensible. It is known that the degree of turbulence have an effect on anti-agglomerants.[26] In addition the bigger volume in the table top wheel and lower pressure than what the rocker cells had, could also play a part in these results. The pressure have a tremendous influence on the solubility of gases in liquids. Henry's law states the quantitative relationship between gas solubility and pressure: The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution, $c \propto P$. Here c is the molecular concentration (mol/L) of the dissolved gas and P is the pressure (in atm) of the gas over the solution.[7,100] The air was removed from the rocker cells by the aid of a vacuum pump, which was not a procedure done in the table top wheel. All this could maybe cause the observed differences between the two apparatuses, and interfere with the inhibition mechanisms. The hydrate formation driving force can be measured in multiple ways. One of them is to measure the subcooling. Subcooling, as it is defined is the difference between the equilibrium hydrate temperature (hydrate dissociation temperature) and the operation temperature at a fixed pressure and system composition.[6,37] By increasing the magnitude of subcooling, the hydrate formation rate will increase.[50] If the subcooling are to be very high, the driving force for hydrate formation may be so strong that the rate of hydrate formation surpass the anti-agglomerant from being effective at separating hydrate particles.[26]

The different apparatuses utilized different subcoolings, and therefore it can be a possible candidate for the observed differences.

None the less the trend was the same for both apparatuses in both distilled water and 1.5wt% NaCl, being that the anti-agglomerants that had unsatisfactory, moderate and satisfactory performance in both 1.5wt% NaCl solution and distilled water behaved similar in the apparatuses. Thus this validate the table top wheel for this anti-agglomerant range in both 1.5wt% NaCl solution and distilled water.

2.5.3 Effect of varying anti-agglomerants chain length in distilled water, 1.5wt% and 7wt% NaCl solution

Only DDBAB and TDBAB were chosen to be tested in 7wt% NaCl, because of their good performance in both distilled water and 1.5wt% NaCl.

Like argued in the previous results, by increasing the NaCl concentration to 7wt% the required anti-agglomerant pass concentration was decreased. This was confirmed by both anti-agglomerants tested. TDBAB had the best performance of the two, with a pass concentration of 500ppm while DDBAB had 1000ppm (table 2.5 and figure 2.29). An increase in the salinity concentration will decrease the hydrate equilibrium temperature, hence the subcooling at the same experimental pressure. Still, hydrates formed at approximately the same temperature.

2.5.4 Effect on anti-agglomerants chain length efficiency by hydrocarbon fluids

The effect of two different brands white spirit, which chemically composition was reported to be the same, were tried out on DDBAB, TDBAB and HDBAB. The reason for choosing these was that both DDBAB and TDBAB had a good performance and HDBAB had a bad performance in one of the white spirits. Only TDBAB, because of its good performance, was tried in all the different hydrocarbon liquids, with distilled water as the aqueous phase in all experiments conducted.

The white spirits, that was claimed to have the same chemical composition, of aliphatic and aromatic hydrocarbons, $> 30\%$ aliphatic hydrocarbons and 15−30% aromatic hydrocarbons, had an effect on two out of three anti-agglomerants tested (table 2.6 and figure 2.30). In both cases where an effect was observed, the effect was diminishing with an increase in the pass concentration for DDBAB and HDBAB. DDBAB had to be increased from 4000ppm to 5000ppm. HDBAB, which already had a pass concentration of 15000ppm, had to be increased beyond the maximum used concentration in this experimental work to get a pass. TDBAB on the other hand showed no observable effect in the different white spirits, with a pass concentration of 5000ppm in both. The fact that the table top wheel being relatively insensitive against anti-agglomerant concentration used, could be causing these effects.

In addition anti-agglomerant disperse the formed hydrates in the hydrocarbon liquid, which they need to function properly, by the use of the hydrophobic tail.[6,60] Therefore different hydrocarbon fluids can induce different effects on these different tail lengths.

In the tests where four different hydrocarbon liquids were used on TDBAB, an effect was influenced (table 2.7 and figure 2.31). As mentioned no observable effect from the white spirits was observed, but when n-decane was used the pass concentration was decreased from 5000ppm to 2000ppm. This was an discernible decrease of 2.5 times resulting in a 60% lower pass concentration, and shows that using an aliphatic compound have a positive effect on this inhibitor. Thus, this shows that different hydrocarbon fluids can induce an effect in the anti-agglomerants. This is a known fact that different hydrocarbon liquids can have natural surfactants.[27,61] As mentioned above, anti-agglomerants disperse the formed hydrates in the hydrocarbon liquid by the use of the hydrophobic tail.[6,60] Therefore different hydrocarbon fluids can induce different effects on these tails. For o-xylene the same concentration as for the white spirits of 5000ppm gave a pass. Only one test on o-xylene was conducted before no more experiments could be safely carried out, reasons to be clarified in the following.

2.5.5 Comparison of the table top wheel with other hydrate inhibition test apparatuses

This equipment was a prototype table top wheel. Therefore before, and during the testing, several issues must be addressed.

Of the other high pressure apparatuses, the table top wheel had both similarities as well as differences. A fuller description of these apparatuses can be found in chapter 1.11.[18,40,75,86,93]

The rocker rig apparatus consist of a bank of small cylindrical pressurized cells rocked back and forth. They often had a ball inside to aid agitation. The maximum working pressure may be about 10.3MPa, thus a broader pressure range than the table top wheel may be applied. Five small balls in addition to the plastic stoppers helped agitate the flow in the table top wheel. These balls was much smaller than the diameter of the half pipe, while in the rocker cells the ball had a little smaller diameter than the cells in which they transverse. Further, these apparatuses had been criticized as not being representative enough for actual representation of the flow regime in a pipeline. This is certainly not the case for the table top wheel, which utilizes a swirling circular motion to move the fluids. Since the rocker rig consists of multiple cells, they can give multiple results for each test run. Hence, each cell can test several different fluids, gases, inhibitor formulations, concentrations and water cuts in a single test run. This cannot be conducted at the current table top wheel design, where one test gives one result. Both of the apparatuses needs a relatively small amount of liquids, although if many cells are used at ones the amount will add up. If the cells was entirely made up of sapphire, the flow regime and potential hydrate formation can be observed, like the acrylic disk on the table top wheel makes possible.

The autoclaves uses only a few hundred milliliters of fluids per test and the agitation was provided by either a magnetic stir bar or blade type agitator-mixer. They have a broad pressure range, up to 35MPa. Therefore, like the table top wheel, which used 60ml fluid, a small amount of fluid was needed to conduct tests. Again, the flow regime between the apparatuses differ, as does the pressures applied. If the autoclave was entirely made of sapphire, the whole flow regime as well as potential hydrate formation can be observed. This was made possible in the table top wheel by the acrylic disk. Also here, one test yields one result.

The closest of the traditional apparatuses in comparison are the traditional wheel apparatuses and the flow loops. This table top wheel, like the traditional wheel apparatuses and the flow loops, have a more realistic simulation of the flow regime in a pipe than what the rocker rigs and autoclaves possesses.

Like the traditional wheel apparatuses, the wheel is spun past the liquid and gas rather than the reverse. Thus, there are no requirement for circulation devices, and the rotation velocity determines the flow regime. A considerable difference between these apparatuses are how they makes the rotation motion. Traditional wheel apparatuses rotates around their horizontal axis, while the table top wheel had a circular swirling motion around its horizontal axis. By this mechanism the liquids were moved around the whole interior of the table top wheel. In these apparatuses pressures up to 25MPa can be applied, whereas the limit for the table top wheel was set to 4MPa. Hence, the traditional wheel apparatuses have a broader range of pressures that they can cope with. The table top wheel had the entire top disk made of acrylic, a transparent material making the whole flow regime visible. The traditional wheel apparatuses had normally two high pressure windows. In addition, these apparatuses are pipes shaped like a wheel. Those that are placed horizontally, like the table top wheel, are 5.1−12.7cm pipe shaped like a wheel of 2m in diameter. The table top wheel on the other hand had a half pipe radius of 1.27cm, and the total diameter was 325.00mm, therefore considerable smaller than the traditional wheel apparatuses.

The flow loops provide the most realistic simulation of pipe conditions available, and come in a range of sizes, both smaller and bigger than the table top wheel. The bench scale version is 1.3cm in diameter and 3m long, thus a smaller diameter on the pipe than the half pipe in the table top wheel. Like the table top wheel turned out to be, these apparatuses provide very repeatable results. The flow loops uses pumps to circulate the gas and fluids around the apparatus. This can be detrimental for the results, since the pumps can crush hydrates, making especially anti-agglomerants experiments difficult to interpret. This was not an issue, as mentioned above, for the table top wheel. Further, the flow loop experiments are time consuming, uses a considerable amount of fluids and the heating and/or cooling process is tedious. Hence, the table top wheel was fairly time efficient, heated and cooled quickly and fluid effective. Thus, it is suitable for use in situations where time and fluids are of the essence.

Another form of small laboratory hydrate test apparatus is the Baker hydrate inhibition test loop. This loop consists of a hollow pipe forming a loop with at least one opening in the loop. The size of the apparatus measured a 2.54cm pipe formed into a 25.40cm in diameter loop. Within the loop there was at least one pig. Therefore, in order to remotely impel the pig to circulate the loop with the fluid, there is at least one impeller adjacent to the loop. This impeller could be a magnet that tracks close to the inner diameter of the loop and impels a small sphere or ball to travel inside the pipe, at speeds up to 3000rpm. Hence, the liquid is moved by the pig while the pipe itself was stationary. The pressure applied can be from 7MPa and above, with or without sight glasses. This whole assembly is placed in a cooling bath. Results from this apparatus is proven to be quite consistent and reproducible. The table top wheel, as mentioned before, had a total diameter of 32.50cm, therefore wither than the Baker loop. Also the pressure that can be applied in the Baker loop was at least 3MPa higher. Eventual hydrate formation and the flow regime in general, could readily be observed through the acrylic disk in the table top wheel. Further, the fluid movement was provided by impelling at least one pig around the interior of the pipe, whereas the whole apparatus was set in motion in the table top wheel. Rotation velocity of the table top wheel was normally 18rpm, but it is easier to achieve higher velocities inside a closed apparatus, than making the whole apparatus move. Both apparatuses utilizes no pumps to circulate the fluid, uses a small amount of fluid and relatively have low level of complexity compared to the large state-of-the-art circulation loops.

2.5.6 Apparatus remarks

First off, the bottom line is that the wheel worked adequate as far as being a prototype. It provided a consistent mean of forming hydrate, and the anti-agglomerant range used here coincided nicely with the same anti-agglomerant range on the rocking cell apparatus. It is space-saving in being relatively small, compared to other wheels and gas hydrate assessment apparatuses in general. Further, each experimental run consumes a small amount of liquid and gas, and it is fairly quick to cool down and/or heat up. It is easily operated and maintained. Both steady state and shout-in/restart condition could be simulated. Since the top disk was made of acrylic, the whole flow motion of the liquid, and eventual hydrate formation, could be observed. This disk also represented a weight saving as well, compared to a stainless steel top. The relatively low pressure used also makes it somewhat safer to operate.

On the other hand to empty the wheel of all its liquids, turned out to be quite a task. Because all connections to the wheel was made through the top disk, either pressure and/or vacuum was needed in order to remove the liquids, but changing the removal of the liquid from manual vacuum to a mechanical provided vacuum made a huge difference. Still, it was almost impossible to remove all liquid with the current methods that were used. The pressurization process was difficult to get exactly to the desirable pressure. This because of that the pressure fluctuated on the electronic interface, sometimes it fluctuated quite a bit. On the final version of the software, extra program loops made the pressure meter lag. Therefore the old version was used during pressurization.

The lag in the software, especially when it comes to pressurization of the wheel, should be sorted out. In this way only one version of it need to be applied in order to operate the wheel. If a graph over the temperature and pressure could be made while the experiment is conducted, it would be possible to observe how far the test had come in form of possible hydrate formation. The time interval between data acquisition worked adequately. Maybe a timer on the acquisition could be made, so that every experiment elapsed the same length in time. In this way the pressure drop can be compared between the different experiments. Because the pressure will decrease as long as hydrate is formed. Therefore the time elapsed must be equal in order for the pressure drops to be compared.

To get the water level in the water bath to be equal and high enough so no air was sucked in, was also not a simple task. Even after the hose was applied to the water bath, the valves had to be adjusted very often because heating or cooling made the pumping rate to fluctuate, possibly because of viscosities differences and that the pumps was affected by the temperatures as well. There exist some accessories to the water heater/cooler that can be requisitioned that monitors the water level in the water bath. By applying this the water level should remain constant. The water bath had a fairly large surface area, which was open to the air. Therefore as time goes by, particles and dust will accumulate and defile the liquid. Hence, a transparent cover could be made and placed over. In addition, if there should occur a power failure or the valves to the water heater/cooler are not looked after the water bath could overflow. Therefore in a future design a spout could be incorporated into the design, so that all the overflow is maintained at one place. Also, if a faster velocity shall be applied to the table top wheel, it can induce resonance waves in the water bath. These waves could result in overflow, therefore breakwaters can be mounted in the water bath to break up the resonance waves.

A video camera should be mounted above the wheel assembly for recording and visual monitoring of the flow regime and eventual hydrate formation. Here the whole sequence of events for a possible hydrate formation could be observed. In addition the video serves as proof for hydrate formation.

Both the pressure gauge and the quick release on the gas valve broke during the course of the experimental work. This could not directly be blamed on the apparatus, maybe more in the way it was sat up in the laboratory. The swirling circular motion could have damaged the wire connection to the pressure gauge, or maybe it was a malfunction. The cause was never determined for why it failed. The quick release for the gas was maybe influenced by the circular motion as well, but it could be caused of excess force when assembled.

As mentioned, the table top wheel flows the liquid purely by an external force. The liquid was thereby moved across the interior of the wheel, rather than the wheel moved pass the liquid. This makes the flow regime more realistic. Further, in order to make the laminar flow regime more turbulent, five stainless steel balls in addition to the plastic stoppers was applied. Perhaps making the connection rod form the motor to the wheel longer could aid in more force to be transferred to the wheel, and hence induce the agitation.

But to make the hydrate formation temperature even higher, perhaps the design of the half pipe could be altered. The half pipe was smooth, so if a waveform (like "speed bumps") were to be applied, it may aid in the mixing process. A small track could be made through the bumps so that the liquid could be easier be drained and does not get held back by the bumps. In addition, this wheel rotated with a swirling circular motion with a tilt. Perhaps a swirling circular motion without this tilt could be applied, by prolonging the rod from the step motor to the wheel and changing the ball joint with a circular track. If enough velocity were to be supplied, the centrifugal force could aid in a more turbulent flow regime.

Acetone will dissolve acrylic, so therefore it cannot be used. This was a drawback with the apparatus. The weakest part of the whole assembly was the acrylic disk. Therefore it dictated the maximum pressure that the wheel could be safely operated with. This pressure, being 4MPa, is substantially lower than what high pressure hydrate inhibition test apparatuses utilize, like all the apparatuses mentioned above. However, the disk was not pressure tested until failure, so the maximum operating pressure was not determined. One positive side effect of this relatively low pressure was that it made it safer to operate. The main benefit of using this acrylic disk was that the whole flow regime and the potential hydrate formation could be observed, being either a plug or slurry. Especially when testing anti-agglomerants, it is beneficial to be able to view the inside of the apparatus. This because observations of fluid flow characteristics, the size and dispersion of the hydrate crystals and whether clusters of hydrates stick to the sides of the apparatus are critical to predict whether a particular candidate will work in the field. Unfortunately, this turned out to be the Achilles heel of the apparatus. The decidedly weakest points on the acrylic disk, thus the weakest points on the whole assembly, was namely the connection points in the disk. At these points cracks stated to emerge, which grew to the point where the wheel could no longer be safely operated.

In order for this prototype to progress, some modification must be done to this acrylic top disk. The cracks emerged at every connection except for at the pressure gauge. This could be that this particular connection had a different dimension than the other. In addition the pressure gauge part that was directly above the connection point, was wither than and close down to this point. This was not the case for all the other connections, which all had a good margin of clearance. Maybe this covering and down force which the pressure gauge provided helped maintain the integrity of the connection. In a future design the connection points could be thicker, or the attributes connected could use a washer to distribute the down force over the connection points. This washer also helps in sealing the possible gaps between the different attributes mounted to the connection points. In general maybe the threads, dimension and/or the angle of the connection holes could be arranged in a different way, which made them more pressure resistant. Further, the sensors in addition to the inlet and outlet hoses as well as gas connections could be mounted to the side of the wheel. In this way all connections to the wheel avoid the acrylic disk and are made through the side of the stainless steel bottom disk. A pipe bend can be used to maintain a "vertical" access to the connections at the side of the wheel.

In addition, the connections could also be mounted to other parts of the bottom disk. If especially the outlet hose were to be mounted at the base of this disk, it could aid in the drainage of the wheel. Another approach could be to make the acrylic disk thicker. Perhaps it could be designed in another way that copes better with pressure, like different shapes inside the disk or use an internal metal mech. Perhaps it could be made out of a more flexible material that would have the ability to deform upon pressure, no so much that it can cause leakages. But then the volume would not be constant. It is always possible to go for a more traditional design of stainless steel with one or more sight glasses. The whole assembly could also be made out of stainless steel, but then no visual observations can be done. Another transparent material could be used, like sapphire, but this would probably be too costly to make a whole disk out of.

One very effective approach could be to lower the pressure used in the experiments. But this pressure is already at a limit of how low it can be. If the pressure is set to low, hydrates may not even form at all. Further, the amount of subcooling also decreases with decreasing pressure.

Therefore if these issues were to be sorted out, this table top wheel is a design worth to go further with, and refine. It possesses an unique way of moving the liquid, namely by the swirling circular motion. This enables the use of cabled sensors since the motion do not cause the cable to be spun around and spiral up. In addition this apparatus have a feature that is important in these types of equipments, the ability to simulate steady state as well as shout-in/restart conditions. The steady state is simulated by the continuous motion of the wheel, while the shut-in/restart is simulated by halter the wheel. Since this apparatus requires a small amount of liquid, it could be used for screening tests. Also, if perhaps a second half pipe was made inside the original, or multiple wheels were mounted on top of each other possibly beside each other, multiple results per test run would be achieved. This could make the apparatus more suitable for screening tests.

Further test that can be conducted would be more anti-agglomerants, varying the water cut, different hydrocarbon liquids, change the subcooling for harsher or milder conditions, change the cooling rate, simulate shut-in/restart conditions, different salinity concentrations and try out kinetic hydrate inhibitors.

2.6 Conclusion

This experimental work had a dual purpose of finding the adequate anti-agglomerant concentration in both 1.5wt% NaCl solution and distilled water and compare these results to the results for the same composition in a rocker rig. Further, the apparatus and method was altered during the experiments.

The table top wheel formed hydrate at a low temperature. Therefore in order to agitate the laminar flow regime, five stainless steel balls was added. They increased the hydrate formation temperature and also made the formation more consistent. Hydrate formation is a interfacial phenomenon, so by making the flow regime more turbulent could aid in the mixing of the phases. Both the formation and dissociation temperature was determined in distilled water, 20% and 33% water cut. In addition the rotation velocity was doubled, but this had no effect on the hydrate formation rate, possibly by not significantly enhancing the turbulence.

In the tests where 1.5wt% NaCl served as the aqueous phase results indicate that increasing the alkyl chain length on the n-alkyl-tri(n-butyl)ammonium bromides up to a certain length, will enhance the performance of the anti-agglomerants. Once over this length, the anti-agglomerants become too hydrophobic and the performance gets impaired. The best performing anti-agglomerant was determined to be TDBAB. Where distilled water was used as the aqueous phase, the tests results was similar to the 1.5wt% NaCl solution. Also here an increase in the alkyl chain length will enhance the anti-agglomerant performance, until a point where it gets diminished. All anti-agglomerants required a higher concentration to achieve the same level of performance compared to the 1.5wt% NaCl solution. The best performing anti-agglomerant was DDBAB. Possible reasons for these observed effects could be caused by the fact that salt are used as thermodynamic inhibitors and hence shift the equilibrium requirements for hydrate formation.

The results for the same constituents in both the table top wheel and the rocker rig was compared. There were some minor differences, like that the table top wheel in general required a higher anti-agglomerant concentration to perform satisfactory, except TDBAB in distilled water which had the same concentration and it did not distinguish that clearly between the anti-agglomerants that performed fairly satisfactory. Further, TDBAB had the best performance in 1.5wt% NaCl solution while DDBAB had the best performance in distilled water in the table top wheel. In the rocker rig DDBAB had the best performance in both 1.5wt% NaCl solution and distilled water. Possible reasons for this could be the fundamental different flow regimes, operation pressure (Henry's law), agitation, subcooling, different volumes between the two apparatuses and the fact that the table top wheel did not distinguish that well between the different anti-agglomerants. From this it can be concluded that the table top wheel was validated at least for this anti-agglomerant range in both 1.5wt% NaCl solution and distilled water.

In addition 7wt% NaCl solution as the aqueous phase was tested on DDBAB and TDBAB, with TDBAB had the best performance, like it also had in 1.5wt% NaCl solution. Possible explanations are probably like the once mentioned above. The effect which two white spirits with seemingly the same chemical composition exerted on DDBAB, TDBAB and HDBAB were examined. Only TDBAB was not affected, and the effect was diminished on the other two. Further, the effect that two other hydrocarbon liquids possessed on the efficiency of TDBAB was examined. Only n-decane possessed an effect, which was enhanced the performance. Postulated mechanisms for this observed effect was that anti-agglomerants dispersed the formed hydrate particles into the hydrocarbon phase, therefore different hydrocarbon liquids can induce different effects on the various alkyl chain lengths.

As a concluding remark, as far as being a prototype the table top wheel functioned adequately and yielded both predictable and reliable test results. Further, the apparatus provide a consistent method for both hydrate formation and inhibitor testing. The apparatus and method was easy to set up, was conducted in a relatively short time, required a minimum amount of test fluids and could simulate both steady state as well as shut-in/restart conditions. In addition, the table top wheel possesses an unique mode of moving the liquid and the acrylic top disk makes it possible for visual observation of the flow regime and possible hydrate formation. However, as the word prototype implies it is not a finished product. Especially when it comes to the acrylic top disk, which cracked after only 59 pressurized experiments. This is a severely defect with the design and must be sorted out. Thus, for the table top wheel to go further in development and eventual implementation the acrylic top disk must be redesigned.

CHAPTER 3: REFERENCES

1. **Vernon L. Snoeyink and David Jenkins**, Water Chemistry, John Wiley & Sons, New York, 1980, 1-2.

2. **M.H. Yousif**, The Kinetics of Hydrate Formation, SPE 28479, Prepared for presentation at the SPE 69th Annual Technical Conference and Exhibition held in New Orleans, LA, U.S.A., 25-28 September, 1994.

3. **Geoff Rayner-Canham and Tina Overton**, Descriptive Inorganic Chemistry, W. H. Freeman and company, New York, 4. Edition 2006, 231, 233-234.

4. **E. D. Sloan Jr. and C. A. Koh**, Clathrate Hydrates of Natural Gases, 3 edition, Vol. 119. Boca Raton, Florida: Chemical Industries, CRC Press, 2008.

5. **Hua Guan**, The Inhibition of Gas Hydrates and Synergy of the Inhibiting Molecules, SPE 131314, Presentation at the CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing, China, 8-10 June 2010, 2010.

6. **L. M. Frostman and J. L. Przybylinski**, Successful Applications of Anti-agglomerant Hydrate Inhibitors, SPE 65007, Prepared for presentation at the 2001 SPE International Symposium on Oilfield Chemistry held in Houston, Texas, 13-16 February 2001, 2001.

7. **Raymond Chang**, Physical Chemistry for the Biosciences, University Science Books, Sausalito, California, 2005, 505, 507.

8. **Malcolm A. Kelland**, personal communication 12/2/2013.

9. **Carolyn A. Koh, Amadeu K. Sum and E. Dendy Sloan**, Gas hydrates: Unlocking the energy from icy cages, Journal of Applied Physucs 106, 061101, American Institute of Physics, 2009.

10. **Amadeu K. Sum, Carolyn A. Koh and E. Dendy Sloan**, Clathrate Hydrates: From Laboratory Science to Engineering Practice, Review, Ind. Eng. Chem. Res., Volume 48, Number 16, 7457-7465, American Chemical Society, 2009.

11. **Donald L. Katz**, Depths to Which Frozen Gas Fields (Gas Hydrates) May Be Expected, SPE 3061, Presented at the SPE 45th Annual Fall Meeting, held in Houston, 4-7 October 1970, Journal of Petroleum Technology, 1971.

12. **M. H. Yousif and E. D. Sloan**, Experimental Investigation of Hydrate Formation and Dissociation in Consolidated Porous Media, SPE 20172, SPE Reservoir Engineering, 1991.

13. **N. I. Papadimitriou, I. N. Tsimpanogiannis and A. K. Stubos**, Gas content of binary clathrate hydrates with promoters, The Journal of Chemical Physics 131, 044102, American Institute of Physics, 2009.

14. **R. Bennett**, Gas Hydrate Research in the Gulf of Mexico, Final Report, DOE/MC/23145-2616 (DE88010279), 1988.

15. **Ardian Nengkoda, Abdulla Harthy, Wael Afify Taha, Hendrikus Reerink, Moh'd Hajri, Hase Alfred, Lamda Muchjin and Suryo Purwono**, Gas Hydrate Problems in Desert of Sultanate of Oman: Experiences and Integrated Inhibition Program, IPTC 13061, Prepared for presentation at the International Petroleum Technology Conference held in Doha, Qatar, 7-9 December 2009, 2009.

16. **A. Corrigan, S. N. Duncum, A. R. Edwards and C. G. Osbome**, Trials of Threshold Hydrate Inhibitors in the Ravenspurn to Cleeton Line, SPE 30696, First presented at the 1995 SPE Annual Technical Conference and Exhibition held in Dallas, 22-25 October, 1996.

17. **Malcolm A. Kelland**, Production Chemicals for the Oil and Gas Industry, CRC Press, Taylor & Francis Group, Boca Raton, Florida, 2009, 5-9, 225-228, 232, 242-243, 405, 409-410.

18. **Malcolm A. Kelland**, History of the Development of Low Dosage Hydrate Inhibitors, Energy & Fuels, An American Chemical Society Journal, 10.1021/ef050427x, 2006, Volume 20, Number 3, 825-847.

19. **Peter Becke, Dagobert Kessel and lradj Rahimian**, Influence of Liquid Hydrocarbons on Gas Hydrate Equilibrium, SPE 25032, Prepared for presentation at the European Petroleum Conference held in Cannes, France, 16-18 November, 1992.

20. **Catherine A. Whitman, Roman Mysyk and Mary Anne White**, Investigation of factors affecting crystallization of cyclopentane clatherate hydrate, The Journal of Chemical Physics 129, 174502, 2008.

21. **Jorge F. Gabitto and Costas Tsouris**, Physical Properties of Gas Hydrates: A Review, Journal of Thermodynamics, Hindawi Publishing Corporation, volume 2010, Article ID 271291, 2009.

22. **Humphrey Davy**, *Phil. Trans. Roy Soc London*, 1811, 101, 30.

23. **E.G. Hammerschmidt**, Ind. Eng. Chem., 1934.

24. **Takashi Makino, Makoto Tongu, Takeshi Sugahara and Kazunari Ohgaki**, Hydrate structural transition depending on the composition of methane + cyclopropane mixed gas hydrate, Fluid Phase Equilibia, Volume 233, Issue 2, 2005.

25. **J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe og B. M. Powell**, Nature (London), 1987.

26. **M. A. Kelland, T. M. Svartaas and L. Dypvik**, Studies on New Gas Hydrate Inhibitors, SPE 30420, Prepared for presentation at the SPE Offshore Europe Conference in Aberdeen, 5-8 September 1995, 1995.

27. **P. K. Notz, S. B. Bumgardner, B. D. Schaneman and J. L. Todd**, Application of Kinetic Inhibitors to Gas Hydrate Problems, SPE 30913, Presented at the 1995 Offshore Technology Conference, Houston, 1-4 May, 1996.

28. **E. D. Sloan, C. A. Koh, A. K. Sum, A. L. Ballard, G. J. Shoup, N. McMullen, J. L. Creek and T. Palermo**, Hydrates: State of the Art Inside and Outside Flowlines, SPE 118534, Distinguished Author Series, 2009.

29. **R. L. Christiansen, Vibha Bansal and E. D. Sloan Jr.**, Avoiding Hydrates in the Petroleum Industry: Kinetics of Formation, SPE 27994, Prepared for presentation at the University of Tulsa Centennial Petroleum Engineering Symposium held in Tulsa, OK, U.S.A., 29-31 August 1994, 1994.

30. **E. Denby Sloan, Carolyn Koh and Amadeu K. Sum**, Natural Gas Hydrates *in* Flow Assurance, Gulf Professional Publishing, USA, 2011.

31. **Saman Alavi, J. A. Ripmeester and D. D. Klug**, Stability of rare gas structure H clathrate hydrates, The Journal of Chemical Physics 125, 104501, 2006.

32. **Carolyn A. Koh and E. Denby Sloan**, Natural Gas Hydrates: Recent Advances and Challenges in Energy and Environmental Applications, American Institute of Chemical Engineering, DOI 10.1002/aic.11219, Volume 53, Number 7, 1636-1643, 2007.

33. **E. Dendy Sloan Jr.**, Natural Gas Hydrates, SPE 23562, Technology Today Series, 1991.

34. **A. Tzirita, P. Jeanjean, J-L. Briaud and W. A. Dunlap**, Detection of Gas Hydrates by In-Situ Testing, OTC 6536, Presented at the 23rd Annual OTC in Houston, Texas, 6-9 May, 1991, 1991.

35. **Richard L. Christiansen and E. Dendy Sloan Jr.**, Mechanisms and Kinetics of Hydrate Formation, in (First) International Conference on Natural Gas Hydrates, Annals of New York Academy of Science, 283-305, 1994.

36. **Malcolm A. Kelland**, Gas Hydrate Management with Chemicals in the Oil and Gas Industry, presentation held at the University of Stavanger, 2013.

37. **B. Fu, S. Neff, A. Mathur and K. Bakeev**, Application of Low-Dosage Hydrate Inhibitors in Deepwater Operations, SPE 78823, Revised for publication from paper SPE 71472, first presented at the 2001 SPE Annual Technology Conference an Exhibition, New Orleans, 30 September-3 October, 2002.

38. **L. D. Talley and G. F. Mitchell**, Application of Proprietary Kinetic Hydrate Inhibitors in Gas Flowlines, OTC 11036, Presentation at the 1999 Offshore Technology Conference held in Houston, Texas, 3-6 may, 1999.

39. **C. R. Burgazli, R. C. Navarrete and S. L. Mead**, New Dual Purpose Chemistry for Gas Hydrate and Corrosion Inhibition, 2003-070, First presented at the 4th Canadian International Petroleum Conference (the 54th Annual Technical Meeting of the Petroleum Society), June 10-12, 2003, in Calgary, Albert, Journal of Canadian Petroleum Technology (JCPT), Volume 44, Number 11, 2005.

40. **E. Dendy Sloan and Carolyn A. Koh**, Clathrates Hydrates of Natural Gases, Second Edition, Revised and Expanded, Marcel Dekker, INC., New York, 1997.

41. **George Tchobanoglous, Franklin L. Burton and H. David Stensel**, Wastewater Engineering Treatment and Reuse, Metcalf & Eddy, Inc., McGraw-Hill Education, 1221 Avenue of the Americas, New York, 4. Edition, ISBN 007-124140-X, 2004, 245-246, 283-293.

42. **J. W. Mullin**, Crystallization, Butterworth-Heinemann, Jordan Hill, Oxford, 4. Edition, ISBN 0 7506 4833 3, 2001.

43. **Yuri F. Makogon, Taras Y. Makogon and Stephen A. Holditch**, Gas Hydrate Formation and Dissociation with Thermodynamic and Kinetic Inhibitors, SPE 56568, Prepared for presentation at the 1999 SPE Annual Technical Conference and Exhibition held in Houston, Texas, 3-6 October, 1999, 1999.

44. **Thomas D. Brown, Charles E. Taylor and Mark P. Bernardo**, Rapid Gas Hydrate Formation Processes: Will They Work?, Energies 2010, 3, 1154-1175, doi: 10.3390/en3061154, ISSN 1996-1073, 2010.

45. **R. L. Christiansen and E. D. Sloan, Jr.**, Mechanisms and Kinetics of Hydrate Formation, Proceedings of the International Conference on Hydrates, Annals of the Ney York Academy of Science, 1994.

46. **R. Alapati, E. Sanford, E. Kiihne and E. Vita**, Proper Selection of LDHI for Gas-Condensate Systems, in the Presence of Corrosion Inhibitors, OTC 20896, Prepared for presentation at the 2010 Offshore Technology Conference held in Houston, Texas, 3-6 May 2010, 2010.

47. **Amadeu K. Sum, Carolyn A. Koh and E. Denby Sloan**, Developing a Comprehensive Understanding and Model of Hydrate in Multiphase Flow: From Laboratory Measurements to Field Applications, American Chemistry Society, Upstream Engineering and Flow Assurance, dx.doi.org/10.10.21/ef300191e, Energy & Fuels, Volume 26, Issue 7, 4046-4052, 2012.

48. **Robin Susilo, Saman Alavi, John A. Ripmeester and Peter Englezos**, Molecular dynamics study of structure H clathrate hydrates of methane and large guest molecules, The Journal of Chemical Physics, 128, 194505, American Institute of Physics, 2008.

49. **Simon R. Davies, John A. Boxall, Carolyn A. Koh, E. Dendy Sloan, Pål V. Hemmingsen, Keijo J. Kinnari and Zheng-Gang Xu**, Predicting Hydrate-Plug Formation in a Subsea Tieback, SPE 115763, Accepted for presentation at the SPE Annual Technical Conference and Exhibition, Denver, 21-24 September 2008, SPE Production & Operations, 2009.

50. **Orlin Lavallie, Ahmed Al Ansari, Stephen O'Neil, Olivier Chazelas, Philippe Glénat and Bahman Tohidi**, Successful Field Application of an Inhibitor Concentration Detection System in Optimising the Kinetic Hydrate Inhibitor (KHI) Injection Rates and Reducing the Risks Associated with Hydrate Blockage, IPTC 13765, Prepared for presentation at the International Petroleum Technology Conference held in Doha, Qatar, 7-9 December 2009, 2009.

51. **J. Davalath and J. W. Barker**, Hydrate Inhibition Design for Deepwater Completions, SPE 26532, First presented at the 1993 SPE Annual Technical Conference and Exhibition held in Houston, 3-6 October, 1995.

52. **Steve Szymczak, Ken Sanders, Marek Pakulski and Timothy Higgins**, Chemical Compromise: A Thermodynamic and Low-Dose Hydrate-Inhibitor Solution for Hydrate Control in the Gulf of Mexico, SPE 96418, First presented at the 2005 SPE Annual Technical Conference and Exhibition, Dallas, 9-12 October, 2006.

53. **S. J. Allenson and A. Scott**, Evaluation and Field Optimisation of Kinetic Hydrate Inhibitors for Application Within MEG Recovery Units, Gas Condensate Field, Mediterranean Sea, SPE 127421, Presentation at the North Africa Technical Conference and Exhibition, 14-17 February 2010, Cairo, Egypt, 2010.

54. **M. H. Yousif and V. A. Dunayevsky**, Hydrate Plug Decomposition: Measurements and Modeling, SPE 30641, Prepared for presentation at the SPE Annual Technical Conference & Exhibition held in Dallas, U.S.A., 22-25 October, 1995, 1995.

55. **Majeed H. Yousif**, Effect of Under-Inhibition with Methanol and Ethylene Glycol on the Hydrate Control Process, OTC 8234, Prepared for presentation at the Offshore Technology Conference held in Houston Texas, 6-9 May, 1996.

56. **Donald L. Katz**, Depths to Which Frozen Gas Fields May Be Expected – Footnotes, SPE 3825, Journal of Petroleum Technology, 1972.

57. **John Boxall, Simon Davies, Carolyn A. Koh and E. Dendy Sloan**, Predicting When and Where Hydrate Plugs Form in Oil-Dominated Flowlines, SPE 129538, Revised for publication from paper OTC 19514, first presented at the Offshore Technology Conference, Houston, 5-8 May 2008, 2009.

58. **Bahman Tohidi, Ali Danesh, R. W. Burgass and A. C. Todd**, Hydrates Formed in Unprocessed Wellstreams, SPE 28478, Prepared for presentation at the SPE 69th Annual Technical Conference and Exhibition held in New Orleans, LA, U.S.A., 25-28 September 1994, 1994.

59. **M. A. Kelland, T. M. Svartaas and L. A. Dypvik**, Control of Hydrate Formation by Surfactans and Polymers, SPE 28506, Prepared presentation at the SPE 69th Annual Technical Conference and Exhibition held in New Orleans, LA, 25-28 September 1994, 1994.

60. **A. P. Mehta, P. B. Herbert, E. R. Cadena and J. P. Weatherman**, Fulfilling the Promise of Low-Dosage Hydrate Inhibitors: Journey From Academic Curiosity to Successful Field Implementation, SPE 81927, Publication from paper OTC 14057, prepared for presentation at the 2002 Offshore Technology Conference, Houston, 6-9 May, 2003.

61. **H. Haghighi, R. Azarinezhad, A. Chapoy, R. Anderson and B. Tohidi**, Hydraflow: Avoiding Gas Hydrate Problems, SPE 107335, Prepared for presentation at the SPE Europec/EAGE Annual Conference and Exhibition held in London, United Kingdom, 11-14 June 2007, 2007.

62. **S. B. Fu, L. M. Cenegy and C. S. Neff**, A Summary of Successful Field Applications of A Kinetic Hydrate Inhibitor, SPE 65022, Presented at the 2001 SPE International Symposium on Oilfield Chemistry held in Houston Texas 13-16 February 2001, 2001.

63. **S. Mokhatab, R.J. Wilkens and K.J. Leontaritis**, Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 2007, 29, 39.

64. Kinetic Inhibition of Natural Gas Hydrates in Offshore Drilling, Production and Processing, DOE/MC/29248-5594 (DE97002241), Annual Report, 1 January-31 December, 1994.

65. **Steen Skjold-Jørgensen, Jan Munck and Peter Rasmussen**, Computations of the Formation of Gas Hydrates, SPE 16034, SPE Publications, 1986.

66. **K.J. Kinnari, C. Labes-Carrier, K. Lunde and L. Aaberge**, International Patent Application WO/2006/027609.

67. **R. Azarinezhad, A. Chapoy, R. Anderson and B. Tohidi**, HYDRAFLOW: A Multiphase Cold Flow Technology for Offshore Flow Assurance Challenges, OTC 19485, Prepared for presentation at the 2008 Offshore Technology Conference held in Houston, Texas, U.S.A., 5-8 May 2008, 2008.

68. **R. Alapati, E. Sanford, E. Kiihne and E. Vita**, Proper Selection of LDHI for Gas-Condensate Systems, in the Presence of Corrosion Inhibitors, OTC 20896, Prepared for presentation at the 2010 Offshore Technology Conference held in Houston, Texas, 3-6 May 2010, 2010.

69. **C. B. Argo, R. A. Blain, C. G. Osborne and I. D. Priestley**, Commercial Deployment of Low-Dosage Hydrate Inhibitors in a Southern North Sea 69km Wet-Gas Subsea Pipeline, SPE 63017, Publication from paper SPE 37255, first presented at the 1997 SPE International Symposium on Oilfield Chemistry held in Houston, 18-21 February, 2000.

70. **P. J. Rensing, M. W. Liberatore, N. Tonmukayakul, C. A. Koh and E. D. Sloan**, *In Situ* Formation and Evolution of Gas Hydrates in Water-in-Oil Emulsions Using Pressure Rheometry, CP1027, The XVth International Congress on Rheology, The Society of Rheology 80th Annual Meeting, American Institute of Physics 978-0-7354-0549-3/08, 2008.

71. **Ulfert Klomp**, The world of LDHI: From conception to development to implementation, Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, British Columbia, Canada, 6-10 July 2008, 2008.

72. **J. A. Moore, L. Ver Vers and P. Conrad**, Understanding Kinetic Hydrate Inhibitor and Corrosion Inhibitor Interactions, OTC 19869, Prepared for presentation at the 2009 Offshore Technology Conference held in Houston, Texas, USA, 4-7 May 2009, 2009.

73. **Manika Varma-Nair, Christine A. Costello, Karla S. Colle and Hubert E. King**, Thermal Analysis of Polymer-Water Interactions and Their Relation to Gas Hydrate Inhibition, Journal of Applied Polymer Science, Volume 103, 2642-2653, 2007.

74. **P. A. Webber**, Fundamental Understanding on the Effects of Anti-Agglomerates Towards Overboard Water Quality, OTC 20841, Prepared for presentation at the 2010 Offshore Technology Conference held in Houston, Texas, USA, 3-6 May 2010, 2010.

75. **Jun Tian and Stephen A. Littlefield**, Hydrate inhibition test loop, International Patent Application, WO 2012/047821 A2.

76. **S. Høiland, K. M. Askvik, P. Fotland, E. Alagic, T. Barth and F. Fadnes**, Wettability of Freon hydrates in crude oil/brine emulsions, Journal of Colloid Interface Science, 287, 217-225, Elsevier, 2005.

77. **Xiaokai Li, Latifa Negadi and Abbas Firoozabadi**, Anti- agglomeration in Cyclopentane Hydrates from Bio- and Co- surfactants, Energy Fuels, 24, 4937-4943, 2010.

78. **Anthony I. Okoh**, Biodegradation alternative in the cleanup of petroleum hydrocarbon pollutants, Biotechnology and Molecular Biology Review, Volume 1 (2), 38-50, 2006.

79. **Jonny Beyer, Arnfinn Skadsheim, Malcolm A. Kelland, Kjetil Alfsnes and Steinar Sanni**, Ecotoxicology of Oilfield Chemicals: The Relevance of Evaluating Low-dose and Long-term Impact on Fish and Invertebrates in Marine Recipients, SPE 65039, Prepared for presentation at the 2001 SPE International Symposium on Oilfield Chemistry held in Houston, Texas, 13-16 February 2001, 2001.

80. **Donald G. Hill, Keith Dismuke, William Shepherd, Henk Romijn, Irena Witt, K. E. Wennberg, Hugues Poitrenaud, Hans Gruner and Daniel Perez**, Reducing Risk of Oilfield Chemicals to Marine Environments - Development Practices, Achievements and Benefits, Prepared for presentation at the SPE International Conference on Health, Safety and Environment In Oil and Gas Exploration and Production held in Kuala Lumpur, Malaysia, 20-22 March, 2002, 2002.

81. **Ronald M. Atlas**, Petroleum Biodegradation and Oil Spill Bioremediation, Marine Pollution Bulletin, Volume 31, Nos 4-12, 178-182, 0025-326X(95)00113-1, 1995.

82. **Ronald M. Atlas**, Bioremediation of Petroleum Pollutants, International Biodeterioration & Biodegradation, 317-327, 0964-8305(95)00030-5, 1995.

83. OSPAR Recommondation 2010/4 on a Harmonised Pre-screening Scheme for Offshore Chemicals.

84. OECD 306, Biodegradability in Seawater, 1992.

85. OECD, Guidance document for the development of OECD guidelines for the testing of chemicals, Number 1, 2009.

86. **Larry D. Talley, Garrick F. Mitchell and Russel H. Oelfke**, Comparison of Laboratory Results on Hydrate Induction Rates in a THF Rig, High-Pressure Rocking Cell, Miniloop and Large Flowloop, Annals of the New York Academy of Sciences, Volume 912, Issue 1, 2006.

87. **T. Austvik, E. Hustvedt, B. Meland, L. Berge and D. Lysne**, Tommeliten Gamma Field Hydrate Experiments, Proceedings of the 7th International Conference on Multiphase Production, Cannes, France, 7-9 June, 1995, 1995.

88. **A. C. Gulbrandsen and T. M. Svartaas,** Influence of Formation Temperature and Inhibitor Concentration on the Dissociation Temperature for Hydrate Formed with Poly Vinyl Caprolactam, Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, British Colombia, Canada, July 6-10, 2008.

89. **V. Mohebbi, A. Naderifar, R. M. Behbahani and M. Moshfeghian,** Investigation of kinetics of methane hydrate formation during isobaric and isochoric processes in an agitated reactor, Chemical Engineering Science 76, 58-65, Elsevier, 2012.

90. **C. Gaillard, J. P. Monfort and J. L. Peytavy,** Investigation of Methane Hydrate Formation in a Recirculating Flow Loop: Modeling of the Kinetics and Tests of Efficiency of Chemical Additives on Hydrate Inhibition, Oil & Gas Science and Technology-Rev. IFP, Volume 54, No. 3, 1999.

91. **Erik G. Dirdal, Chandrakala Arulanantham, Hamidreza Sefidroodi and Malcolm A. Kelland**, Can cyclopentane hydrate formation be used to rank the performance of kinetic hydrate inhibitors?, Proceedings of the 7th International Conference on Gas Hydrates, Edinburgh, Scotland, United Kingdom, 17-21 July, 2011.

92. **Shuqiang Gao**, Hydrate Risk Management at High Watercuts with Anti-agglomerant Hydrate Inhibitors, Energy & Fuels, Volume 23, 2118-2121, 2009.

93. **Ron K. Berger and Norman D. McMullen**, Lessons Learned from Troika's Flow Assurance Challenges, OTC 13074, Prepared for presentation at the Offshore Technology Conference held in Houston, Texas, 30 April-3 May 2001, 2001.

94. **Are Lund, Olav Urdahl and Sigrid S. Kirkhorn**, Inhibition of gas hydrate formation by means of chemical additives-II. An evaluation of the screening method, Chemical Engineering Science, Volume 51, Number 13, 3449-3458, 1996.

95. **Bo-Hui Shi, Jing Gong, Chang-Yu Sun, Jian-Kui Zhao, Yao Ding and Guang.Jin Chen**, An inward outward natural gas hydrates growth shell model considering intrinsic kinetics, mass and heat transfer, Chemical Engineering Jornal, 171, 1308-1316, 2011.

96. **Pei Cheng Chua and Malcolm A. Kelland**, Study of the Gas Hydrate Anti-Agglomerant Performance of a Series of n-Alkyl-tri(n-butyl)ammonium Bromides.

97. **Christophe Duchateau, Jean-Louis Peytavy, Philippe Glénat, Tong-Eak Pou, Manuel Hidalgo and Christophe Dicharry**, Laboratory Evaluation of Kinetic Hydrate Inhibitors: A Procedure for Enhancing the Repeatability of the Test Results, Energy & Fuels, Volume 23, 962-966, 2009.

98. **Lars Henrik Gjertsen and Finn Hallstein Fadnes**, Measurments and Predictions of Hydrate Equilibrium Conditions, Annals New York Academy of Science, 722-734.

99. **B. Tohidi, R. W. Burgass, A. Danesh, K. K. Østergaard and A. C. Todd**, Improving the Accuracy of Gas Hydrate Dissociation Point Measurements, Annals New York Academy of Science, 924-931.

100. **Chang**, Chemistry BIK230 General Chemestry, University of Stavanger, Ninth Edition, McGraw-Hill, 2007, 105-107.

APPENDIX A: RESULTS AND BLUEPRINTS

In all, both successful and unsuccessful, 69 experiments were conducted. Many alterations to both the method and apparatus were done, some issues with the apparatus arose and different experiments were conducted, a description of all in the comment part, table A.1.

Table A.1. All experiments conducted, not all successful. In the comment part a description of each experiment can be found.

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
18.02.13	15000	OBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	28.43	Solid, white, hydrate plug. It seemed like hydrate formed after 1h and 51min, but the liquid moved freely.	E
19.02.13	15000	DBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (1h 45min)	26.86	Plug of hydrate all around the top of the wheel. After 30min on 0^{o}C a hydrate slurry was made. After 1h more viscous and deposits. 1h and 15min more viscous and more deposits. In order for minimizing the amount of air in the water bath, the valves that control the flow rate both out and in to the water cooler was turned.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
11.02.13	1000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (10min)	35.4	Hydrate plug. First test with chemical added (AA). A start/stop switch was mounted on one of the electronic box lids.	D
14.02.13	3000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (1h 21min)	33.32	Hydrate plug, a slushy plug. Washed two times with Distilled water to get rid of any possible liquid from last time. The gas inflow to the wheel was secured.	D

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
20.02.13	3000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (1^{o}C in wheel) (13min)	34.64	Slushy plug. This is the same experiment as on 14.2, except that the rotation speed was doubled at 4^{o}C on the water cooler, from 18rpm to 36-38rpm. This had no effect on hydrate formation, and normal speed (18rpm) was continued used. A electronic device was mounted that helped on the interference on the temperature probe in the wheel. Now this temperature in the wheel could also be used. The water bath was emptied to get excess to the temperature probe so it could be switched out with an identical one that had been calibrated.	D

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
15.02.13	4000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (2h 9min)	31	Hydrate slurry. Looked better than at partial water concentration. Because the particles are "drier" and more easily dispersed.	A
12.02.13	5000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (1h 55min)	26.1	A hydrate slurry was formed. New software interface was created. Now data could be logged. The pressure meter lags because of more program loops.	A
06.02.13	250	DDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	$1,9^oC$ in wheel	35.46	Solid hydrate plug.	E
13.03.13	2000	DDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	27.8	Slushy hydrate plug.	D

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
14.03.13	3000	DDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	25.45	Hydrate slurry with deposits.	B
26.04.13	500	DDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	28.97	Slushy hydrate plug with some free water.	C
25.04.13	1000	DDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	27.1	Hydrate slurry with minor deposits. In this experiment the original white spirit was used again.	B
01.03.13	4000	TDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (over weekend)	18.34	Slushy plug. First test over a weekend. At 0.8^{o}C in the wheel, small deposits in it. At 0.2^{o}C (1h and 7min on 0^{o}C in water cooler) hydrate slurry formed. Have gone from sticky hydrates to more powder like, dry, hydrates.	C

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
26.02.13	5000	TDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (2h 27min)	29.5	Fine hydrate slurry. After 31min on 0^{o}C more and more hydrate particles formed in the bottom of the wheel. After 1h a hydrate slurry was formed.	A
22.02.13	1000	TDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (2h 46min)	33.3	Slushy plug. Looked allot like 3000ppm DDBAB. After 7min, at 1.1^{o}C in the wheel, there were a fine slurry at the bottom of the wheel. Balls stopped, maybe because of that they hit the temperature probe. After 15min the pressure was 35.30bar and the slurry was still fine.	B/C
25.02.13	2000	TDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight, 19h 50min)	25.78	A white hydrate slurry. Small deposits in the bottom of the wheel.	A/B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
22.03.13	250	TDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (over weekend)	25.61	Slushy hydrate plug. Some free moving liquid around the plug. The pressure measuring fluctuated quite a bit.	D
21.03.13	500	TDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	25.68	Hydrate slurry.	A
05.03.13	10000	HDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight, 22h 54min)	20.62	Hydrate slurry with deposits.	C
11.03.13	15000	HDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	19.7	Hydrate slurry with deposits.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
27.02.13	1000	HDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	1.5^{o}C in wheel	34.72	A hydrate plug. The plug was white and lumpy. Maybe a little slushy.	D/E
28.02.13	2000	HDBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (2h 4min)	30.4	Hydrate slurry with minor deposits. At 0.7^{o}C in the wheel hydrate slurry with deposits formed.	B
04.03.13	1000	ODBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	1.7^{o}C in wheel	34.33	Slushy plug. At 3.7^{o}C in the wheel small hydrate deposits. 2 min later a slushy plug was formed.	D
07.02.13	10000	ODBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^{o}C (overnight)	20	Hydrate slurry with fine deposits, but mostly dispersed hydrates. It had fine hydrate slurry in the beginning, turned worse overnight.	C

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
08.02.13	15000	ODBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	21.1	Hydrate slurry formed. Looked better than 10000ppm in 15000ppm NaCl, because no build up of deposits.	B
21.02.13	30000	ODBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC	30.5	Fine hydrate slurry. No deposits.	A
30.04.13	4000	CBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	23.83	Slushy hydrate plug formed at one place in the wheel, with free water.	D
29.04.13	5000	CBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	20.75	Hydrate slurry with deposits.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
20.03.13	6000	CBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	19.29	Hydrate slurry with deposits. The same experiment as on the 19.3, but here the water cooler held.	B
02.05.13	3000	CBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	14.59	Hydrate slurry with deposits. Suspect a gas leak.	B
13.05.13	3000	CBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	21.21	Hydrate slurry with major deposits. Almost not flowing, viscous. New quick release arrived and mounted. Also the gas valve connection to the wall was lowered. Same experiment as on the 2.5.	C

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Effekt, Europris AS)											
15.03.13	4000	CBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	21.54	Hydrate slurry with deposits.	B
18.03.13	5000	CBAB	20ml AA solution	40ml White spirit	15000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	15.93	Hydrate slurry with deposits. Looked the same as 4000ppm, but the pressure drop was higher. The cable mount to the pressure gauge was turned so that the pressure measurements now was more stable.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Kemetyl Norway AS)											
16.04.13	4000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	26.33	Little slushy, Hydrate plug. This was the first test with new pressure gauge and new type white spirit. Therefore an old experiment (15.2) was executed again for validation. Old experiment gave rank A, the same experiment gave rank D with new white spirit. A leak in the drainage hose was sealed.	D
19.04.13	4000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	22.87	Slushy hydrate plug. The plug was only present at one place, free water. This is the same experiment as on the 16.4, with the same result, and with original white spirit on the 15.2. Used the sink to make a vacuum in order to drainage the last amount of liquid from the wheel.	D

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Kemetyl Norway AS)											
17.04.13	5000	DDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	19.74	Hydrate slurry with deposits. An experiment that has been conducted before (12.2) was conducted again for validation of the new white spirit. Previous experiment gave rank A. All the connections to the wheel was secured with wire.	B
23.04.13	2000	DDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl	Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	26.14	Hydrate slurry with deposits. New Pressure gauge and white spirit.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
White Spirit (Naphtha (petroleum), hydrodesulfurized heavy, > 30% aliphatic hydrocarbons, 15-30% aromatic hydrocarbons). (Kemetyl Norway AS)											
18.04.13	5000	TDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	20.61	Hydrate slurry. An experiment that has been conducted before (26.2) was conducted again for validation of the new white spirit. Same result as the one before.	A
22.04.13	15000	HDBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC (overnight)	19.93	Slushy hydrate plug. The plug was all over the wheel, seemed dry. This is the same experiment as on the 11.3 which gave rank B, but with new white spirit and pressure gauge.	D

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
n-Decane ($C10H22$, 1L=0,73Kg, M=142,29g/mol, Assay (GC, area%) ≥94%, Density (d 20^{o}C/4^{o}C)= 0,728-0,732). (Merck Schuchardt OHG)											
23.05.13	1000	TDBAB	20ml AA solution	40ml n-Decane		Water in oil emulsions. The n-Decane went cloudy when pressurized.	40	0^{o}C (overnight)	30.55	Solid, lumpy and clear hydrate plug, with free water, also clear.	E
22.05.13	2000	TDBAB	20ml AA solution	40ml n-Decane		Water in oil emulsions. The n-Decane went cloudy when pressurized.	40	0^{o}C (overnight)	27.43	Hydrate slurry with deposits, looked similar to 3000ppm.	B
21.05.13	3000	TDBAB	20ml AA solution	40ml n-Decane		Water in oil emulsions. The n-Decane went cloudy when pressurized.	40	0^{o}C (overnight)	21.41	Hydrate slurry with deposits, may be somewhat more deposits than on 4000ppm.	B
15.05.13	4000	TDBAB	20ml AA solution	40ml n-Decane		Water in oil emulsions. The n-Decane went cloudy when pressurized.	40	0^{o}C (overnight)	19.79	Hydrate slurry with deposits. More deposits than 5000ppm TDBAB.	B
14.05.13	5000	TDBAB	20ml AA solution	40ml n-Decane		Water in oil emulsions. The n-Decane went cloudy when pressurized.	40	0^{o}C (overnight)	19.04	Hydrate slurry with deposits.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
o-Xylene (C8H10, 1L=0,88Kg, M=106,16g/mol, Assay (GC, area%) ≥98%, Density (d 20^{o}C/4^{o}C)= 0,878-0,881). (Merck Schuchardt OHG)											
24.05.13	5000	TDBAB	20ml AA solution	40ml o-Xylene		Water in oil emulsions, little white and sticking to the walls. The o-Xylene went all white when pressurized.	40	0^{o}C (overnight)	17.37	Hydrate slurry with deposits.	B

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Only Distilled water											
24.01.13		No chemical added	Distilled water (>50ml)				30	2.9^{o}C	24	Plenty of hydrate. Hydrate plug. First test without leaks. Silicone grease on the two disk parts, and tightened the screws, helped. Pressure gauge must be calibrated. Have only the water cooler temperature, not the actual temperature in the wheel. Measured a deviation of 1.265^{o}C for water cooler to the wheel. Electronic things in general to be sorted out.	E
28.01.13		No chemical added	Distilled water (>50ml)				40	1.4^{o}C (2h)	20	Plenty of hydrate. Hydrate plug.	E
29.01.13		No chemical added	Distilled water (50ml) and a quarter spatel of Ocma clay			Cludy	40	2.3^{o}C	35	Plenty of hydrate. Hydrate plug. The Ocma clay seemingly did not have any effect on the hydrate formation temperature (onset temperature). Hydrate started melting at 16.5^{o}C.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Only Distilled water											
30.01.13		No chemical added	Distilled water (50ml)				40	9.6^{o}C	37.8	Plenty of hydrate. Hydrate plug. Added 5 stainless steel balls (4mm diameter) to help on making the hydrate formation temperature to increase and more reliable, which it did. They were partially hindered from moving by some sort of grease. The temperature probe was tried calibrated, but the engine interfered on the signals. An extra valve was mounted on the piping from the water cooler.	E
31.01.13		No chemical added	Distilled water (50ml)				40	11^{o}C	34.7	Plenty of hydrate. Hydrate plug. Maybe hydrate formed earlier, somewhat hard to observe. Many tiny air bubbles in the water bath.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Only Distilled water											
01.02.13		No chemical added	Distilled water (50ml)				40	10.2^{o}C	37.5	Plenty of hydrate. Hydrate plug. There were some stops in the rotation of the wheel because of some engine adjustments during the cool down. This could maybe interfered with the hydrate formation. A leak in the flushing hose, right at the connection to the valve on the wheel, was sealed. More 10% MEG in Distilled water was added to the water bath and the water cooler, to help on clarifying the view to the wheel. Hydrate not melted on 14^{o}C. From 15^{o}C, increased the temperature, 0.1^{o}C, every 15 min till 16^{o}C. Almost all hydrate melted.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Distilled water and white spirit											
04.02.13		No chemical added	12ml Distilled water	48ml white spirit		Water in oil emmulsions. The white spirit whent white when pressurized.	40	5^{o}C	30.8	Hydrate plug along the bottom of the wheel, long lump. Cleaned the wheel with white spirit in order for removing some of the silicone grease.	🟥 E
05.02.13		No chemical added	12ml Distilled water	48ml white spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	5.8^{o}C	36.9	Hydrate plug. More gas will dissolve in the white spirit (oil phase). Therefore the wheel needs to be pressurized several times until the required pressure is stable. After hydrate was formed, set the water cooler to 10^{o}C, for 15 min, 11^{o}C for 15 min. From 11.1^{o}C, increased 0.1^{o}C every 10min, to 11.5^{o}C. Hydrates melted at 11.4-11.5^{o}C. Started to flush and clean 3 times with Distilled water before every experiment from now on.	🟥 E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Distilled water and white spirit											
06.02.13		No chemical added	12ml Distilled water	48ml white spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	3.8^{o}C	36.8	Hydrate plug. The rotation speed was not on maximum, turned up during the experiment. The flushing hose blow off the wheel from the pressure from the air gun. Reattached and washed two more times with Distilled water. When almost all liquid was turned into hydrate, heated up to 10^{o}C for 15 min, 10.5^{o}C for 15min, 11^{o}C for 15 min. From 11.1^{o}C to 11.7^{o}C, increased by 0.1^{o}C every 10 min. At 11.3^{o}C almost all hydrate where melted.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Distilled water and white spirit											
07.02.13		No chemical added	20ml Distilled water	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	3.5^oC	36.7	Hydrate plug. After hydrate formation, heated to 11.4^oC for 15 min, almost all hydrate melted. The gas valves to the wheel was reattached to the wall. Started to fill the wheel with the water phase first and then the oil phase, since most of the AAs are water soluble.	E
08.02.13		No chemical added	20ml Distilled water	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	4.9^oC		Hydrate plug. Heated up to 11.3^oC for 15 min after hydrate formation. Increased by $0,1^oC$ every 15min until 11.6^oC. Almost all hydrate melted, but there were however some small lumps that seemed like hydrate that not melted.	E

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^{o}C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Experiments that for various reasons could not be conducted											
13.02.13		No chemical added	Nothing added	Nothing added	Nothing added		40	0^{o}C (overnight)	39.95	The wheel was pressurized to check for leaks. A leak emerged from one of the inner screws, a tiny stream of bubbles. The screw was next to the pressure gauge. After 15 min the pressure was roughly the same. Extracted the liquid and cleaned with white spirit. Pressurized again. At about 30bar, the leak emerged at the same place, and an additional leak at one of the outer screws, number 3 to the left from the temperature probe. At 40bar, however, the leaks stops. The pressure meter fluctuates on the last digits. No motion, cooled down to 0^{o}C overnight, then heated up again. Conclusion, no significant leaks.	

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Experiments that for various reasons could not be conducted											
19.03.13	6000	CBAB	20ml AA solution	40ml White spirit		Water in oil emulsions. The white spirit went white when pressurized.	40	0^oC		A tubing in the water bath now made the water intake to always stay under water level. This eliminated the air bubbles, thus clarify the vision. The water bath emptied itself, thus no cooling overnight.	
26.03.13	1000	DDBAB	20ml AA solution	40ml White spirit	70000 ppm NaCl					Could not pressurize because the pressure meter was stuck on 47.57 bar no matter what. By positioning the pressure gauge cable in different angles, the pressure changed, but this did not help much this time, only temporarily. It looks like the water level is stable with the tubing this time.	

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Experiments that for various reasons could not be conducted											
02.04.13										The pressure was still stuck on 47 bar. No experiment conducted. Emptied the water bath in order to get excess to the pressure gauge.	
04.04.13										The pressure gauge was removed and examined.	
09.04.13										Emptied the wheel. The original pressure gauge was broken. A new pressure gauge could be used, not the same as the original one.	
10.04.13										The new pressure gauge was mounted to the wheel. First pressure test showed some leaks. Took on some Teflon tape and the second pressure test worked fine, no leaks.	

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (°C) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Experiments that for various reasons could not be conducted											
24.04.13										Moved around the water cooler in order to get the water level stable. Moved the water cooler back to the original position, because no better result.	
03.05.13							40	(Room temperature over weekend)	6.65	Pressurized to 40 bar to confirm whether there are gas leaks or not, which there were. The gas leak came from both the inlet valve and the gas inlet/outlet connections.	
06.05.13										The quick release gas connection to the wheel broke. A new one is ordered.	
16.05.13										Tweaked around with one of the Valves to make the water level in the water cooler to be higher on 0°C. Secured the gas intake to the wheel again.	

Date	Concentration (ppm)	Chemical	Aqueous phase	Oil phase	NaCl	Initial change	Initial pressure (bar)	Temperature before T_o (^oC) or (time on T_o)	Pressure drop (bar)	Comment	Rank
Experiments that for various reasons could not be conducted											
27.05.13										There had formed some cracks in the acrylic top disk of the wheel, on all the connections except for the pressure sensor. Unsafe to run any test.	
28.05.13										Disassembled the wheel from the water bath so that it can be moved to further investigations.	

1.A Blueprints from the apparatus

The blueprints from the table top wheel apparatus are provided in the following.

Outline and measurements for the water bath, figure A.1.

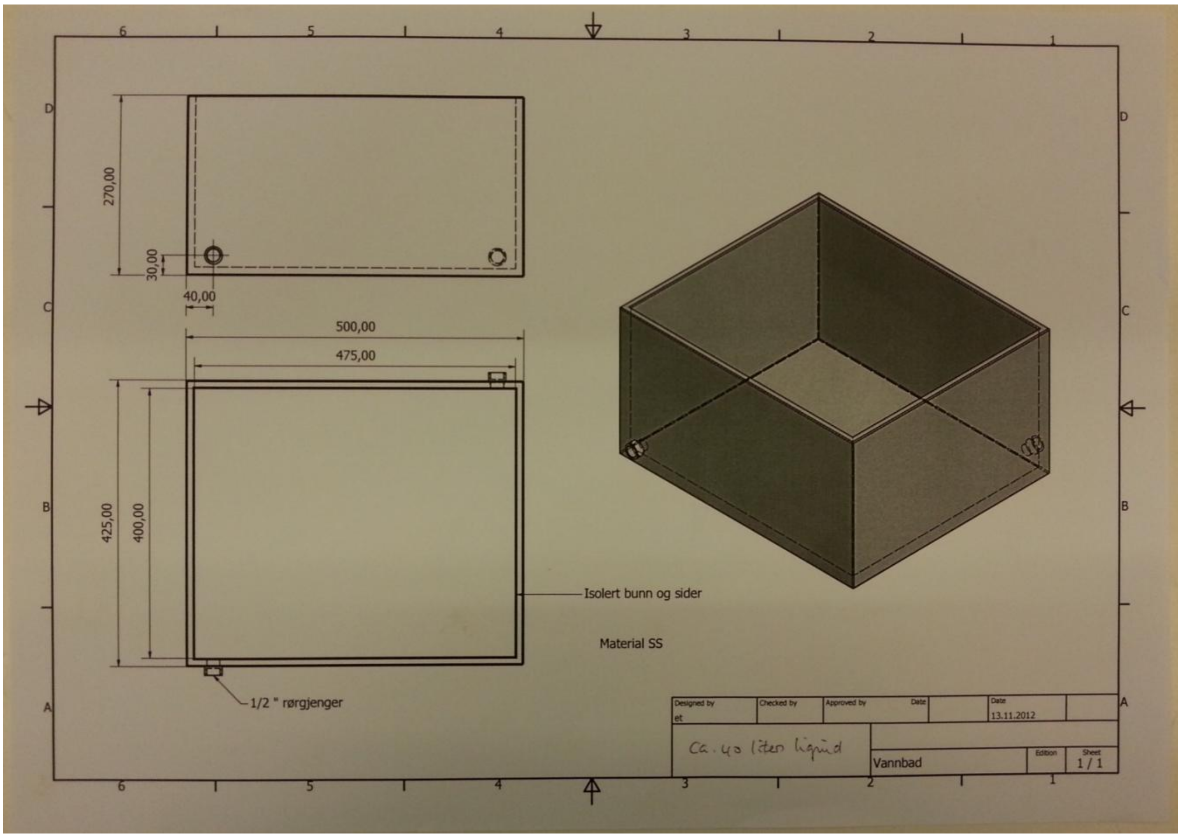
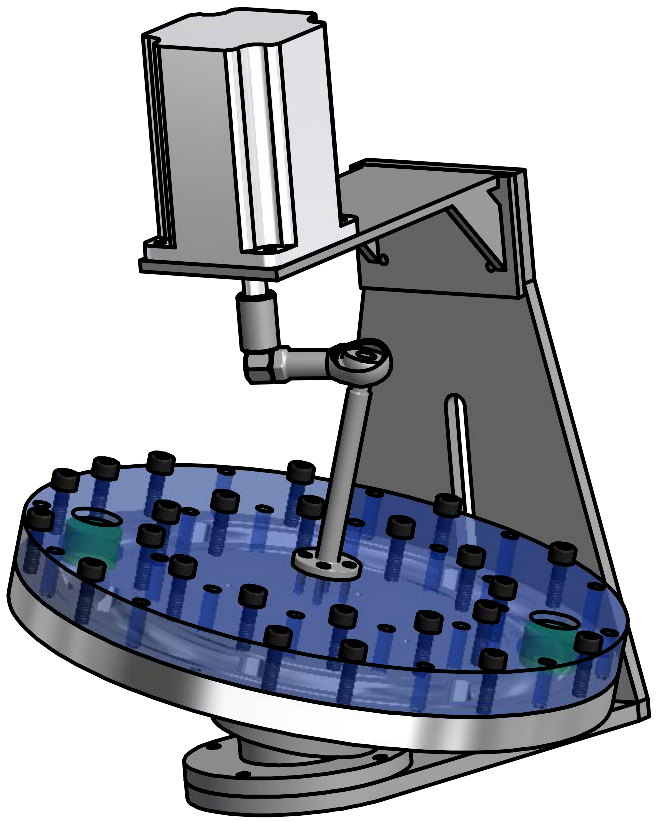
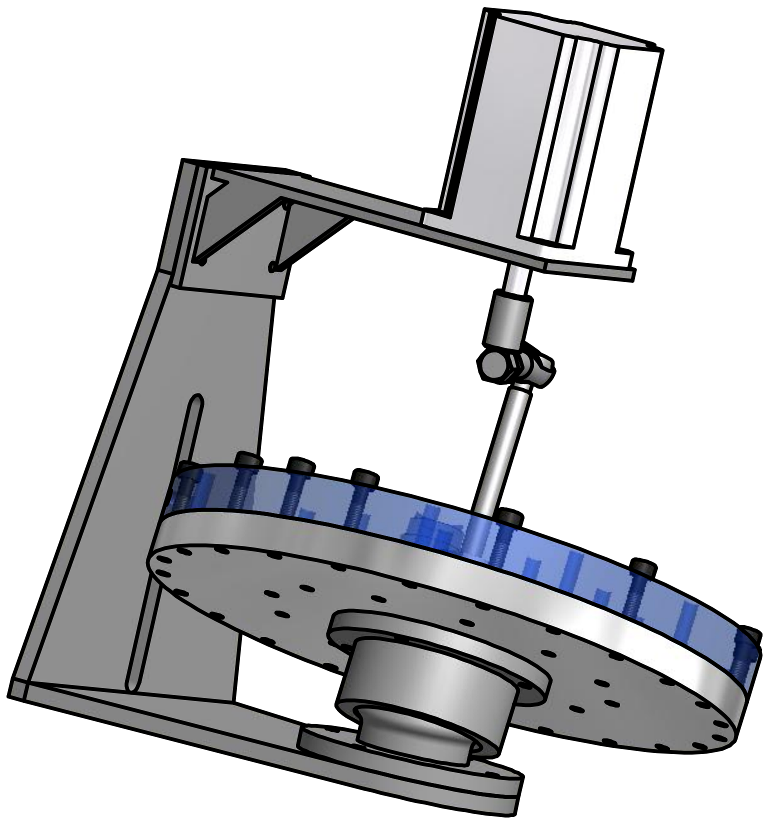


Figure A.1. The blueprint for the water bath.

Blueprints for the table top wheel are given in the following.





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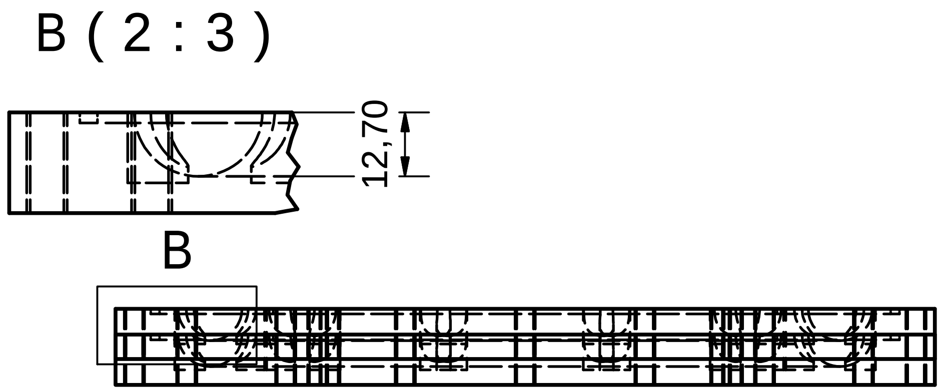
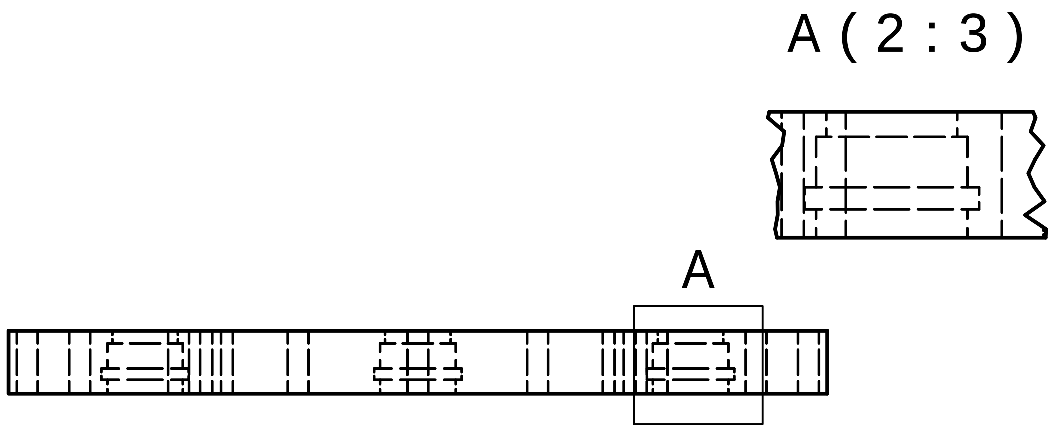
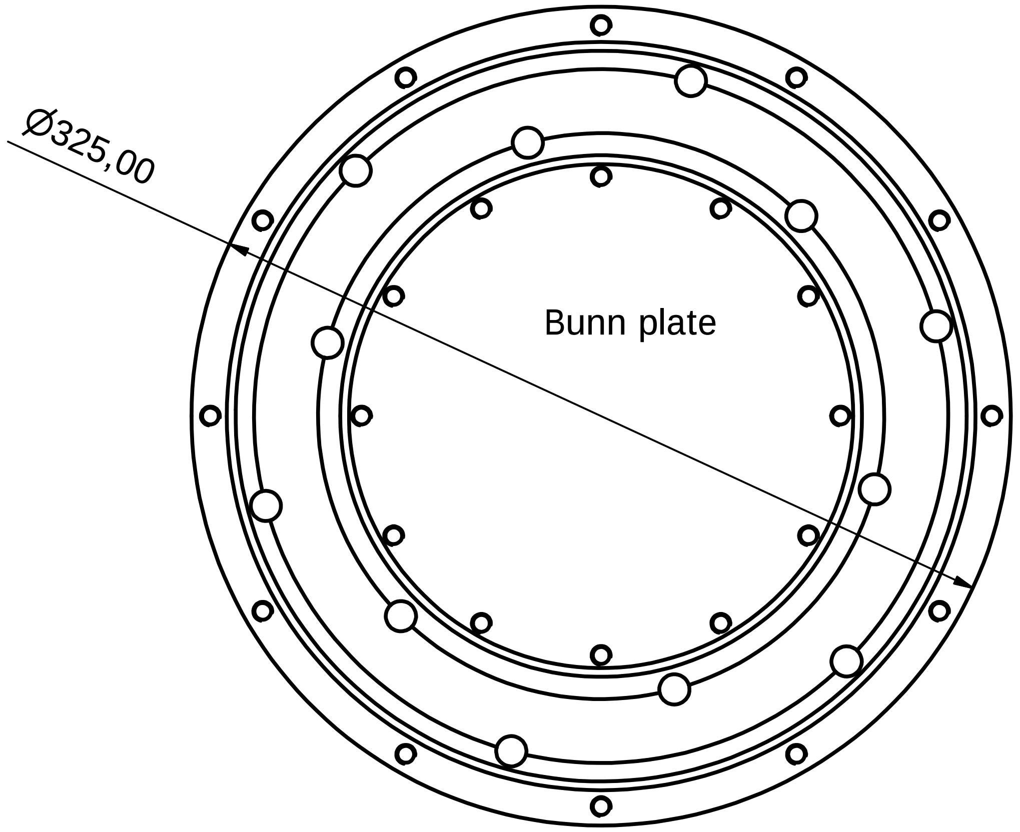
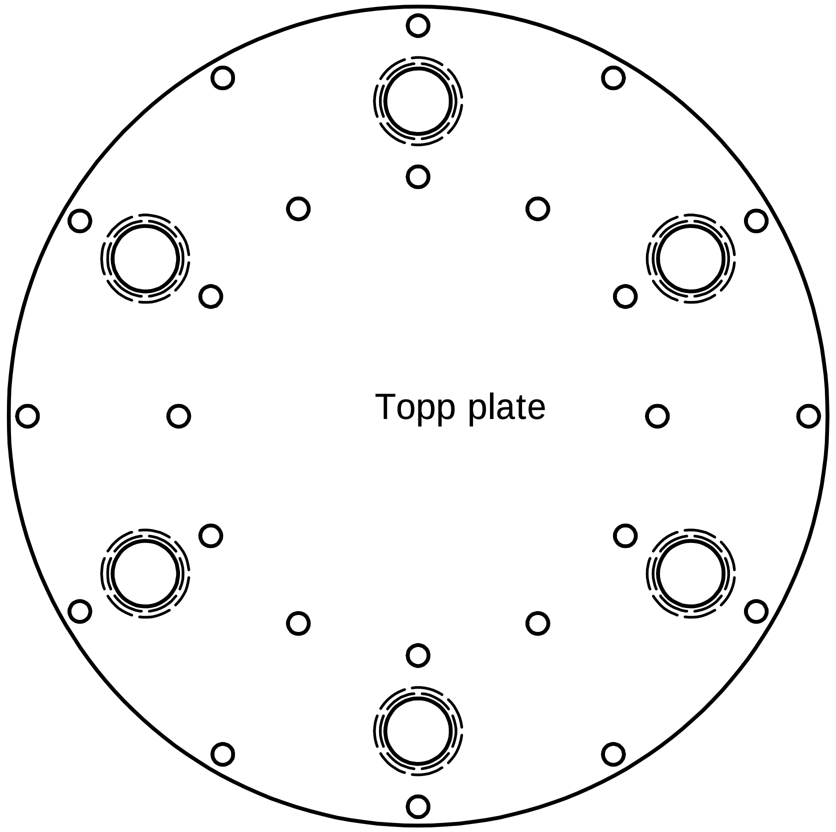
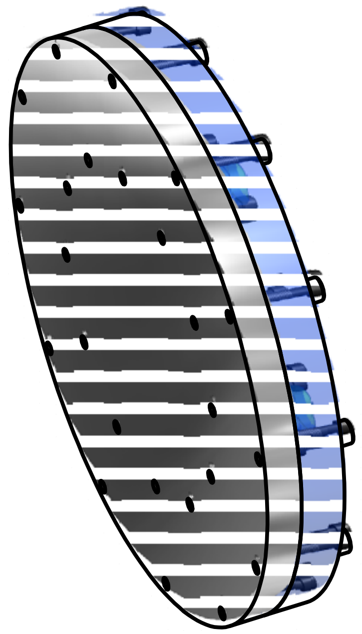
Assembly	Assembly 4	Edition	Sheet 1 / 1











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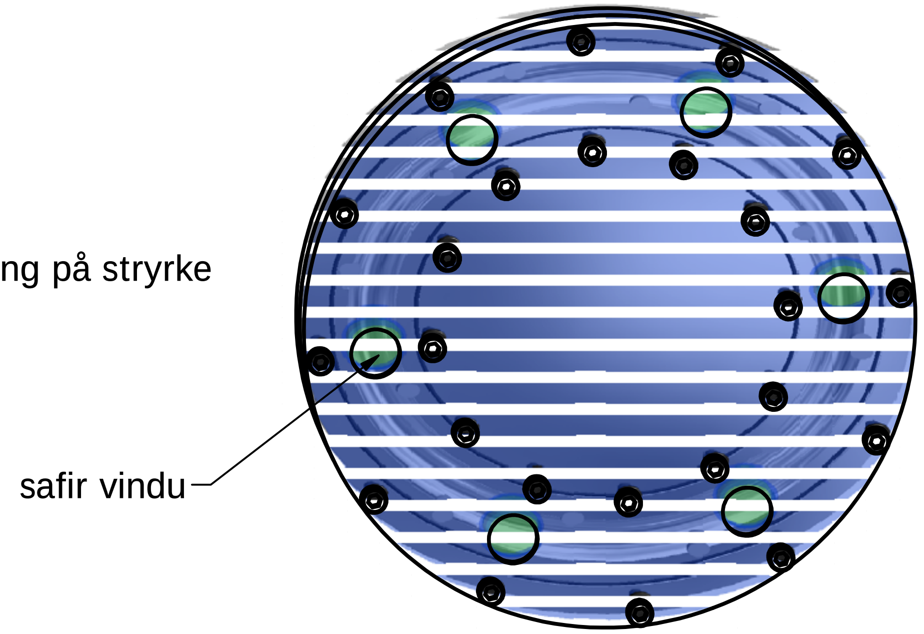
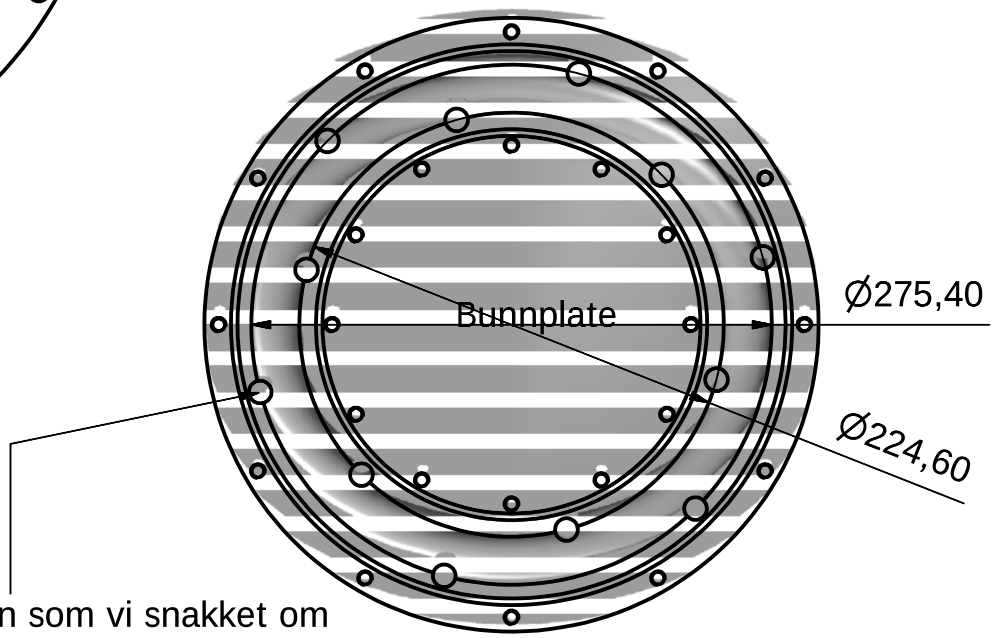
Er det slik du kan tenke deg?
Jeg må ta en ordentlig gjenomgang på stryrke beregningen.





Dette er restriksjonen som vi snakket om diameter 12mm

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APPENDIX B: THF RIG EXPERIMENTS

Meanwhile the new prototype apparatus was finalized, tests on a THF (tetrahydrofuran) rig were conducted. THF makes hydrate Structure II, which predominates in the field. The apparatus gives multiple results for each test run, thus excellent for screening test.

1.B Experimental equipment

During the conduction of the experiment, the following equipment was used: A water heater/cooler, a plastic water bath, glass beakers (80 and 40mL), hollow glass rods and a rack to hold the beakers and the hollow glass rods, figure B.1.

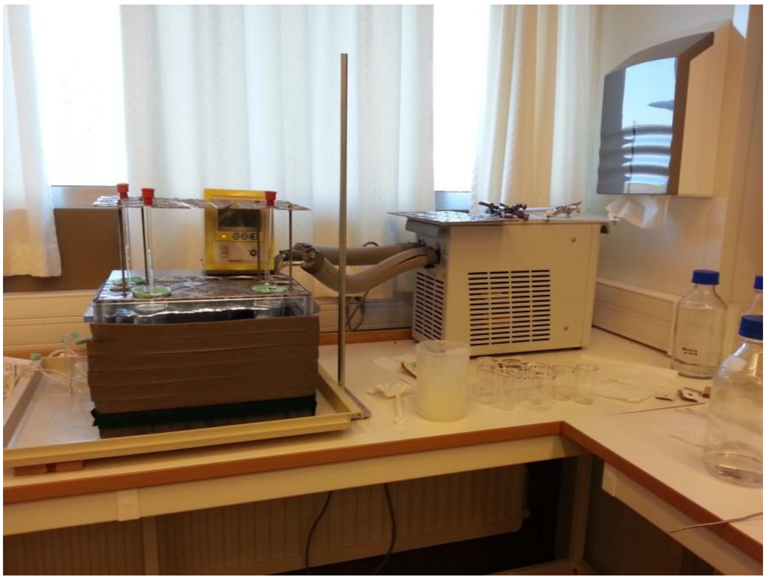

Figure B.1. The THF rig with the water bath together with the rack to hold both the glass rods and beakers on top of it. In addition the thermostat was also there. All this to the left. To the right is the water heater/cooler.

The liquid in the water bath was made up of distilled water and glycol. The glycol was added in order to prevent ice formation in the water cooler, since the water heater/cooler was operated in the range from −0.5 to −2.5°C. The rack was placed on top of the water tank. Here the beakers and rods where held in place. In the bottom of the water bath there were some lights that helped on making it easier to observe crystal growth and to make sure that the glass rods were not in contact with the beakers. The water heater/cooler was of the type LAUDA DLK 10 and was a through flow cooler with accuracy ±0.05°C. Its minimum and maximum temperature was −15°C and 150°C respectively. The temperature could be set, interval of 0.1°C, and it was shown on a digital display on the thermostat which was of the type LAUDA E 200.

2.B Experimental procedure

The water bath was set to the decided temperature, normally −0.5°C, and the rack was placed on top of the tank. In a needed number of beakers the required amount of inhibitor was weight out. Then THF was added up to the 40 or 80mL mark. The beakers was then placed into the water tank with 1 minute interval and held in place by the rack. Some ice was collected in a container and the hollow glass rods were placed into it. This was stored in a freezer that held approximately −15°C, to make sure that the ice had a uniform temperature. Meanwhile, with 5 minutes interval, the beakers were stirred in order for the liquid inside them to reach the water bath temperature for 20 minutes. Then the ice container was collected and the hollow glass rods were filled with ice and putted one in each beaker with 1 minute interval. Only the tip of the glass rod was in contact with the THF solution, in order to nucleate THF hydrate formation. It was important that all ice was removed from the outside of the rods so that they did not initiate hydrate crystallization. After 1 hour the rods were taken out and examined for crystal growth. If it was possible the ice structure was noted and possibly weight, figure B.2. By doing so the rate for THF crystal growth (g/h) at the tip of the hollow glass rods could be measured. Eventual crystal growth on the glass rod, not connected to the tip was ignored. Sometimes there were massive crystal growth, so massive that they grew out to the edge of the beakers, making it impossible to weigh them properly. The average growth rate of 4−8 experiments was recorded, in which the spread in growth rates was about 20−25%.

Figure B.2. An example of how a THF crystal might appear.

If there were THF crystal growth, different crystal morphology could arise from various inhibitors used. These morphologies were tried interpreted:
RP: Regular pyramidal crystals
TnP: Thin plates
TkP: Thick plates
CS: Crumpled sheets
RE: Regular pyramids but with rounded edges

The THF solution was made by mixing 26.28g NaCl (assay > 99.5% from VWR international) in 170g THF (density 0.995g/mL from VWR international), then adding distilled water to reach 900mL. This gives THF to H_2O molar ratio of 1:17, containing 36000ppm NaCl. THF is immiscible in water, but the NaCl helps in making it into one phase.

Since this was only a temporary arrangement, thus not many inhibitors were tested. The inhibitors used were TBPB (tetrabutylphosphonium bromide, 98%), TPAB (tetrapentylammonium bromide, > 99%) and $Bu_3iHexP^+Br^-$, all of which on different concentrations. The first two inhibitors where supplied by Sigma-Aldrich, while the third was prepared in the laboratory. On the basis of this relatively small test results, no significant conclusion could be drawn from these experiments.