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MASTER'S THESIS

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Abstract

This thesis presents the development of a methodology for testing paraffin dispersants.

Wax deposition is one of the main problems related to offshore production and transportation of crude oil. In the petroleum industry today paraffin inhibitors are the most commonly used chemicals to prevent wax deposition. In countries where environmental regulations are stipulated on biodegradation, the use of these non-biodegradable polymers restricts the use of such chemistry. Service companies are then only allowed to use biodegradable chemicals, which limits the chemicals to paraffin dispersants for paraffin control.

There was no standard technique defined to properly performance test paraffin dispersants. Based on this, a methodology for testing paraffin dispersants was developed.

The aim of this thesis was to develop a standard methodology for testing paraffin dispersants where the wax deposition was driven by shear dispersion rather than a thermal gradient, and to evaluate the performance of different types of paraffin dispersants in order to identify the best performers. In addition, different types of wax prevention chemicals were added to a crude oil sample, and the wax crystal structure and the effect of the chemicals was analysed.

Two different types of crudes were tested, and a number of tests were performed using a wax loop. When testing crude A having a wax content of 20.4%, one was able to obtain wax deposition driven by shear dispersion rather than a thermal gradient, and one could clearly differentiate between a good and bad performer when adding different types of paraffin dispersants to the crude oil sample. When repeating the methodology on crude D having a higher wax content and WAT, it was possible to obtain wax deposition driven by shear dispersion rather than a thermal gradient. Despite of this it was not possible to perform any further testing on crude D.

When looking at the structure of paraffin wax crystals at the microscope, the addition of different types of wax prevention chemicals did not result in a significant change in wax crystal structure. However, the addition of different types of wax prevention chemicals did influence the amount and size of wax crystals and the WAT of the crude.

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Nomenclature

W_m = Rate of wax crystal deposition due to molecular diffusion

ρ_r = Wax crystal density

A = Surface area available for deposition

D_m = Molecular diffusion coefficient

dC/dT = Solubility coefficient of the wax crystals in the crude

dT/dy = Radial temperature gradient at the pipe wall

m_b = Mass of wax deposited by Brownian motion

t = Time

ρ_d = Density of the solid wax

D_B = Brownian motion diffusion coefficient of the solid wax crystals

A = Surface area available for deposition

C^* = Concentration of solid wax out of the solution

r = Radial coordinate

D_s = Shear dispersion coefficient

a = Particle diameter

γ = Oil shear rate at pipe wall

C^*_w = Volume fraction concentration of solid wax of solution at the wall

F_g = Gravity force

r_p = Particle radius

ρ_p = Density of particle

ρ_f = Density of fluid

g = Acceleration due to gravity

F_f = Frictional force

r_p = Particle radius

μ = Viscosity of the fluid

υ = Velocity fall of particle

S_{WS} = Spreading coefficient for water and a solid

γ_{SO} = Interfacial tension between a solid and oil

γ_{WO} = Interfacial tension between water and oil

γ_{SW} = Interfacial tension between a solid and water

$d\gamma$ = Change in surface or interfacial tension of the solvent

Γ_I = The surface excess concentration of any component of the system

$d\mu_i$ = Change in chemical potential of any component of the system

Re = Reynolds number

D = Hydraulic diameter of the pipe

u = Average fluid velocity

ρ = Density of the fluid

μ = Dynamic viscosity of the fluid

q = Volumetric flow rate

A = Cross sectional area of flow

D = Diameter of the pipe

ρ = Density of the crude

m = Mass of the crude

V = Volume of the pycnometer

Abbreviations

WAT = Wax appearance temperature

WDT = Wax dissolution temperature

PPDs = Pour point depressants

EVA = Ethylene/vinyl acetate

PVT = Pressure volume temperature

GC = Gas chromatography

Chapter 1 Introduction

Wax deposition is one of the main problems related to offshore production and transportation of crude oil. When the temperature decreases and the pipeline is cooled down during production, paraffin compounds present in the crude oil will precipitate and lead to wax deposition. This leads to flow assurance challenges, and causes a loss of revenue to the petroleum industry.

The standard methodology for paraffin control includes either static and dynamic test methods or viscosity modification. The static and dynamic test methods are designed to show the improvement of pour point control, deposition control and yield stress, while viscosity modification imparted by the application of chemistry modifies the paraffin crystal growth and/or dispersion of crystals due to crystal modification.

In the petroleum industry today paraffin inhibitors are the most commonly used chemicals to prevent wax deposition, although some limitations do exist. When the wax appearance temperature (WAT) downhole is the same as or close to the reservoir temperature, the application of paraffin inhibitors are limited by the fact that they only function effectively when applied above the WAT. In most regions around the world the use of this crystal modification chemistry is acceptable. However, in countries where environmental regulations are stipulated on biodegradation, the use of these non-biodegradable polymers restricts the use of such chemistry. Service companies are then only allowed to use biodegradable chemicals, which at the present time limits the chemicals to dispersants for paraffin control.

There is currently no standard technique defined to properly performance test paraffin dispersants. Dispersants can be applied at a temperature below the WAT and are designed to prevent both agglomeration and deposition, but most test methods do not show improvements due to the test methodology.

1.1 Thesis objectives

The objectives of this master thesis include:

- Developing a standard methodology for testing paraffin dispersants, where the wax deposition is driven by shear dispersion rather than a thermal gradient. The methodology should be a practical solution for industrial use.
- Evaluate different types of paraffin dispersants in order to identify the best performers.
- Looking at the structure of paraffin wax crystals at the microscope, and how addition of different wax prevention chemicals affects the WAT and the wax crystal structure.

Chapter 2 Theory

2. 1 Paraffin wax

2.1.1 Paraffin wax definition

The term paraffin wax is used for a mixture of solid hydrocarbons. These solids are made up of long-chain (>C18), normal or branched alkane compounds, which are naturally present in crude oils and some condensates. Cyclic alkanes and some aromatic hydrocarbons may also be present. The pipeline wax deposition is caused by the normal alkanes (also known as n-paraffin waxes) that deposit on the pipeline wall. Waxes in crudes are of longer chain-alkanes, which make the waxes in crudes harder to control than those in condensates. Soft waxes are usually observed when the molecular size is 18-25 carbon atoms, while hard crystalline waxes have 25-50 or more carbons in the chain. The size of the molecules in the paraffin waxes has an impact on the melting point, as increasing the size of the molecules increases the melting point. This means that the higher the melting point, the more difficult it is to keep the paraffin wax from forming deposits. [1]

2.1.2 Wax appearance temperature

The wax appearance temperature is defined as the temperature at which the first wax crystals begin to precipitate from the crude oil. This is a very important measurement when it comes to production and handling of crude oil. Under reservoir conditions (temperature range from 70-150°C and pressure range of 8000-15000 psi) the wax remains dissolved in the crude oil. When the crude oil is being produced and leaves the reservoir and flows through cold environment pipelines, the temperature of the crude oil close to the pipe wall will decrease below the WAT. Wax components will then precipitate out of the crude oil and lead to solid deposition on the pipe wall. The WAT can be as high as 50°C or above for some crude oils and depends on pressure, bubble point and oil composition. [1, 2]

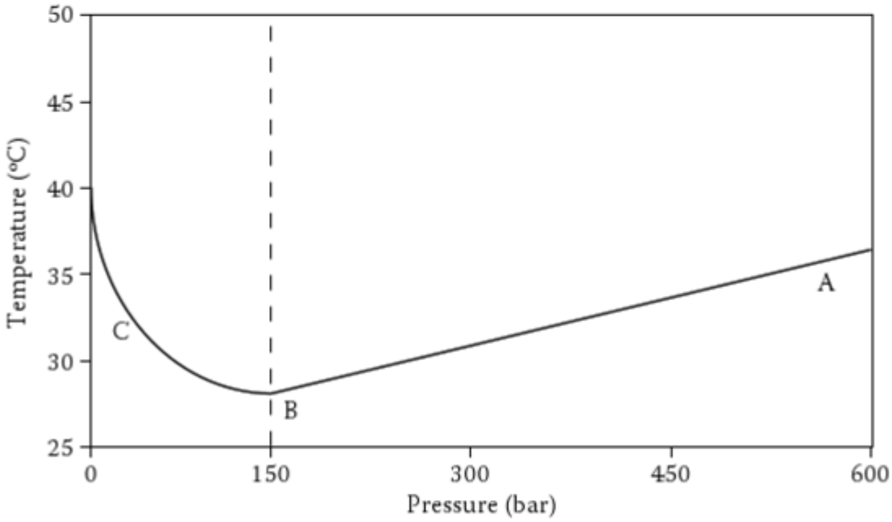

Figure 1: Typical phase diagram for wax precipitation [1]

Figure 1 shows a typical phase diagram for wax precipitation. At point A the crude oil is under reservoir conditions. As the crude oil is being produced the pressure decreases and the light ends expand in greater proportion to the dissolved waxes, which leads to an increase of the solubility of the wax and a lower WAT. At point B (the bubble point), the volume ratio of light ends to heavy ends is at its greatest and the WAT is at its lowest. At point C the pressure is further reduced. This results in liberation of dissolved gases and light ends to the gas phase, which reduces the solubility of the wax and increases the WAT. [1]

2.1.3 Wax dissolution temperature

The wax dissolution temperature (WDT) is defined as the temperature at which all the precipitated wax crystals in the crude oil are dissolved. The WDT can be determined by using microscopy, with observing a droplet of crude oil that is first cooled down below the WAT. The crude oil droplet is then heated up and one can observe the wax crystals being dissolved. When the last wax crystal is dissolved the WDT is found. The WDT has a higher temperature than the WAT.

2.1.4 Pour point

The pour point of crude oil is defined as the lowest temperature at which movement of the crude is observed. The pour point of crude oil can be found by performing a pour point test, where you have a sample of crude oil that is first heated up and then cooled down using a specified rate, while observing the movement of the crude at every third degree. The procedure for this is found in attachment no 2. When the crude reaches its pour point, the sample will not be frozen solid. The paraffins in the crude will crystallize and form a matrix of wax crystals, which holds the bulk of the liquid portion of the crude within it. When the liquid portion of crude is trapped within the wax crystal matrix, the wax crystals will prevent the liquid in the crude from flowing. Normally the pour point is 10 - 15°C below the WAT. [3]

2.2 Wax deposition mechanism

At high temperatures and pressures, any paraffin waxes within the crude oil will be in solution. As the temperature goes below the WAT, wax crystals will start precipitating from the crude oil. These crystals will deposit at the surface of the surrounding system, e.g. on the flowline during production. In addition, loss of low molecular weight hydrocarbons (light ends) to the gas phase will occur as the pressure drops during production, resulting in a reduced solubility of the waxes in the crude. It is important to know that the wax can deposit even if the bulk oil is at a temperature above its WAT. This is caused by a temperature differential between the bulk oil and the outer surface of the line. Crude oil near the pipe wall may experience a temperature below WAT, which leads to wax crystallization. Deposition is a low-energy state and occurs at a lower temperature, which make the lattice obtained stable. This makes deposition a preferred state for the crystals.

The wax deposition mechanism is primarily driven by molecular diffusion of wax molecules, shear dispersion of wax crystallites and Brownian diffusion of the wax crystallites. [1, 4]

2.2.1 Factors affecting wax deposition

Wax deposition is affected by several factors. In laminar flow below the WAT, the shear deposition mechanism becomes apparent and the wax deposition will increase with increased flow rate. This is explained by the fact that more particles will have the availability to deposit at the surface. The oil in the tubing will also have longer residence time in laminar flow, which affects the wax deposition. At low flow rates, the laminar boundary layer is thicker and hence more deposition occurs. As the flow rate increases to a turbulent flow regime, wax deposition will gradually decrease initially due to the thinning of the laminar boundary layer. Wax deposited at higher flow rates will be harder and more compact.

Another factor that affects the wax deposition is the cooling rate, together with the temperature differential between the bulk of the solution and the cold surface. An increase in the temperature differential leads to an increase in wax deposition. Wax deposition occurs only when the temperature of the surface of the pipeline wall is below the WAT of the solution. Initially, the thickness of the wax layer increases and the rate of wax deposition is high. This wax layer then acts as insulation and reduces the effective temperature differential, thus slowing the rate of molecular diffusion and the wax deposition down. The size and number of crystals formed are also an important factor for wax deposition. At a high cooling rate, the wax will precipitate out in smaller crystals. A larger number of crystals will be formed, because of the large number of crystallisation sites available. At a lower cooling rate, the process of crystallization will be more uniform.

Temperature differential will also affect the composition of deposited wax. If the temperature differential is high, the cooling will be rapid. This leads to simultaneously crystallization of both lower and higher melting waxes, which forms a weak porous structure with cavities full of oil.

Wax deposition can also be a function of surface properties. During wax deposition, wax crystals adhere to the pipe surface. Paraffin wax deposited on a surface is held in place by both absorption forces and surface roughness. It is found that paraffin deposition increases with surface roughness due to the availability of nucleation sites, e.g. the amount of wax deposited on a smooth surface will be less than wax deposited on steel. [4]

2.2.2 Molecular diffusion mechanism

If the temperature of the pipe wall is lower than the WAT, there will be a temperature gradient across the fluid from the core to the wall, and wax crystals will be transported towards the wall. This can occur even if the bulk fluid is above the WAT, and is called the molecular diffusion mechanism. The rate of transport towards the wall is given by the Fick diffusion equation: [5]

$$W_m = p_r A D_m \frac{dC}{dT} \frac{dT}{dy}$$

W_m = Rate of wax crystal deposition due to molecular diffusion

ρ_r = Wax crystal density

A = Surface area available for deposition

D_m = Molecular diffusion coefficient

dC/dT = Solubility coefficient of the wax crystals in the crude

dT/dy = Radial temperature gradient at the pipe wall

2.2.3 Brownian diffusion mechanism

When wax crystals precipitate out of the oil solution, they will be continuously bombarded by thermally agitated oil molecules. These collisions will lead to a small random Brownian movement of the suspended wax crystals. If a concentration gradient exists for these crystals, Brownian movement of the small, solid wax crystals will lead to a net transport. This net transport of the particles is similar to diffusion. The Brownian diffusion mechanism is given by the following equation: [5, 6]

$$\frac{dm_b}{dt} = \rho_d D_B A \frac{dC^*}{dr}$$

m_b = Mass of wax deposited by Brownian motion

t = Time

ρ_d = Density of the solid wax

D_B = Brownian motion diffusion coefficient of the solid wax crystals

A = Surface area available for deposition

C^* = Concentration of solid wax out of the solution

r = radial coordinate

2.2.4 Shear dispersion mechanism

During production of crude oil through the pipeline there will be a thin laminar sub-layer adjacent to the pipe wall. When suspended solid particles are being transported in a fluid with a laminar flow regime below the WAT, the particles will tend to move at the mean speed and in the direction of the surrounding fluid. The velocity of the particles increases with the distance to the pipe wall, and the particles rotate with an angular velocity, which is half the fluid shear rate. Rotating particles will impart a circulatory motion to a layer of fluid adjacent to the particle, due to fluid viscosity. This region of rotating fluid exerts a drag force from the neighbouring particles, and when the particle concentration is high, a significant number of multilateral interactions will occur. These interactions will result in a net lateral transport and a dispersing of the particles.

For low volumetric fractions of precipitated solids, the shear dispersion coefficient is given by: [5]

$$D_s = \frac{a^2 \gamma C_w^*}{10}$$

D_s = Shear dispersion coefficient

a = Particle diameter

γ = Oil shear rate at pipe wall

C^*_w = Volume fraction concentration of solid wax of solution at the wall

2.3 Wax crystal structure

Precipitation of wax crystals often results in the formation of sub-micron spherical wax particles that settle under the influence of gravity. Paraffin waxes have specific gravities around 0.8 to 0.85, while field waxes usually have specific gravity higher than 0.9. Field waxes usually co-precipitate with asphaltenes and resins if they are present, which causes higher specific gravity. Asphaltenes and resins are considered responsible for causing the formation of amorphous spherical wax crystal particles rather than wax needle crystals. Crystallized wax particles agglomerate to form very large micron-level particles where the molecular weights run in the hundreds of thousands or millions.

Plate form, needle form and mal or imperfect crystal formations are the three most generally recognized crystalline forms of wax. In general, larger molecules lose its kinetic energy and crystallize first, but the crystalline behaviour of wax is also dependent upon the properties of the crystallizing medium. If the crude oil is viscous and contains a high amount of resins and asphaltenes, the crystals will be small and spherical and create an amorphous wax. Figure 2 shows an example of amorphous wax particles that have crystallized in a crude oil containing asphaltenes and resins:

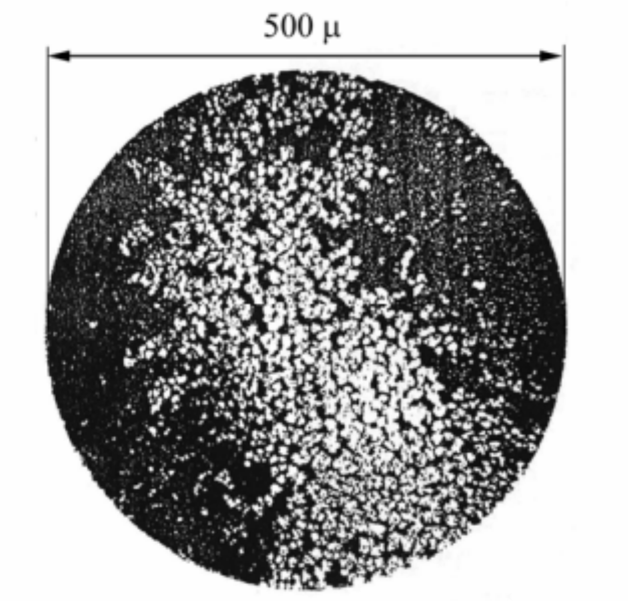

Figure 2: Amorphous wax particles [7]

If the crude oil is more liquid the wax crystals will be large and needle or plate like, and create a pressible type of wax. Figure 3 shows an example of needle-like particles that have crystallized in a crude oil that does not contain any asphaltenes or resins [7]:

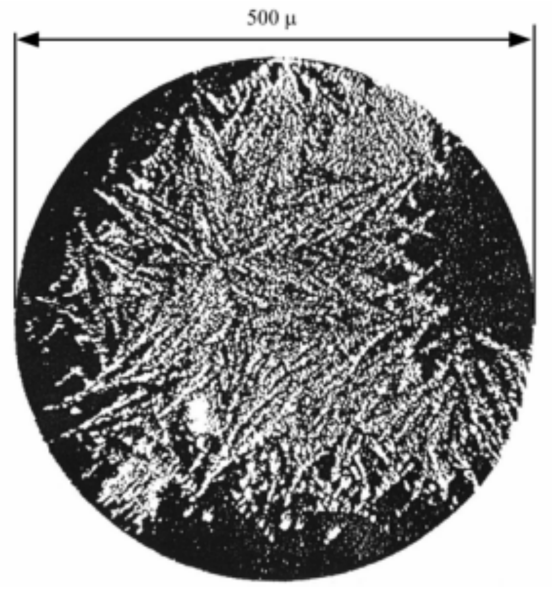

Figure 3: Needle-like wax particles [7]

2.3.1 Stoke's law

Stoke's law is a mathematical equation that is used to find the minimum settling velocity of small spherical particles in a fluid medium. Since most field wax particles are spherical, Stoke's law can be used to find the settling velocities of the particles. Spherical particles tend to settle under the influence of gravity in fluid mediums, and the gravity force is given by:

$$F_g = \frac{4}{3}\pi r_p^3 (\rho_p - \rho_f)\, g$$

F_g = Gravity force
r_p = Particle radius
ρ_p = Density of particle
ρ_f = Density of fluid
g = Acceleration due to gravity

The frictional fluid force that resists the fall of particles is given by:

$$F_f = 6\pi r_p \mu \upsilon$$

F_f = Frictional force
r_p = Particle radius
μ = Viscosity of the fluid
υ = Velocity fall of particle

The gravitational force causing the particle fall is constant, while the friction force resisting the fall is a function of the velocity. When the values of the gravity force and the frictional force is equal, a minimum settling velocity of the particles are found. When combining the two previous equations the minimum settling velocity is given as:

$$\upsilon = \frac{2}{9}(\rho_p - \rho_f)\frac{g r_p^2}{\mu}$$

It is important to remember that Stoke's law makes the following assumptions:

- The gravitational force is constant
- The particles are spherical

- The settling of the particles is not influenced by the presence of other particles or molecules
- Laminar flow. There are no convection currents present in the fluid [7]

2.4 Problems caused by wax deposition

Wax deposition is a major problem in the petroleum industry. Paraffin waxes contained in petroleum mixtures can precipitate when the temperature decreases during oil production, transport through pipelines or storage. Wax deposition is especially problematic in offshore wells, where the distance between the platform and subsea facilities can be 20 to 60 km. Along that distance, there is a potential risk of crude oil being cooled down below the WAT. When the crude oil is being cooled down below the WAT, wax crystals deposit at the surface of the pipeline and lead to several problems. As the wax crystals deposit at the surface of the pipeline the pipe diameter will be reduced and the roughness of the pipe wall increase, which leads to a reduced flow rate. In some cases the pipe can be completely blocked, which leads to a stop in the production and huge economical losses. Reduction in pipe diameter and blockage of the pipe can occur down hole if the well temperature is low, or topside in cold climate or subsea transportation.

Figure 4: Wax deposition in a subsea pipeline [8]

Increased viscosity and gelling of the crude due to high amounts of wax precipitation in the crude is also a problem when it comes to wax deposition. When the crude is cooled down the waxes separate out as plastic crystals, which interact together to form a three-dimensional structure where the crude becomes trapped. This leads to an increased viscosity of the crude, together with reduced flow ability and a pressure loss in the pipeline. If the production line is shut-in, the crude cools further down below the WAT, and a gel results at zero shear rate. If the yield stress of the gel exceeds the maximum pipeline pressure, the line cannot be restarted.

Reduced operating efficiency and down time during production due to wax deposition leads to huge economical losses, and there is also a safety hazard due to deposits interfering with the operation of valves and instruments. Because of this it is very important to have good wax control strategies during production and transportation of crude oil, to avoid problems caused by wax deposition. Wax removal can be both costly and technically challenging, especially in deep water pipelines. [1, 9]

2.5 Wax control strategies

It is important to have good wax control strategies during production and transportation of crude oil. This can be both chemical and non-chemical treatment techniques. A combination of non-chemical techniques such as insulation and pigging of the pipeline together with an optimum selection of preventative chemicals and remediation products are commonly used in the industry. Some of the most commonly used non-chemical treatment options include:

- Pigging: This is the most commonly used method of wax control, which includes physical removal of wax by pigging the pipeline. A pig is launched down into the pipeline and will mechanically scrape wax from the pipeline wall and redistribute it within the crude in front of the pig. This leads to a much thinner and smoother deposit on the pipe wall which results in a reduced pipe wall friction and reduced pressure drop. Pigging is a technique that must be carried out frequently in order to avoid large build-ups of wax. If not, the large amount of wax deposits will result in insufficient pressure to push the pig through the pipeline, as the wax accumulates in front of it. Pigging requires shut down of the system, which leads to down time and stop in the production. In some cases the process of pigging results in the loss of 1-3 days of production, which can be very expensive. A combination of pigging and chemical injection is the most optimum combination.

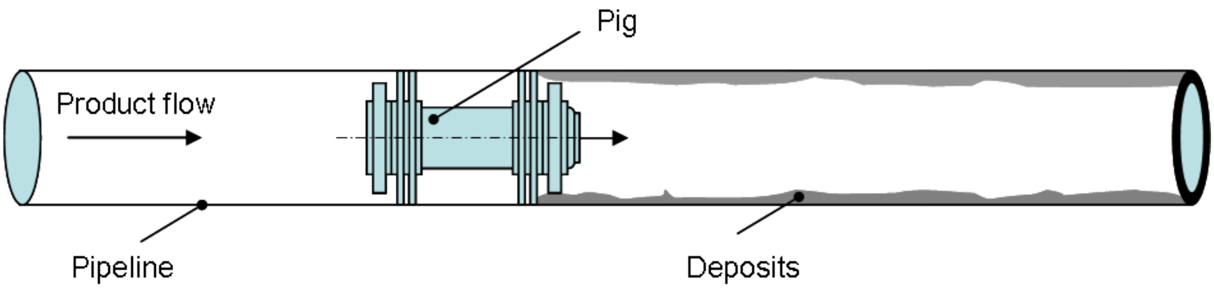

Figure 5: Illustration of pipeline pigging [10]

- Thermal insulation and pipeline heating: Insulation of the pipeline is unlikely to resolve a severe wax problem, but if the temperature can be maintained above the WAT then no wax will form. Burying a pipeline in sediments or soils will insulate the pipeline, while hot water jackets and electrical current can be used as potential heat sources to heat up the pipeline.
- Hot oiling: A portion of the crude oil is heated up to a temperature significantly above the WAT, and circulated down the pipeline. This is the most commonly used technique for down-hole wax treatment in on-shore fields. The product and treatment can be put into the storage tank, but the need for a large heat source and the potential hazard to workers is a major disadvantage. Steam or hot water is also used.

A number of factors need to be considered when evaluating different wax treatment techniques. Chemical treatments and insulation of the pipeline are used to prevent wax deposition, but at a certain point there will be a need for non-chemical treatments like pigging. Some of the most commonly used chemicals to prevent wax deposition include crystal modifiers, paraffin inhibitors, paraffin dispersants, pour point depressants and wax solvents. In this master thesis the main focus will be on chemical wax prevention and the use of dispersants. [11, 12]

2.6 Chemical wax prevention

The potential for wax deposition and the need for chemical treatment are varying during the operation of a field. Some oil and gas fields may only have potential for wax deposition during low flow conditions, while others may have potential for wax deposition when the pipeline is shut in and the system is experiencing low temperatures.

Chemical wax prevention offers the most cost effective option for the majority of oil and gas fields. Generally, non-chemical treatments require greater initial capital investment than chemical treatments, but have lower operational costs than chemical dosing. Chemical treatments are dosed only during the period when there are operating problems, while non-chemical treatments are designed for extended or continuous use.

The first step in designing a chemical treatment is to establish the nature of the precipitating solid and to characterize the crude oil by analysis. The chemicals are added on a continuous basis to reduce the rate of deposition of waxes to the surfaces and to prevent significant increases in the viscosity of the crude. In some geographical areas the most important is the viscosity control while in other areas it is the prevention of deposition. High molecular weight polymers have been identified to be effective for both situations. In situations where the main function of the polymer is to prevent wax deposition it is termed a wax crystal modifier or inhibitor, or a pour point depressant or a wax inhibitor when the polymer is used to control viscosity. [11]

2.6.1. Crystal modifiers

Some high molecular weight polymers modify the wax crystal size, shape and adhesion properties to metal surfaces. These polymers prevent paraffin wax deposition by co-crystallizing with the waxy molecules as they precipitate from the crude oil, which reduces the rate of growth of wax crystals and the rate of agglomeration. As the wax crystals nucleate and come out of the solution their shapes are changed by the polymers, so that it does not form needles, or cohere crystalline structures or matrices.

For a crystal modifier to be successful two key qualities are required. It should precipitate in crude oil at about the same temperature as the wax and contain structural sequences capable of co-crystallisation with wax. Successful crystal modifiers are polymeric or high molecular weight organic molecules with both straight chain hydrocarbons and polar groups within the same molecules. These polymers are characterized by the presence and frequency of pendant side chains along the backbone and the molecular weight. The effect of the crystal modifiers strongly depends on the interaction of polar groups on the side chains with the paraffin wax molecules.

It is important to know the fact that crystal modifiers do not completely stop the formation of wax crystals; they will only slow down the process of wax crystal growth. This means that at a certain point it will be necessary to pig the pipeline or use a solvent that is able to remove the wax. Wax crystals modifiers are formulated in hydrocarbon solvents (usually aromatics) in order to get rapid dispersion into the oil phase, and should be continuously added to the crude at a temperature above the WAT. [11]

2.6.2 Pour point depressants

Pour point depressants (PPDs) are chemicals that affect the pour point of the crude oil and improve the flow characteristics. They are polymers with pendant hydrocarbon chains that interact with the paraffins in the crude oil and inhibit the formation of large wax crystal matrices. The interactions delay the wax crystal formation and growth, decrease the crudes pour point while affecting the size and the shape of the wax crystals. [1, 3]

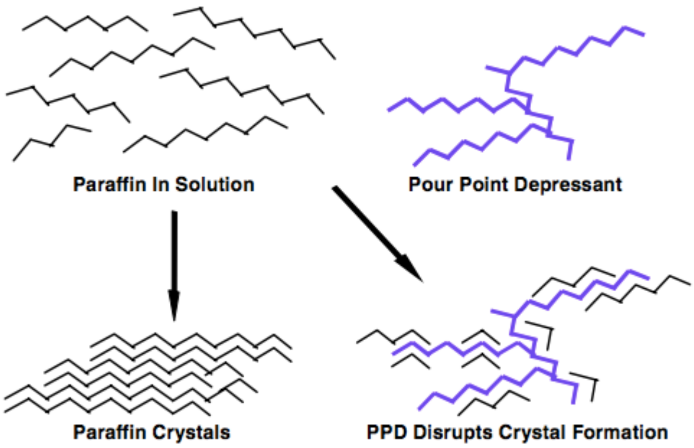

Figure 6: Mechanism of pour point depressant [3]

Figure 6 shows the mechanism of PPDs. When a PPD is added to a crude oil the paraffin crystals are kept apart from each other by the PPD backbone, and because of this the paraffin crystals are no longer able to form three-dimensional structures that inhibit flow.

The concentration of PPDs depends on the severity of the wax problem, but typical dosages are 100-2000 ppm. High concentrations of PPDs can be difficult to handle in cold climates due to their high solidification temperature. PPDs must be injected into the pipelines before the bulk temperature drops below the WAT. The main classes of PPDs are:

- Ethylene polymers and copolymers:
  The most common and well-known type of ethylene copolymers are ethylene/vinyl acetate (EVA) copolymers, which are random copolymers of low molecular weight. The effectiveness of EVA copolymers is determined by the percentage of vinyl acetate in the copolymer, together with the presence of asphaltenes in the crude. The side chains in the vinyl acetate croups are disrupting the wax crystallization process with lowering the WAT or pour point. However, a high percentage of vinyl acetate will have a negative impact on the performance with decreasing the cocrystallization with waxes. Generally, about 25%-30% vinyl acetate content gives an optimum performance for EVA copolymers.

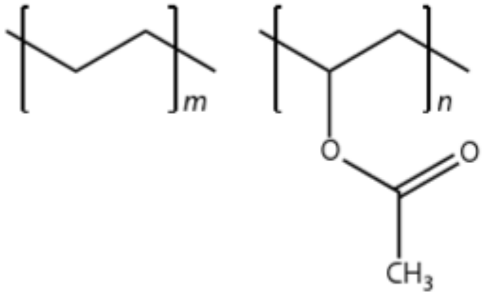

Figure 7: Chemical structure of EVA [1]

- Comb polymers: Comb polymers are known as more effective PPDs than EVA copolymers. Comb polymers have a polyvinyl backbone with several long-chain groups, and are able to cocrystallize with waxes through van der Waals interactions. They are also able to place a steric hindrance on the wax crystal, which interferes with proper alignment of new incoming wax molecules and terminates the growth. This reduces the pour point, prevents wax crystals from agglomerating and sometimes prevents sticking to the pipe walls. Comb polymers are usually made from one of two classes of monomers: (meth)acrylic, maleic anhydride or both. The optimum length of the side chains depends on the lengths of the alkanes in the waxes.

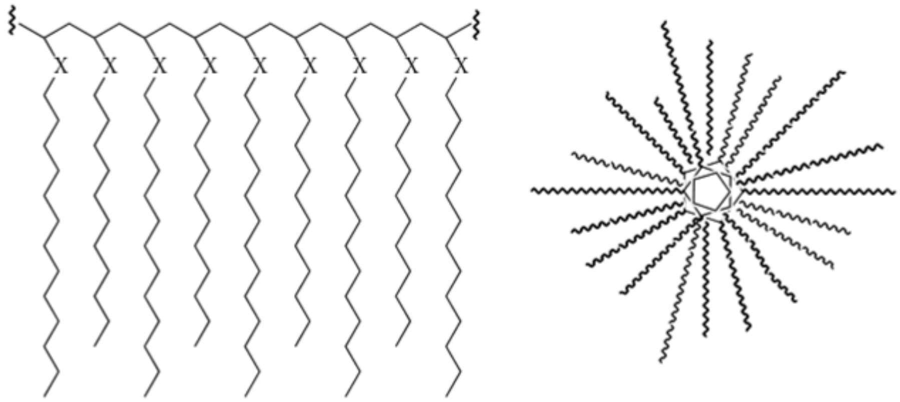

Figure 8: Chemical structure of a comb polymer (left) and structure looking down at the helical backbone (right) [1]

- Miscellaneous polymers:

  Alkylphenol-formaldehyde resins are miscellaneous polymers that are used as PPDs and flow improvers. Phenol is first reacted with a long-chain α-olefin and then condensed with aldehyde to make the resins. Used on their own, they are not as effective as comb polymers.

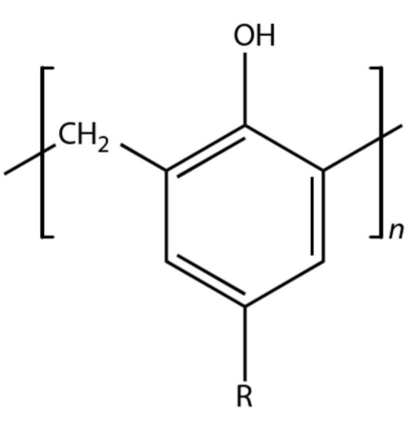

Figure 9: Chemical structure of alkylphenol-formaldehyde resins [1]

2.6.3 Paraffin dispersants

Paraffin dispersants are surfactants that absorb onto pipe surfaces, reducing the ability of wax crystals to stick together and to stick to the pipe surface. This could be done by changing the wettability of the pipe surface to water-wet, and/or by creating a weak layer where the wax crystals grow and are later sheared off by a turbulent flow regime. They also have the ability to coat growing wax crystals, decreasing their tendency to agglomerate and to stick to the pipe surface. The overall effect of this is less accumulation on the pipe wall. Paraffin dispersants can be dosed continuously for inhibitory effect, or applied in a batch mode down the wellbore. They can also be bled into the production stream through small tubing. Typically dosages of paraffin dispersants are 50-300 ppm.

Ideally, paraffin dispersants should be able to break up accumulated masses of paraffin wax, but in practice, the dispersants usually need the assistance of polymeric wax inhibitors to enhance their performance. Paraffin dispersants have had limited success in the field used on their own. [1, 13]

2.6.4 Surfactants

Surfactants (also known as surface active agents) play a key role in many well treatments due to their unique properties. Surfactants are used to reduce surface tension, change wettability, mobilize residual oil and disperse corrosion inhibitors. They are also used as anti-sludge agents, emulsifiers to prepare acid-diesel emulsions and demulsifiers. When present at low concentration in a system, surfactants have the ability to absorb on to various surfaces and associate in the bulk of solutions and form micellar structures. This is the reason that surfactants have this wide range of applications. The properties of surfactants depend on the size of the head group, tail length and configuration of the tail, surface charges, ionic strength, pH value, presence of impurities, co-surfactants and temperature. [14, 15]

2.6.4.1 Types of surfactants

Surfactants have a hydrophilic head and a hydrophobic tail, which is composed of a hydrocarbon or a fluorocarbon chain. The hydrocarbon group generally consist of a hydrocarbon chain with 10-22 carbon atoms, and the chain may include oxygen atoms, benzene ring, amide groups, ester groups or double bonds.

Hydrophilic groups

The hydrophilic group of a surfactant is usually referred to as the head group, and is either strongly polar or charged. Surfactants are classified into several groups based on the charge of the hydrophilic head. The following is some of the major groups:

- Anionic surfactants: These include carboxylates, sulfonates, sulfates and phosphates, and carry negative charges when they ionize in aqueous solutions.
- Cationic surfactants: Carry positive charges when they dissociate in water. Contains primary, secondary or tertiary amines or quaternary ammonium structures.
- Non-ionic surfactants: Does not carry any charge. The surfactant molecules dissolve in the aqueous phase by hydrogen bonds via a chain of ethylene oxide or propylene oxide groups. Non-ionic surfactants are used extensively in low-temperature detergency and as emulsifiers.
- Amphoteric/zwitterionic surfactants: The charge depends on the pH of the aqueous solution, both positive and negative charges nay be present. These surfactants are used to generate viscosity in-situ.
- Combinations: Combinations of the above head group types are increasingly being used within a single surfactant. The most common are hose that have both non-ionic and anionic groups, such as the alkyl ethoxy sulfates. [14, 15]

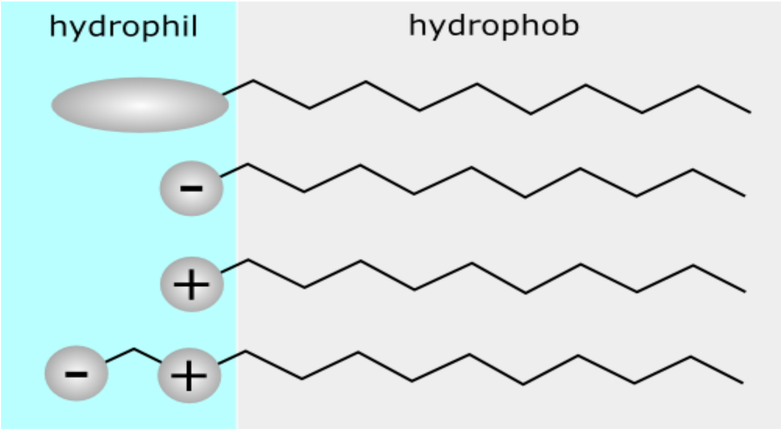

Figure 10: Surfactant classification: Non-ionic, anionic, cationic and zwitterionic [16]

2.6.4.2 Wetting by surfactants

Wetting is in general defined as the displacement from a surface of one fluid by another, and it always includes three phases where at least two are liquids. This can be a solid and two immiscible liquids, a gas and two immiscible liquids or three immiscible liquids. Wetting is a process that involves surfaces and interfaces, and to some degree all surfactants have the ability to change the wettability of a surface.

Water has a relatively high surface tension (72 mN/m), but it does not spontaneously spread over covalent solids that have surface free energies less than 72 mJ/m^2. It is therefore often necessary to add a surfactant to water to enable the water to wet a solid or liquid surface. Adding a surfactant to water modifies the interfacial tensions of the system. Spontaneous spreading of water decreases the free energy of the total system, and the change in free energy is called the spreading coefficient. The spreading coefficient for water and a solid is given by:

$$S_{WS} = \gamma_{SO} - \gamma_{WO} - \gamma_{SW}$$

S_{WS} = Spreading coefficient for water and a solid
γ_{SO} = Interfacial tension between a solid and oil
γ_{WO} = Interfacial tension between water and oil
γ_{SW} = Interfacial tension between a solid and water

For water to wet a surface spontaneously, the spreading coefficient must be positive. Adding a surfactant to the water may result in a positive value for the spreading coefficient, which leads to spontaneous spreading of water. When water is spontaneously spread on a surface it can hold a uniform film of water that is stable at any thickness. However, the addition of a surfactant to water does not always increase the wettability. A surfactant that orients itself with the hydrophilic head group away from the surface can make the surface more water-wet. On the other hand, if the surfactant orients itself on a surface such that the surfactant molecules have the hydrophobic tail groups away from or along the surface, the water-wetting will decrease while the oil-wetting will increase. Specific structural characteristics can increase or decrease the packing of surfactant molecules and influence the modification of surface wetting. Milton J. Rosen has made some general observations of modifications to hydrophobic tail groups that can be applied to the water/solid interface:

- Increasing the length of the hydrophobic tail group: This can increase the tendency of the surfactant to absorb at an interface, and improve the packing of the surfactant molecules at an interface.
- Introducing branching or undersaturation: Can cause looser packing of surfactant molecules at the interface.
- Presence of an aromatic nucleus: Can increase absorption of the surfactant onto polar surfaces and cause looser packing of surfactant molecules at the interface.
- Presence of a polyoxypropylene chain: The surfactant absorption onto polar surfaces can be increased. [17, 18]

2.6.4.3 Reduction of surface and interfacial tension by surfactants

One of the most commonly measured properties of surfactants in solution is reduction of surface or interfacial tension. It depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface or interfacial excess concentration of the surfactant. This can be shown by the Gibbs equation, which is one of the most fundamental of interfacial phenomena:

$$d\gamma = -\sum_i \Gamma_i d\mu_i$$

$d\gamma$ = Change in surface or interfacial tension of the solvent
Γ_i = The surface excess concentration of any component of the system
$d\mu_i$ = Change in chemical potential of any component of the system

The molecules at the surface of a liquid have potential energies, which are greater than those of similar molecules in the interior of the liquid. Because of this, an amount of work equal to the difference in potential energy is needed to bring a molecule from the interior to the surface of the liquid. Surface tension, or the surface free energy per unit area, is a measure of this work. It is the minimum amount of work that is required to bring a sufficient amount of molecules from the interior to the surface to expand it by unit area. Surface tension is defined as the force per unit length at a right angle to the force, which is required to pull the surface molecules apart in order to permit expansion of the surface by movement of molecules from the underlying phase.

If a surfactant is added to a system of two immiscible phases like heptane and water, the surfactant will be absorbed at the interface between the two phases and orient itself with the hydrophilic group (head) towards the water and the hydrophobic group (tail) towards the heptane. This is illustrated in the following figure:

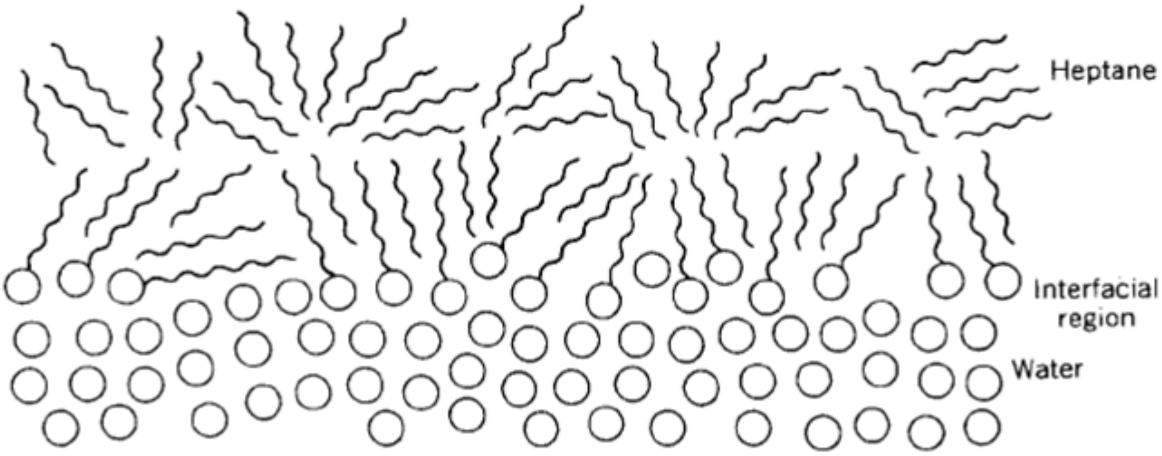

Figure 11: Heptane-water interface with absorbed surfactant [17]

When the original interface with water and/or heptane molecules is replaced by the surfactant molecules, the interaction across the interface will be changed. On one side the interaction across the interface will be between hydrophobic group of the surfactant and the heptane, and between the hydrophilic group of the surfactant and the water molecules on the other side of the interface. These interactions will be much stronger than the original interaction between the heptane and the water molecules, which leads to a significant reduction of the interfacial tension.

In general, good surface or interfacial tension reduction is shown only by those surfactants that have an appreciable, but limited, solubility in the system. To be able to compare the surfactants performance in reducing surface or interfacial tension, one has to distinguish between the efficiency of the surfactant and its effectiveness. The efficiency of a surfactant in reducing surface tension reflects the concentration of the surfactant at the interface, relative to that in the bulk liquid phase. This can be measured by taking the ratio of the concentration of the surfactant at the surface to that in the bulk liquid phase, at equilibrium. For surfactants in aqueous solutions the efficiency increases with increase in the hydrophobic character of the surfactant. The effectiveness of a surfactant is a measure of the maximum reduction in tension that can be obtained, regardless of the bulk phase concentration of surfactant. This can be measured by the amount of reduction, or surface pressure, attained at the critical micelle concentration. [17]

2.6.5 Wax solvents

Wax solvents are used to remove existing deposits in the pipeline when the extent of deposition is no too severe. There is a wide range of solvents that can be used for the purpose of removing deposits. However, the choice of solvent must be a compromise between optimum performance and ideal handling and safety profile. The most commonly used hydrocarbon solvents include gasoline, trichloroethylene, toluene, xylene, napthas, carbon disulphide and terpenes. Carbon disulphide and chlorinated solvents are very effective, but are not permitted due to toxicological and environmental reasons. Xylene is an aromatic hydrocarbon that is very effective, and is used widely for treatment of wax deposition in pipelines. Both heat and agitation speed up process of dissolving. It is not absolutely necessary to use heat with a solvent, but it is important to know the fact that hot solvents dissolves wax crystals faster than cold solvents. [11]

2.7 Wellbore flow performance

2.7.1 Types of flow

Wellbore flow can be divided into several broad categories, depending on the flow rate, the fluid properties and the flow geometry. In most production wells the flow is multiphase, with at least two phases present. Single-phase flow can be found in some production wells and in most injection wells. The flow geometry in the wellbores is usually flow through a circular pipe, and the flow may be in any direction relative to the gravitational field. Pressure volume temperature (PVT) behaviour and rheological characteristics are fluid properties that must be considered when describing the wellbore fluid performance.

When one is talking about fluid flow, one is often referring to the flow of an ideal fluid. It is presumed that an ideal fluid has no viscosity, which is an idealized situation that does not exist. However, when one is talking about the flow of a real fluid, the effects of viscosity are introduced. This results in the development of shear stresses between neighbouring fluid particles when they are moving at different velocities. When an ideal fluid is flowing through a pipeline, all particles will move in parallel lines with equal velocity. The velocity adjacent to the wall in the flow of a real fluid will be zero, and increase rapidly within a short distance from the wall.

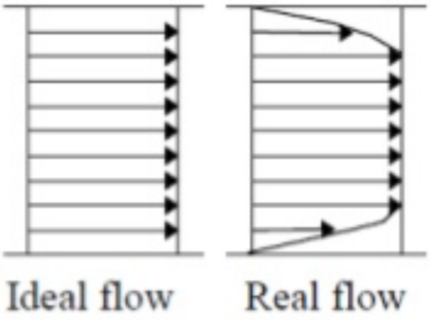

Figure 12: Velocity profile of an ideal fluid and a real fluid [19]

Fluids can also be classified as incompressible or compressible fluids. Liquids are relatively incompressible, and they are generally treated as incompressible fluids. [20, 21]

2.7.2 Laminar and turbulent flow

Depending on the value of Reynolds number, flow can be characterized as being either laminar or turbulent. The Reynolds number is dimensionless and is the ratio of the inertial forces to the viscous forces in a flowing fluid. For flow in a circular pipe the Reynolds number is given by:

$$Re = \frac{Inertial\ forces}{Viscous\ forces} = \frac{Du\rho}{\mu}$$

Re = Reynolds number
D = Hydraulic diameter of the pipe
u = Average fluid velocity
ρ = Density of the fluid
μ = Dynamic viscosity of the fluid

When calculating the Reynolds number it is important that all variables are expressed in consistent units to make the Reynolds number dimensionless. The average fluid velocity, u, is the volumetric flow rate divided by the cross-sectional area of flow:

$$u = \frac{q}{A}$$

q = Volumetric flow rate
A = Cross sectional area of flow

For flow in a circular pipe the cross-sectional area is calculated by the following equation:

$$A = \frac{\pi}{4} D^2$$

D = Diameter of the pipe

When the Reynolds number is below 2100 the flow is characterized as laminar flow. Laminar flow is characterized by a smooth and constant fluid motion where the fluid moves in distinct laminae, and the likelihood of laminar flow increases with an increase in viscosity. When the Reynolds number is in the range between 2000 and 4000, the flow is in a critical region called the transition zone, where it can be either turbulent or laminar depending on several factors. Turbulent flow occurs when the Reynolds number is larger than 4000, and is characterized by eddy currents that lead to fluctuating velocity components in all directions. The dispersion of solutes contained in the fluid, the frictional pressure drop behaviour and the velocity profile in the pipe are all factors that are strongly influenced by the fact that the flow is laminar or turbulent. [20, 22]

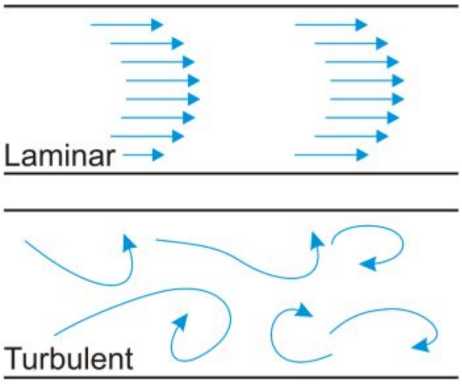

Figure 13: Laminar and turbulent flow [23]

Chapter 3 Development of methodology

3.1 The selection of test equipment

The cold finger test is a commonly used test method for testing paraffin inhibitors. This test requires the paraffin inhibitor to be applied above the WAT, in order to show its performance. If not, the effectiveness of the paraffin inhibitor will be reduced. For paraffin dispersants, this test would not indicate or show any results in preventing wax deposition. Paraffin inhibitors work by inhibiting wax crystal growth and deposition, and the wax crystals that are precipitating out of the crude oil will deposit on the cold finger through molecular diffusion. The amount of wax deposited on the cold finger from a blank sample of crude oil is compared to a sample of crude oil containing a paraffin inhibitor, and the performance and effect of the inhibitor can be determined.

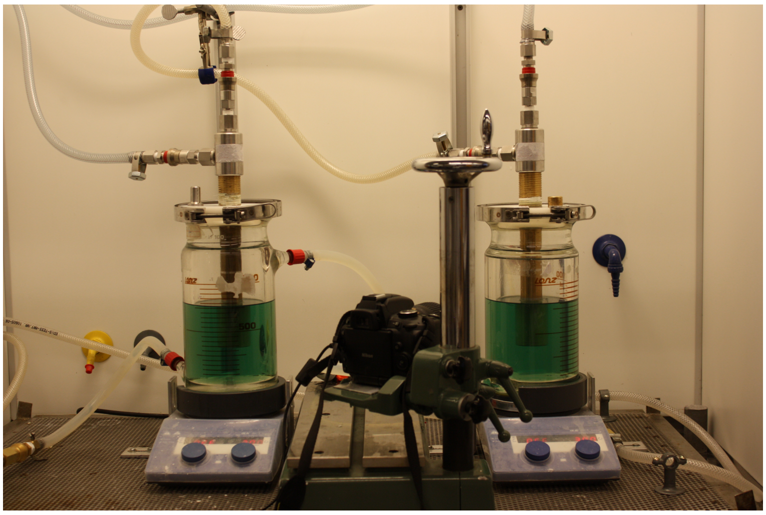

Figure 14: Experimental setup of cold finger test equipment [24]

When adding a paraffin dispersant to a crude oil sample using the cold finger test, the dispersant will coat the growing wax crystals and decrease their tendency to agglomerate and deposit on the cold finger surface. In addition, the dispersant will also absorb on to the surface of the cold finger, reducing the ability of wax crystals to deposit on its surface. This makes the cold finger test not preferable for this thesis objective. If any wax crystals do adhere to the surface, the wax would be soft and mushy due to the coating of wax crystals, and the amount of wax deposited would not have been measurable. It is on that basis that the cold finger test is not a preferable test method to use when developing a methodology for testing paraffin dispersants.

The wax flow loop, on the other hand, is very suitable when developing a methodology for testing paraffin dispersants. The wax flow loop simulates pipeline conditions, and enables testing of a crude oil sample and the efficiency of paraffin dispersants under realistic conditions.

3.2 The wax flow loop

The core of the wax flow loop is a coil that is working as the test pipeline. The test pipeline can be exchanged, which enables tests with variable line length and diameters for different test approaches. A treated or untreated sample of crude oil is preheated to a set temperature, and then circulated into the wax loop using an injection pump with a constant flow rate. The flow rate and the temperature of the pump, pre-heater, thermostat and post-heater can be set from the command window. When the crude oil sample is pumped through the test pipeline, wax crystals will start to precipitate out from the crude oil and deposit on the surface of the test pipeline, which is cooled down to a set temperature by using a water bath. When the crude oil sample has passed through the test pipeline the crude oil is reheated by the post-heater to a temperature above the WDT, and is circulated back to the crude oil container. It is important that the crude oil container is heated up to a temperature above the WAT, in order to dissolve all the remaining wax crystals before it re-enters the wax loop.

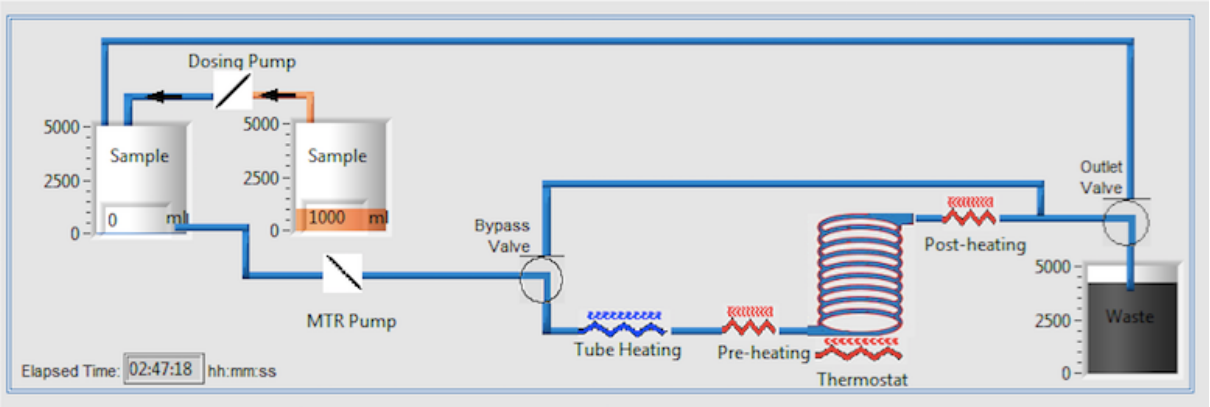

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Figure 15: Schematic drawing of the wax loop

The wax deposition will result in a reduced diameter of the pipeline that causes a differential pressure increase, and thermal insulation caused by the wax deposition may result in a reduction of differential temperature over the pipeline. The differential pressure and temperature is monitored by the wax loop, and the differential pressure and temperature versus time are shown as graphs on the computer screen. These results are used to evaluate the performance and efficiency of the paraffin dispersant. As the wax crystals precipitate out of the crude oil and deposits on the surface of the test pipeline, the diameter of the test pipeline will be reduced and the differential pressure will increase. At a certain point this will lead to a blockage of the pipeline, which will be clearly indicated on the graphs as pressure build-ups. When running a blank sample of crude oil it is fairly straight forward to compare the effect with adding a dispersant, looking at the pressure build-ups from the blank sample and compare it with a crude oil sample containing a paraffin dispersant. This makes the wax flow loop a suitable method for developing a standard test method for testing paraffin dispersants, and evaluate the performance of different dispersants.

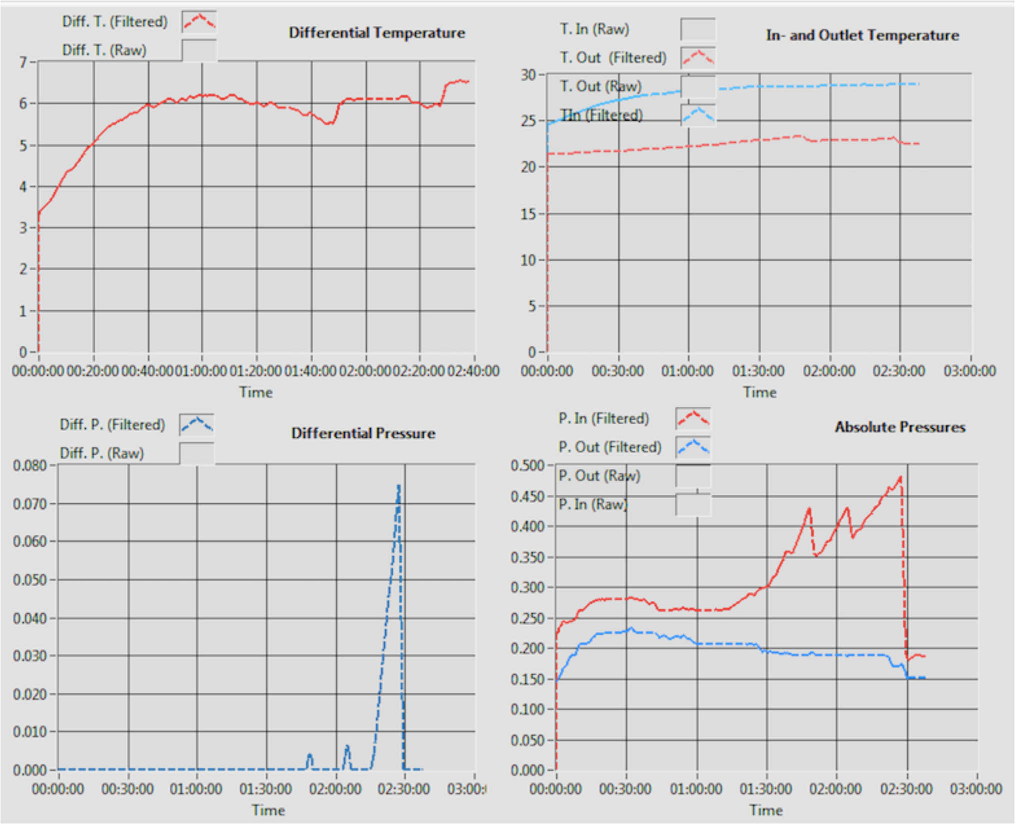

Figure 16: Differential and absolute pressure (bar) and temperature (°C) versus time

Figure 16 shows the results from the wax loop computer with differential and absolute pressure versus time. As wax deposits and the differential pressure increases, the differential temperature decreases due to the thermal insulation of the pipeline. The pressure builds up before the wax is sheared off by the increasing pressure and flow rate, causing a decrease in pressure and temperature before it builds up again. This print screen shows the results from a blank crude oil sample. In theory, running the test with adding a paraffin dispersant to the crude oil sample should delay the pressure build-ups, and make the pressure build-ups appear over a longer time period.

3.3 Hypothesis

In order to develop a methodology for testing paraffin dispersants several criteria are made. First of all, it is necessary to simulate a scenario of the field where the crude oil is entering the test pipeline below the WAT. The wax particles will then precipitate out of the crude oil, deposit onto the test pipeline wall and one will be able to observe the effects of the wax deposition. In addition, it is important that the wax deposition mechanism is driven by the flow, and not by a thermal gradient.

In order to obtain wax deposition that is driven by the flow rather than a thermal gradient, several set parameters have to be adjusted. First of all, it is necessary to set a low flow rate, in order to ensure a laminar flow regime. If the flow rate is too high and the flow is turbulent, the wax deposition will not be driven by the flow. The temperature of the stirrer has to be set at a temperature above the WAT, in order to ensure that no wax particles are precipitating out of the crude oil before entering the wax loop. The temperature of the pump also needs to be set at a temperature above the WAT, but below the temperature of the stirrer. The pre-heater should be set to a temperature below the WAT in order to reach a temperature below the WAT before entering the test pipeline. This is, as mentioned earlier, the main criteria. In order to obtain a wax deposition driven by the flow rate rather than a thermal gradient, the temperature differential between the inlet of the test pipeline and the test pipeline has to be as low as possible. If the temperature of the test pipeline is set as close to the inlet temperature as possible, this should not be a problem. The temperature of the post-heater, which is positioned at the end of the test pipeline, should be set at a temperature above the WDT. This is to ensure that all the wax particles are re-dissolved before the crude oil enters the stirrer, and is circulated back into the wax loop.

When it comes to the wax deposition, the aim of this methodology is to obtain significant pressure build-ups during a reasonable time period. A significant pressure build-up is classified as a pressure increase of at least 0.1 bar at the inlet of the test pipeline. If one is able to develop a standard test method, a paraffin dispersant can be added to the crude oil sample, comparing the test results with a blank crude oil sample. The paraffin dispersant should be run two times the blank crude oil sample in order to compare the effects on the wax deposition together with the pressure build-ups. If the paraffin dispersant does not show any pressure build-ups that are exceeding the blank sample during a time period of two times the blank, the paraffin dispersant is classified as a good performer. On the other hand, if the paraffin dispersant shows a pressure build-up that exceeds the blank sample within the time period of two times the blank, the dispersant is showing a bad performance on the crude oil sample.

If one can get the wax loop into the right conditions and all these criteria are fulfilled, one should be able to develop a methodology for testing paraffin dispersant where the deposition is driven by the flow rather than a thermal gradient, and to distinguish between a good and bad performer of paraffin dispersants. In order to confirm that a standard methodology for testing paraffin dispersants is achieved, several types of crudes should be tested.

It is important to mention that this development of methodology is not about developing a set of standard set values. Different types of crudes will have different wax contents, compositions and physical differences, which means that a set of standard set values used on a crude with a low wax content will not work on a crude with a high wax content. The set values have to be adjusted to each individual crude in order to obtain wax deposition driven by the flow rather than a thermal gradient.

3.4 The test pipeline

The test pipeline connected to the wax loop is exchangeable. When selecting a test pipeline for the wax loop, two test pipelines with different diameters were available; a 4 mm diameter and a 2 mm diameter test pipeline. When selecting a test pipeline for developing the methodology for testing paraffin dispersants the advantages and disadvantages were evaluated. The 4 mm diameter test pipeline gives a more uniform deposition and a longer deposition rate, while the 2 mm diameter test pipeline gives more rapid pressure build-ups due to the small diameter. One will also observe a higher number of pressure build-ups with a 2 mm than a 4 mm diameter test pipeline. It would be preferable to have a low number of pressure build-ups in order to see a much clearer difference when adding a dispersant, and it is on that basis that the 4 mm diameter test pipeline was selected for the development of methodology for testing paraffin dispersants.

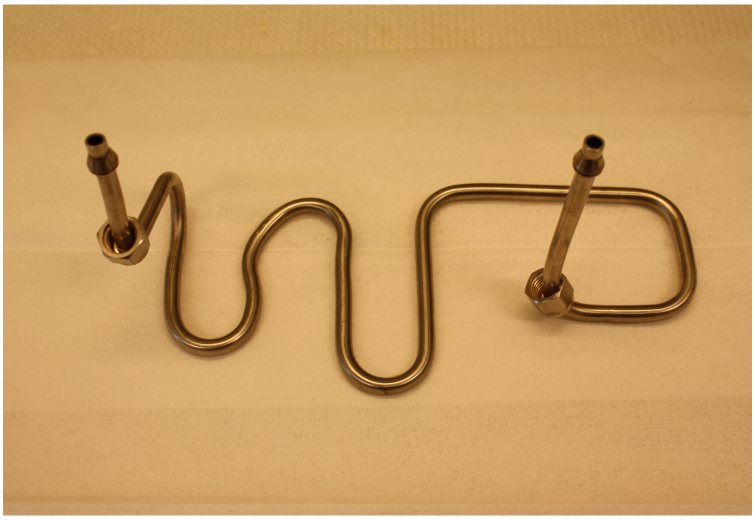

Figure 17: The 4 mm test pipeline

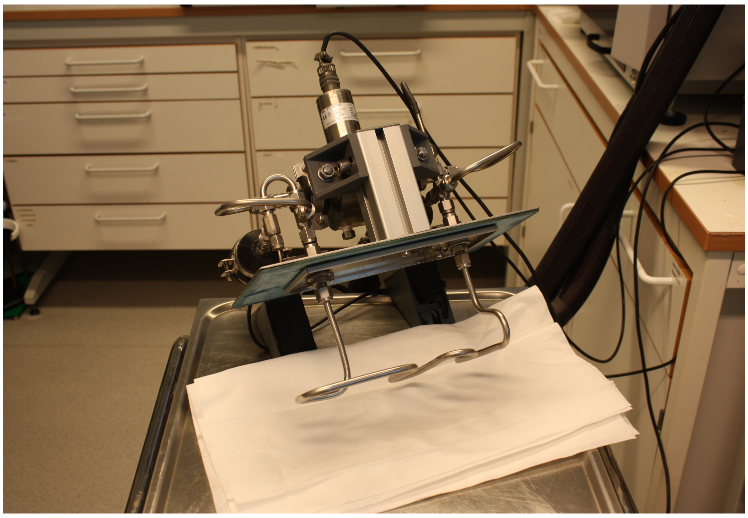

Figure 18: Test pipeline connected to the wax loop

Chapter 4 Results and discussion

4.1 Crude oil selection and characterization

In order to find a suitable crude for the development of methodology for paraffin dispersants three stock tank oils from the North Sea were tested. Viscosity, pour point, wax appearance temperature and wax dissolution temperature were tested in compliance with the procedures in appendix 1, 2 and 3.

4.1.1 Viscosity profile

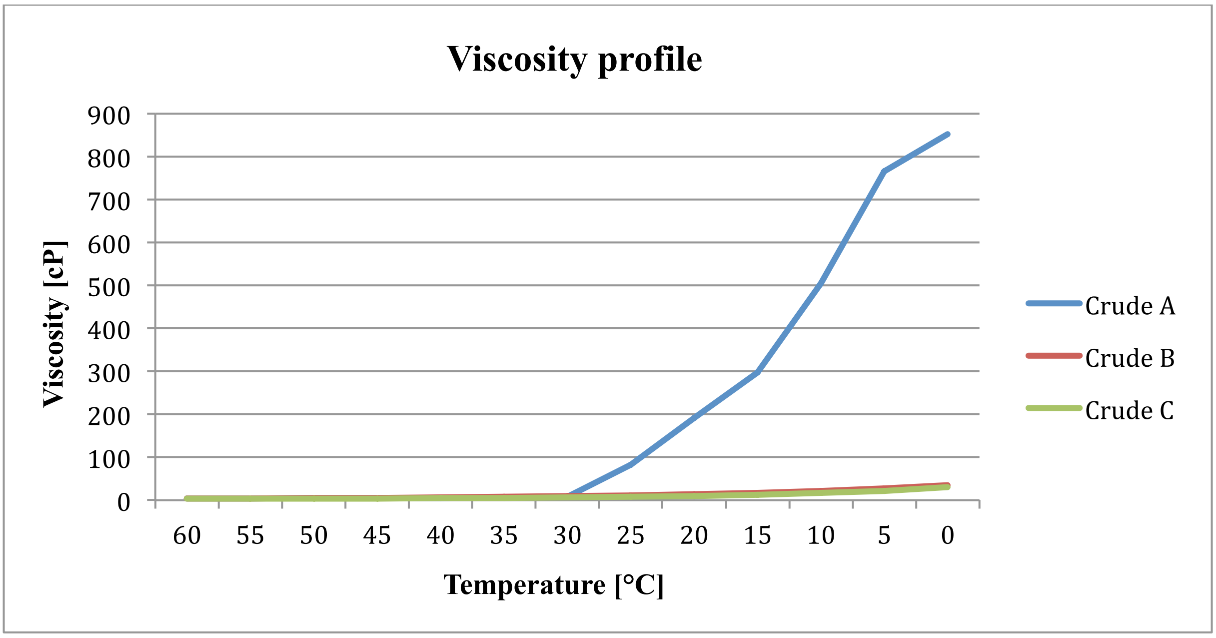

Figure 19: Viscosity profile of the different crudes

The viscosity profiles of the three North Sea crudes were found after performing a viscosity test in compliance with the procedure in appendix 1. From the graph one can see a significant difference between crude A and crude B and C. The viscosities of the three North Sea crudes are quite similarly until the temperature reaches 30°C. Then crude A shows a linear increase in viscosity from 30 – 0 °C. Crude A has a maximum viscosity of 853 cP, while crude B and C have a maximum viscosity of 35 and 30 cP respectively.

4.1.2 Pour point

Crude	Pour point [°C]
Crude A	24
Crude B	Not found
Crude C	Not found

Table 1: Pour point

The pour point of crude B and C was not possible to find when performing the pour point test. The minimum temperature of the water bath is -30°C, and the crudes were still pourable at a temperature of -30°C. This means that it was simply not possible to determine the pour point of the crudes with the equipment available. Crude A stopped being pourable at a temperature of 21°C. The pour point of a crude is found by adding 3°C to the temperature at which the crude is no longer pourable, which means that the pour point of crude A was 24°C. The fact that crude A clearly has a higher pour point than crude B and C indicates a higher wax content.

4.1.3 WAT and WDT

Crude	WAT [°C]	WDT [°C]
Crude A	38,5	54,5
Crude B	34,5	51,5

Table 2: WAT and WDT

At this point crude C was eliminated and the WAT and WDT were not measured, due to its low pour point and viscosity. Crude A and B were quite similar with a difference of 4 and 3°C in WAT and WDT respectively.

4.1.4 Crude oil selection

When selecting a crude oil for the development of methodology for paraffin dispersants the properties of the crudes were evaluated. Crude A and B had a quite similarly WAT and WDT, but showed a significant difference in pour point and viscosity profiles. A high pour point indicates high wax content, which will contribute to pressure build-ups and blockages. If the wax content of the crude oil is very low, as indicated in crude B, it would have been difficult to get clear pressure build ups due to small amounts of wax deposition when performing tests on the wax loop. When using a crude oil with a low pour point and low viscosity it may also take longer time to get a pressure build up, than with using a crude with high viscosity and pour point. When selecting a crude for the development of methodology it is preferable with a crude that has a high wax content, in order to get clear pressure build-ups when performing tests at the wax loop. A crude is considered to have a high wax content when there is more than 10% wax, and a low wax content when there is less than 4% wax. [25] An analysis received from M-I Swaco showed that crude A has a wax content of 20.4 %, which means that crude A has a high wax content. On that basis, crude A was selected for the development of methodology.

4.1.5 GC- analysis

A gas chromatography (GC) analysis of crude A was performed with the following result:

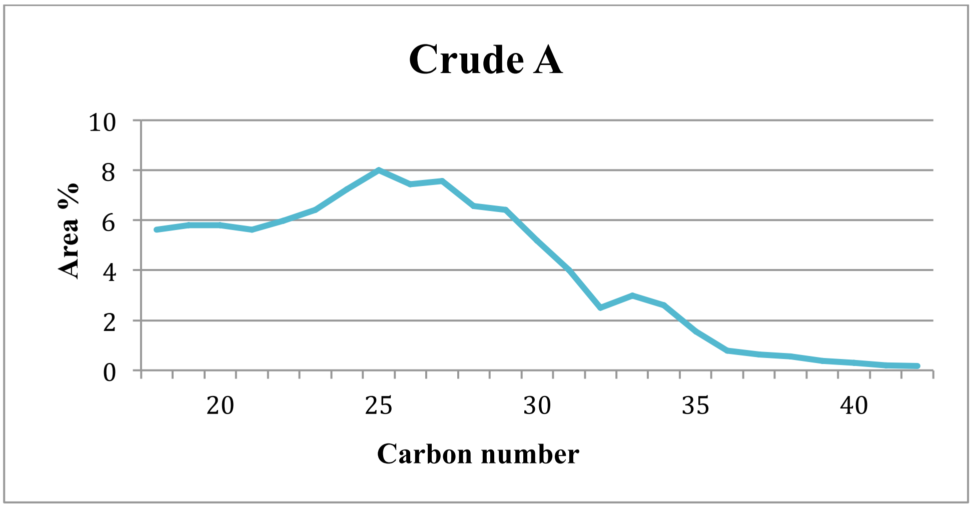

Figure 20: GC-analysis of crude A

Figure 20 shows the paraffin carbon chain distribution in crude A. From the graph one can see that Crude A has carbon numbers as high as C42, which means that the wax crystals that are precipitating out of Crude A will be hard wax crystals.

4.1.6 Density of the crude

The density of crude A was determined by using a pycnometer. The mass of the crude was measured at 40°C, and the density was calculated by using the following equation:

$$\rho = \frac{m}{V} = \frac{8.758\ g}{10.477\ cm^3} = 0.836 \frac{g}{cm^3} = 836\ kg/m^3$$

ρ = Density of the crude
m = Mass of the crude
V = Volume of the pycnometer

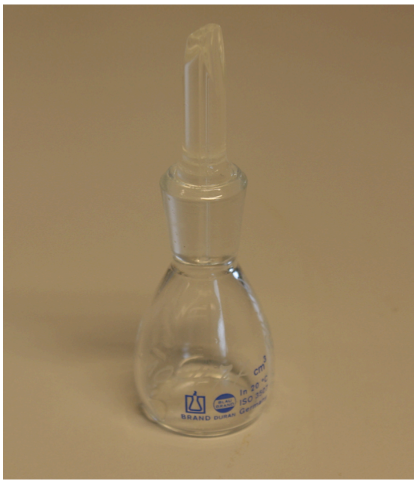

Figure 21: The pycnometer

4.1.7 API gravity of the crude

The API gravity is a value used to classify a crude oil as light, medium, heavy or extra heavy. The API value for each classification is:

- Light crude = API > 31.1
- Medium crude = 22.3 < API > 31.1

- Heavy crude = API < 22.3
- Extra heavy crude = API < 10

The API gravity of crude A was calculated by the following equation [26]:

$$API\ gravity = \frac{141.5}{Spesific\ gravity\ of\ the\ crude} - 131.5 = \frac{141.5}{0.836\frac{g}{cm^3}} - 131.5 = 37.76$$

The API gravity of crude A was calculated to be 37.76, which means that crude A is classified as a light crude oil.

4.2 Development of standard methodology for testing paraffin dispersants

In order to develop a standard methodology for testing paraffin dispersants a number of tests were performed on the wax loop. The tests were performed in compliance with the procedure in appendix 4. A blank sample of crude A was tested, and the set values were adjusted to obtain an optimum deposition with significant pressure build-ups. After performing a number of tests with adjusting the set values, the following values were set as a standard:

Stirrer	
Motor	100 rpm
Heating	45°C = WAT + 6.5°C
MTR pump	
Heating	40°C = WAT + 1.5°C
Heaters	
Pre-heater	OFF
Post-heater	70°C = WDT + 15.5°C

Table 3: Standard set values

The temperature of the stirrer was set to 45°C, which is 6.5°C above the WAT of crude A. With a temperature of 45°C no wax crystals will precipitate out from the crude oil before entering the wax loop. The pre-heater was turned off in order to ensure that the crude was being naturally cooled down by the flowline to a temperature below the WAT before entering the test pipeline. When the crude is cooled down by the flowline to a temperature below the WAT, the temperature differential between the inlet of the test pipeline and the test pipeline is reduced to a minimum. Obviously, the temperature differential between the inlet of the test pipeline and the test pipeline also depends on the set value of the thermostat and the flow rate. The development of a standard set value for the thermostat and the flow rate will be shown later in this chapter. The post-heater was set to a temperature of 70°C in order to ensure that all wax crystals were dissolved before entering the stirrer, and circulated back into the wax loop.

4.2.1 Adjusting the thermostat temperature

The temperature of the thermostat is controlling the temperature of the test pipeline. In order to ensure that the wax deposition is not driven by a thermal gradient, the temperature of the thermostat must be as close to the inlet temperature of the test pipeline as possible. It is important to mention that a number of tests with different thermostat set values were performed. The following sections are showing the final adjustments of the thermostat temperature to obtain deposition within a reasonable time frame for testing.

4.2.1.1 Thermostat temperature at 25° C

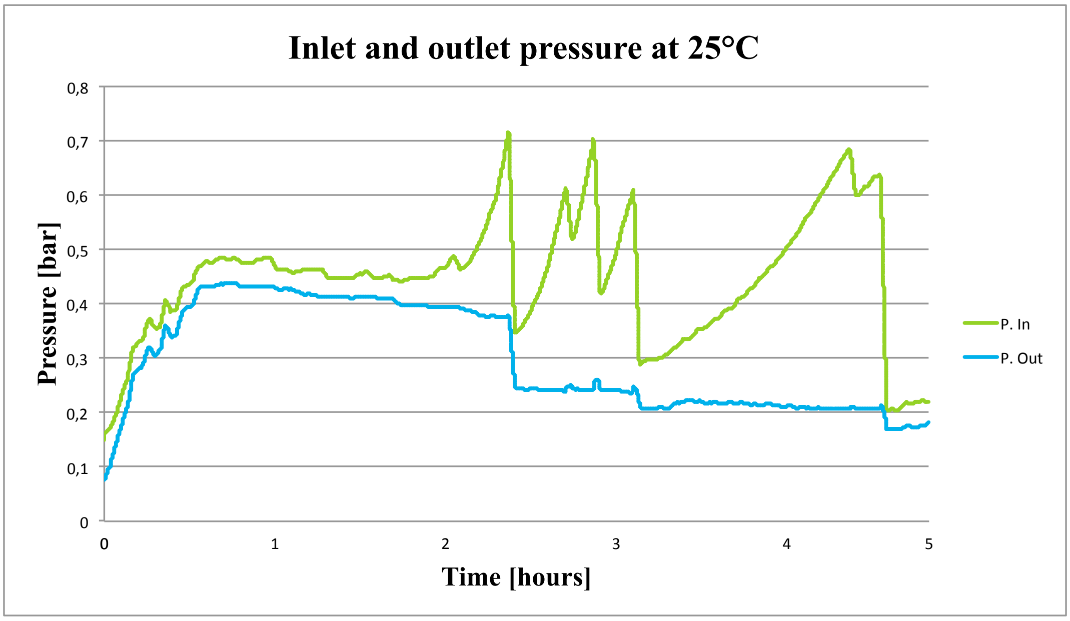

Figure 22: Inlet and outlet pressure at 25°C

Figure 22 shows the inlet and outlet pressure of the test pipeline using the standard set values described in chapter 4.2, together with a thermostat temperature of 25°C and a flow rate of 30 ml/min. Using a flow rate of 30 ml/min ensures a laminar flow regime. This has been calculated and is presented in appendix 5. The wax loop records a measurement every second, which makes the results presented in the graph very accurate. After two hours a significant pressure build-up of 0.26 bar was observed. As the wax crystals deposit on the pipeline wall the inlet pressure increases, until it reaches a maximum and the wax crystals are sheared off from the pipeline wall. However, when the wax crystals have been sheared off due to the high inlet pressure, the inlet pressure immediately starts to increase and the pressure build-ups are repeated during a time period of three hours. This can be explained by the fact that when the inlet pressure reaches a maximum, only a layer of wax crystals are sheared off, which means that some wax crystals may still be adhering to the pipeline wall. When the inlet pressure has decreased, the wax crystals that are precipitating out of the crude oil will not only adhere to the pipeline wall, but also to the remaining wax crystals, and the inlet pressure will immediately start to increase again.

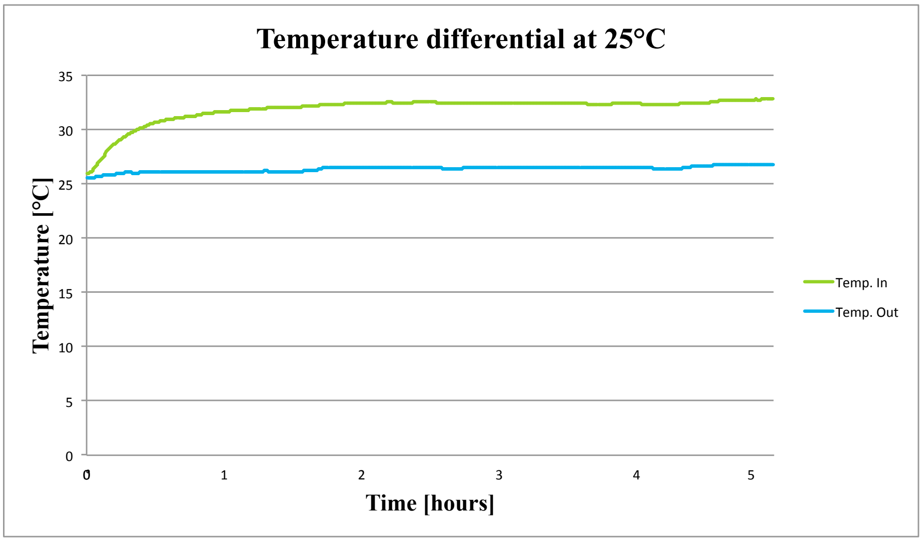

Figure 23: Temperature differential at 25°C

Figure 23 shows the temperature differential between the inlet and outlet of the test pipeline during a time period of five hours. Initially, the temperature of the inlet is 25.5°C, which is very close to the temperature of the test pipeline. From the graph one can see that the temperature differential initially is approximately zero before it increases due to the thermal insulation of the pipeline caused by the wax deposition. The maximum temperature differential is 6°C.

4.2.1.2 Thermostat temperature at 20°C

A thermostat temperature of 25°C resulted in significant pressure build-ups after two hours. In order to expedite these pressure build-ups, a thermostat temperature of 20°C was set. The standard set values were used together with a flow rate of 30 ml/min.

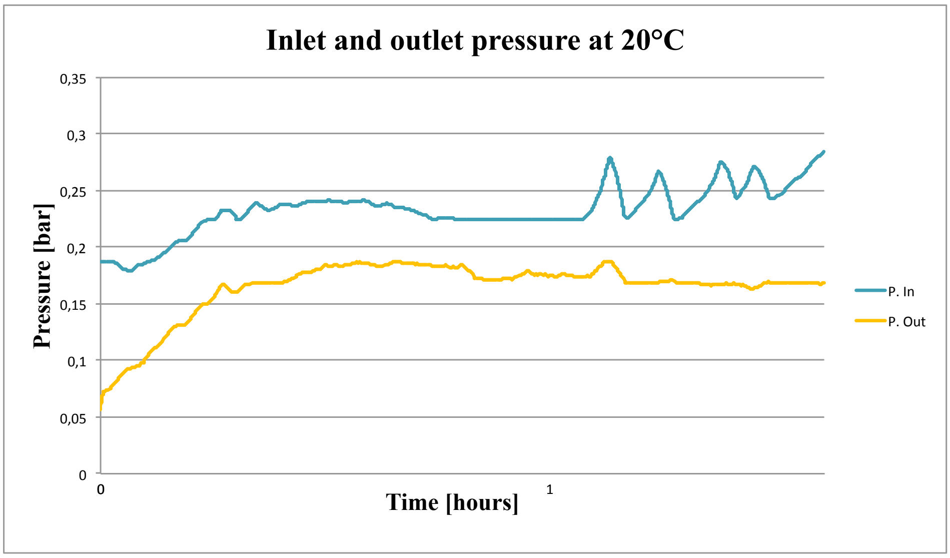

Figure 24: Inlet and outlet pressure at 20°C

From figure 24 one can see pressure build-ups after one hour. Using a thermostat temperature of 20°C expedited the pressure build-ups, however, the pressure build-ups were not as significant as when using a thermostat temperature of 25°C.

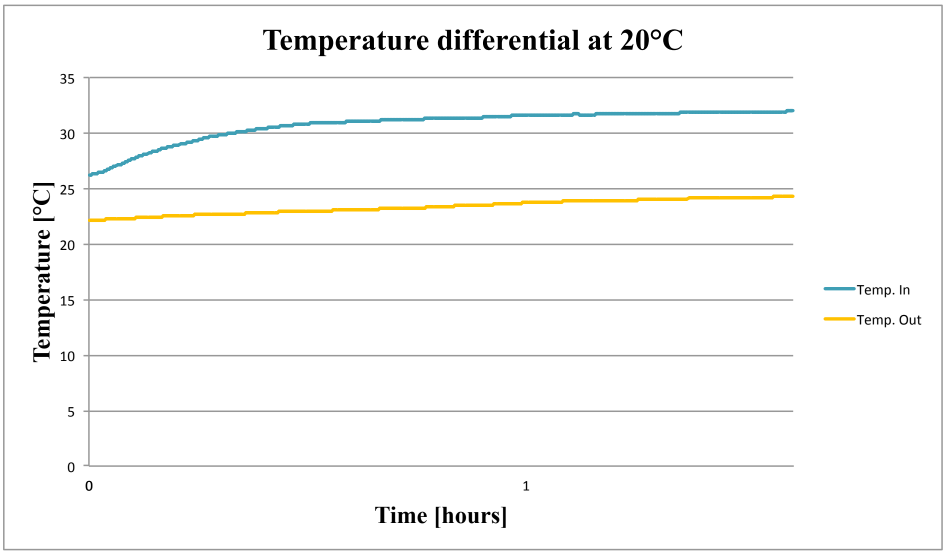

Figure 25: Temperature differential at 20°C

Initially, one can see that decreasing the thermostat temperature resulted in an increase in temperature differential along the test pipeline, with an inlet temperature of 26.2°C and an outlet temperature of 22.1°C. The maximum temperature differential is 8°C.

4.2.2 Adjusting the flow rate

In order to increase the pressure build-ups the flow rate was decreased from 30 to 20 ml/min. The standard set values described in chapter 4.2 was used, together with a thermostat temperature of 20°C. A decrease in the flow rate increases the residence time of the crude oil in the test pipeline, which leads to more rapid wax deposition.

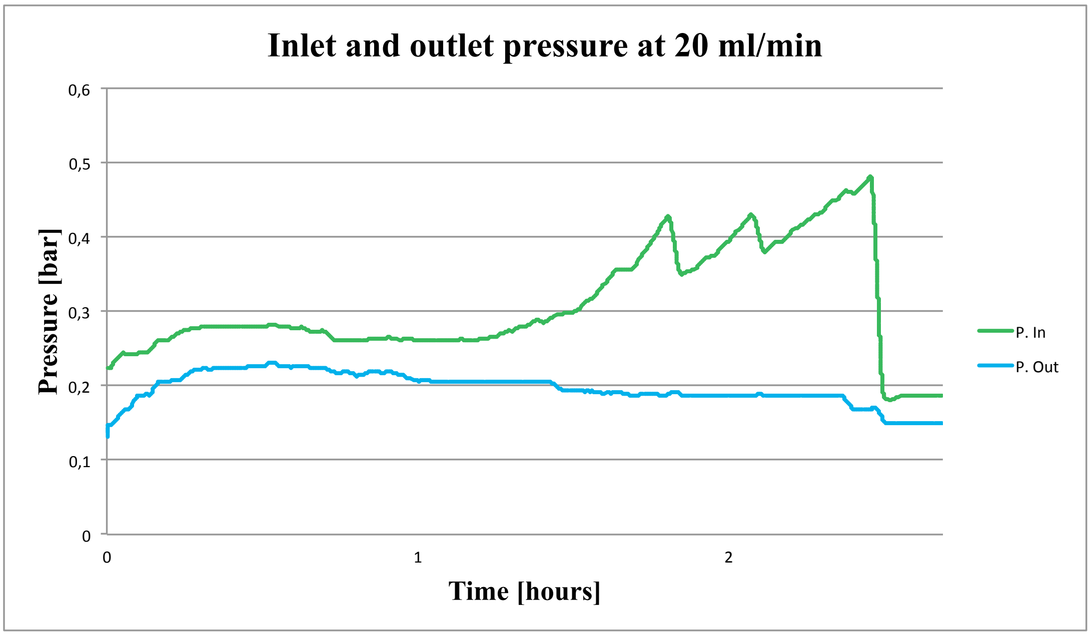

Figure 26: Inlet and outlet pressure at 20 ml/min

From figure 26 one can see that decreasing the flow rate to 20 ml/min was successful. After 1 hour and 20 minutes the inlet pressure started increasing from 0.26 to 0.42 bar, which is a higher pressure increase than with using a flow rate of 30 ml/min. One can observe three pressure build-ups within a time period of 1 hour, before the inlet pressure reaches a maximum and the wax crystals are sheared off by the increasing pressure and flow rate. The test was repeated with the exact same set values, with the following result:

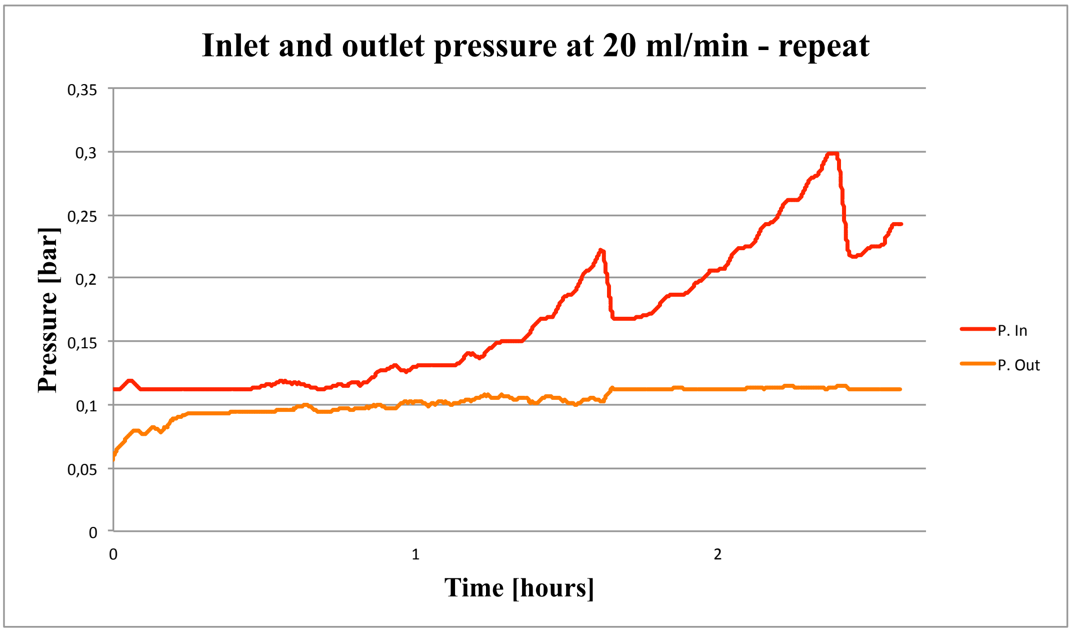

Figure 27: Inlet and outlet pressure at 20 ml/min – repeat

In order to make it easier to compare the results the inlet pressure from both tests was compared:

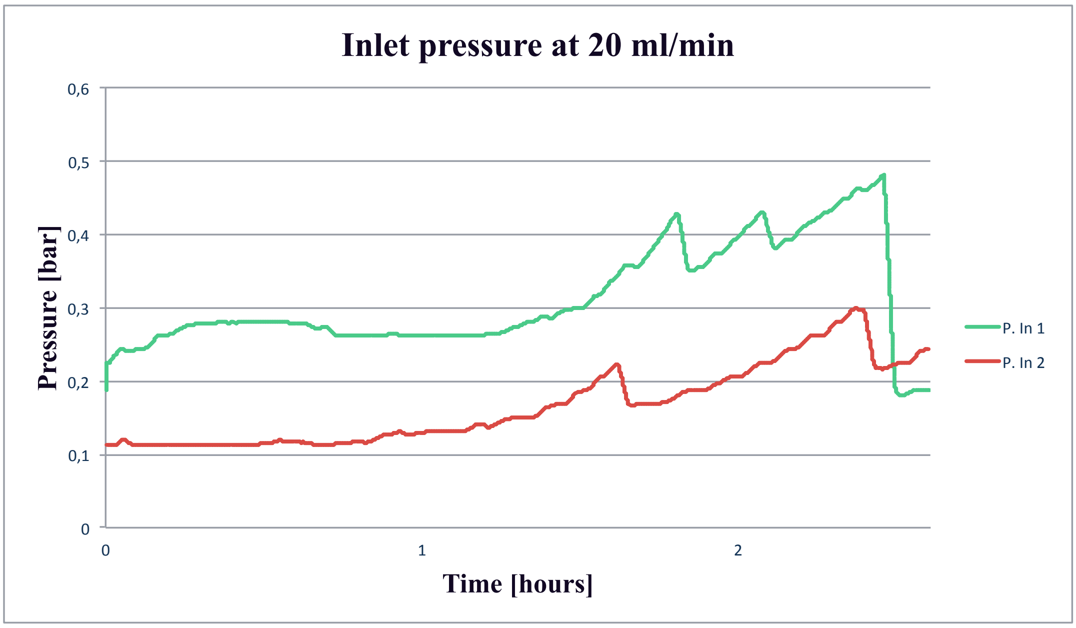

Figure 28: Inlet pressure at 20 ml/min

Figure 28 shows the inlet pressure presented in figure 26, compared with the inlet pressure from the repeat of the test. The same procedure and set values were used during both tests.

From the graph one can see that the tests are showing the same trends within the same time period. It is important to remember that the aim of this project is to develop a practical industrial solution. Which means, that as long as the two tests are showing the same trends and behaviour within the same time period, it is possible to draw conclusions and to extract useful information from the results. The wax deposition will not be uniform along the test pipeline, which results in blockages of different significance. This explains the difference in pressure and pressure build-ups.

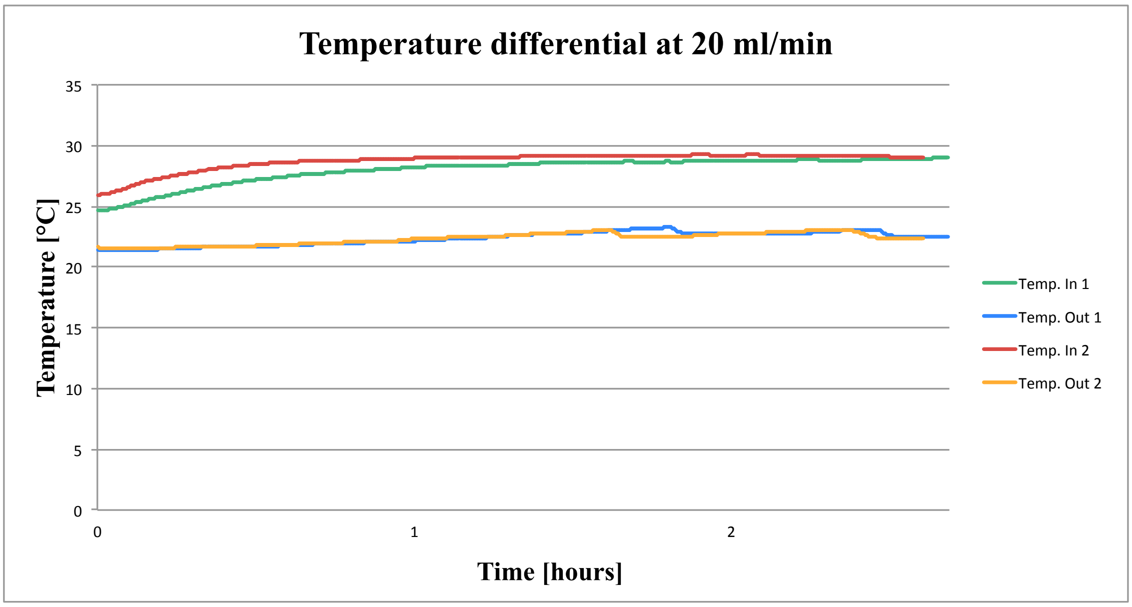

Figure 29: Temperature differential at 20 ml/min

Figure 29 shows the temperature differential along the test pipeline from the two tests. From the graph it is fairly straightforward to see that the two tests are showing the same trends during the same time period in temperature differential. Initially, T. In 1 and T. In 2 is showing a temperature of 24.6°C and 26.9°C respectively, while both T. Out 1 and T. Out 2 is showing a temperature of 21.6°C. These are acceptable values. Decreasing the flow rate resulted in a reduced temperature differential along the pipeline, with a maximum temperature differential of 6 and 6.5°C respectively.

Since the two tests were showing the same trends and behaviour during the same time period, the following values were set as standard set values when performing tests with crude A on the wax loop:

Stirrer	
Motor	100 rpm
Heating	45°C = WAT + 6.5°C
MTR pump	
Flow rate	20 ml/min
Heating	40°C = WAT + 1.5°C
Heaters	
Pre-heater	OFF
Post-heater	70°C = WDT + 15.5°C
Thermostat	
Heating	20°C = WAT – 18.5°C

Table 4: Standard set values for crude A

With these standard set values all the requirements were obtained: clear pressure build-ups within a reasonable time period, a pressure build-up of at least 0.1 bar and a reduced temperature differential between the inlet of the test pipeline and the test pipeline. This means that with the standard set values for crude A, one has obtained wax deposition that is driven by shear dispersion rather than a thermal gradient.

4.3 Testing paraffin dispersants

Four types of paraffin dispersants were added to a sample of crude A and tested in order to differentiate between a good and bad performer.

Dispersant	Type of dispersant
Dispersant 1	Metal salt of sulphonate surfactant
Dispersant 2	Hyperbranched polymer
Dispersant 3	Sulphonate surfactant/amine salt
Dispersant 4	Blend of polyacrylate and sulphonate surfactant/amine salt

Table 5: Types of paraffin dispersants

A concentration of 500 ppm was used during each test, which is a standard starting dosage rate used when testing the performance of paraffin dispersants at M-I Swaco. Each dispersant were tested twice during a time period of five hours, which is two times the blank crude oil sample. The dispersants were tested twice in order to draw good conclusions and to extract useful information from the results. The standard set values for crude A were used, and each test was tested in compliance with the wax loop procedure in appendix 4.

In the following sections only the inlet pressure is presented, and compared with the inlet pressure from the first tested blank sample of crude A, presented in figure 26. The inlet pressure says a lot about the performance of the paraffin dispersants, as an increase in the inlet pressure indicates an increase in wax deposition along the test pipeline. When choosing a blank crude oil sample to compare the results from the paraffin dispersants with, the value of the initial inlet pressure was analysed. All the paraffin dispersants tested showed an initial inlet pressure close to the initial pressure of the blank crude oil sample presented in figure 26, which is the reason for choosing this blank crude oil sample to compare the results with.

4.3.1 Dispersant 1

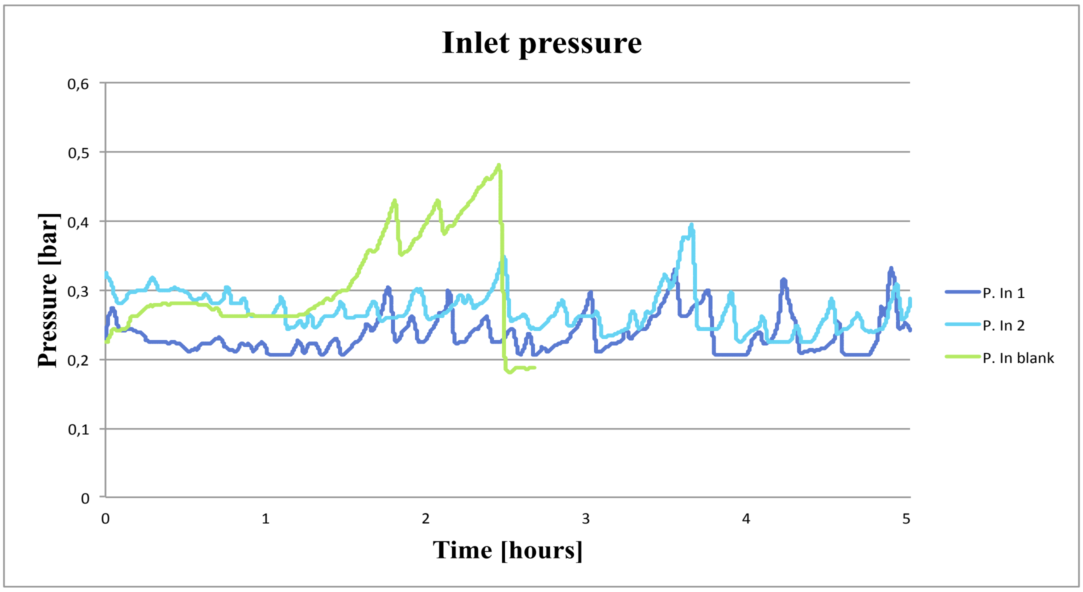

Figure 30: Inlet pressure dispersant 1

Dispersant 1 is a metal salt of sulphonate surfactant. A concentration of 500 ppm of dispersant 1 were added to crude A and tested during a time period of five hours. Two tests were performed and compared to a blank sample of crude A, which is presented in the graph. From the graph one can see small oscillations when adding dispersant 1 to the crude oil sample. The dispersant coats the wax particles and makes the wax more soft and mushy, which means that the wax deposited handles less pressure before it is sheared off. When not adding a dispersant, the wax particles becomes harder and stick better to the surface of the test pipeline, and handles a lot more pressure before it gets sheared off. This explains the reason behind the different curves. The two tests with adding dispersant 1 to the crude oil sample showed a similar trend in pressure increase during the time period of five hours. Dispersant 1 did not exceed the pressure increase of the blank sample during a time period of five hours, which classifies dispersant 1 as a good performer.

4.3.2 Dispersant 2

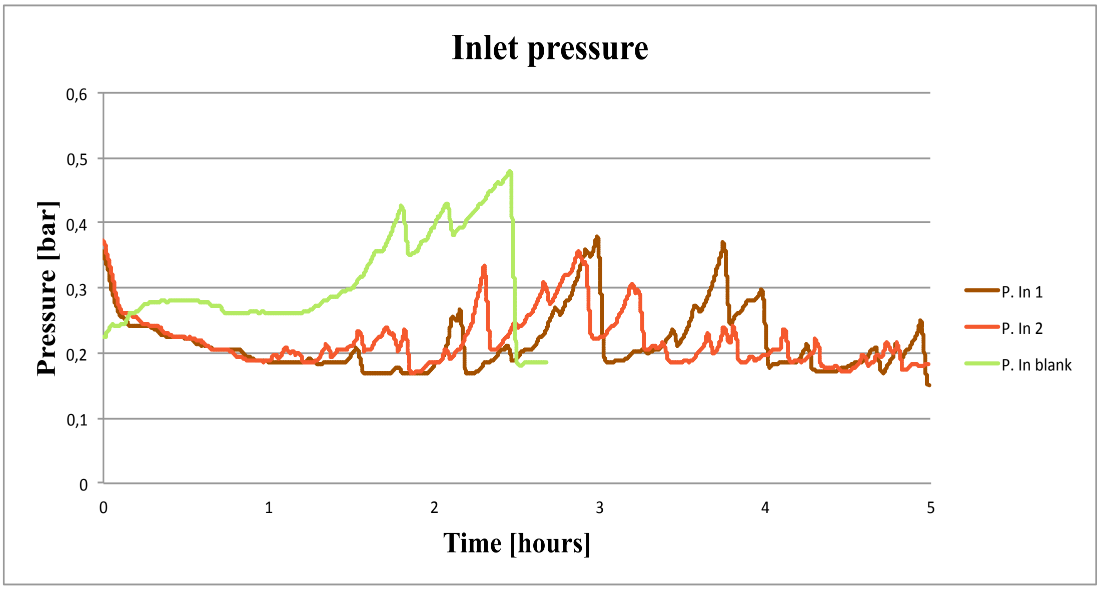

Figure 31: Inlet pressure dispersant 2

Dispersant 2 is a hyperbranched polymer. During the first hour of the tests with adding dispersant 2 to the crude oil sample, one can observe approximately the same values in inlet pressure. After this the pressure increases are varying, however they are showing the same trends during the same time period. As mentioned earlier, this is explained by the fact that the wax deposition will not be uniform along the test pipeline, which results in different significance of pressure increases. The tests with adding dispersant 2 to the crude oil sample did not exceed the inlet pressure of the blank crude oil sample during a time period of five hours, which classifies dispersant 2 as a good performer.

4.3.3 Dispersant 3

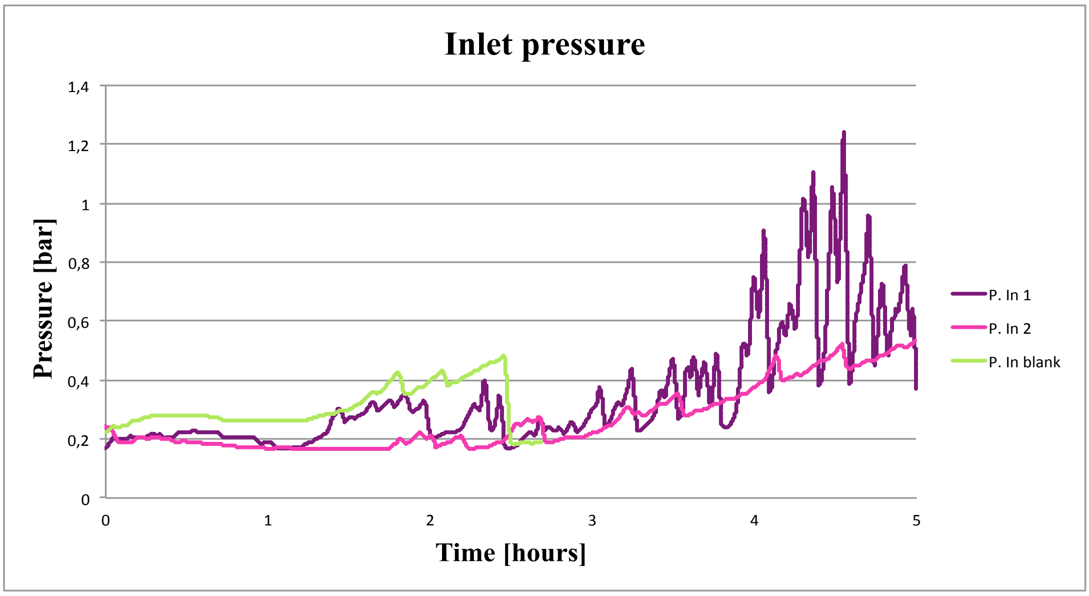

Figure 32: Inlet pressure dispersant 3

Dispersant 3 is a sulphonate surfactant/amine salt. The two tests with adding dispersant 3 to the crude oil sample showed similar trends during the first hour of the test. After this the pressure increases was of different significance. P. In 1 shows a pattern with oscillations, while P. In 2 shows a more linear increase during the same time period. However, after approximately four hours, both tests are showing a pressure increase that is exceeding the blank crude oil sample. Because of this, dispersant 3 was classified as a bad performer.

4.3.4 Dispersant 4

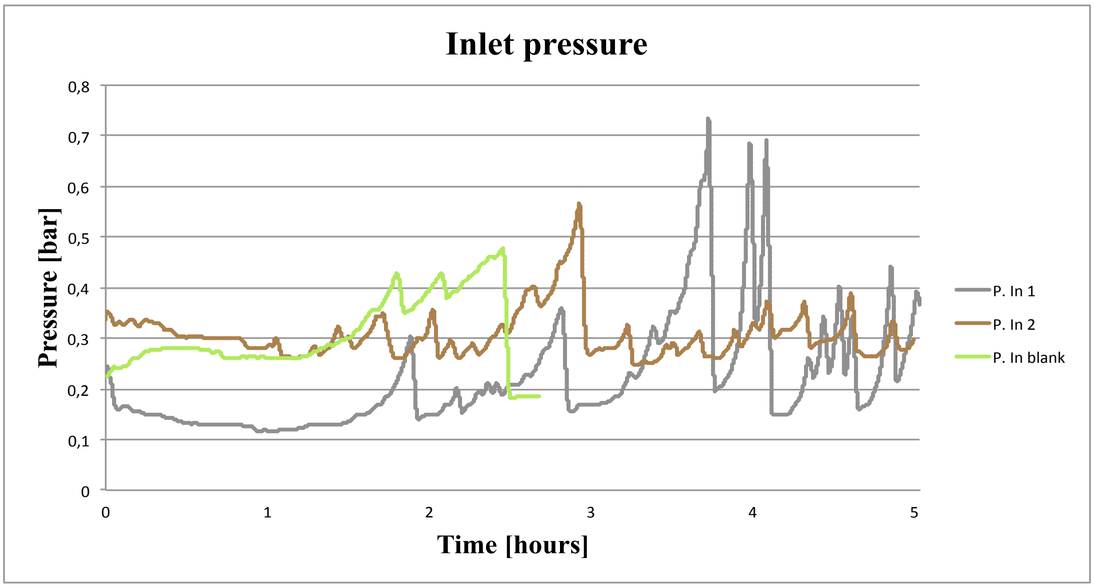

Figure 33: Inlet pressure dispersant 4

Dispersant 4 is a blend of polyacrylate and sulphonate surfactant/amine salt. From the graph one can see varying results between the two tests with adding dispersants 4 to the crude oil sample. However, both tests do exceed the inlet pressure of the blank crude oil sample during a time period of five hours, which classifies dispersant 4 as a bad performer.

4.4 Testing a new type of crude

In order to confirm that a standard methodology for testing paraffin dispersants was developed, it was necessary to repeat the methodology with another type of crude. A stock tank oil from Africa was selected, and viscosity, pour point, WAT and WDT were tested in compliance with the procedures in appendix 1, 2 and 3.

4.4.1 Viscosity profile

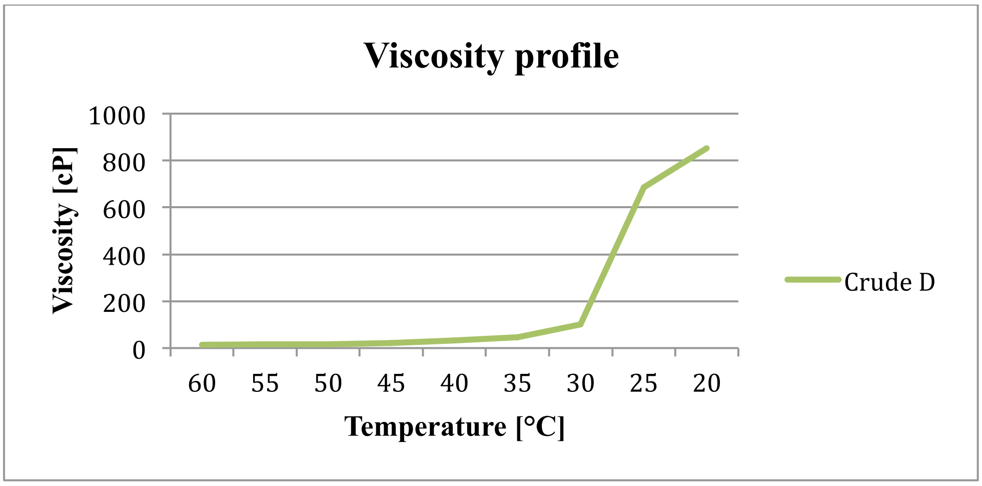

Figure 34: Viscosity profile of crude D

From the graph one can see that when crude D is reaching a temperature of 30°C, the crude is showing a significant increase in viscosity. From 30 - 25°C the viscosity is increasing from 100 to 686 cP respectively. At a temperature of 20°C, crude D has reached its maximum viscosity with 853 cP. After this the viscosity readings stopped, which means that the crude was solid and the spindle was unable to rotate. This indicates that crude D has a much higher wax content than crude A, and will most likely have a higher pour point, WAT and WDT.

4.4.2 WAT, WDT and pour point

WAT	55°C
WDT	65°C
Pour point	36°C

Table 6: WAT, WDT and pour point

Crude D did have a much higher WAT, WDT and pour point than crude A, as expected. Crude D stopped being pourable at a temperature of 33°C, which means that the pour point was calculated to be 36°C.

4.4.3 GC – analysis

A GC – analysis of crude D was performed with the following result:

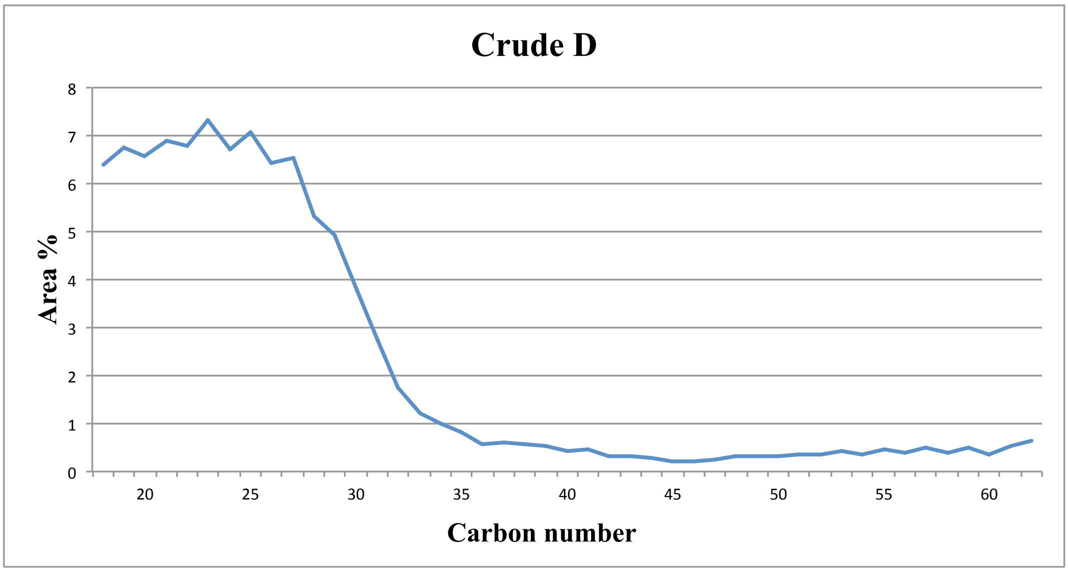

Figure 35: GC - analysis crude D

Figure 35 shows the paraffin carbon chain distribution in crude D. From the graph one can see that Crude D has carbon numbers > C60, which means that the wax crystals that are precipitating out of Crude D will be hard wax crystals.

4.4.4 Density of the crude

The density of crude D was determined by using a pycnometer. The mass of the crude was measured at 40°C, and the density was calculated by using the following equation:

$$\rho = \frac{m}{V} = \frac{8.957\ g}{10.477\ cm^3} = 0.855 \frac{g}{cm^3} = 855\ kg/m^3$$

4.4.5 API gravity of the crude

The API gravity of crude D was calculated by the following equation:

$$API\ gravity = \frac{141.5}{Spesific\ gravity\ of\ the\ crude} - 131.5 = \frac{141.5}{0.855\,\frac{g}{cm^3}} - 131.5 = 33.99$$

The API gravity of crude D was calculated to be 33.99, which means that crude D is classified as a light crude oil, when referring to the API classification presented in section 4.1.7.

4.5 Repeat of the methodology

In the following sections the steps in adjusting the set values for crude D is presented.

4.5.1 Thermostat temperature at 50°C

After testing the properties of crude D one could see that crude D had a high pour point, viscosity profile, WAT and WDT. It was also reasonable to estimate that crude D did have a higher wax content than crude A. Because of this, it was necessary to start with high set temperatures in order to see the behaviour of crude D and how the crude responded with pressure build-ups. In addition, the wax loop is very sensitive to blockages when testing a crude with a high wax content, since both the test pipeline and the plastic tubes are having a small diameter.

With taking this into account, Crude D was tested with the following set values:

Stirrer	
Motor	100 rpm
Heating	80°C = WAT + 25°C
MTR pump	
Flow rate	20 ml/min
Heating	65°C = WAT + 10°C
Heaters	
Pre-heater	60°C = WAT + 5°C
Post-heater	80°C = WDT + 15°C
Thermostat	
Heating	50°C = WAT – 5°C

Table 7: Set values crude D

The heating of the stirrer was set to a temperature of 80°C, in order to ensure that no wax particles were precipitating out of the crude before entering the wax loop. Also, the heating of the MTR-pump was set to a temperature above the WAT in order to ensure that no wax particles were precipitating out of the crude and causing damage to the pump. A flow rate of 20 ml/min ensures a laminar flow regime. This has been calculated and is presented in appendix 5. The test pipeline was set to a temperature of 50°C, which is 5°C below the WAT. The temperature of the post-heater was set to 80°C, in order to ensure that all wax particles were dissolved before re-entering the stirrer and being circulated back into the wax loop.

The set values presented in table 7 gave the following result:

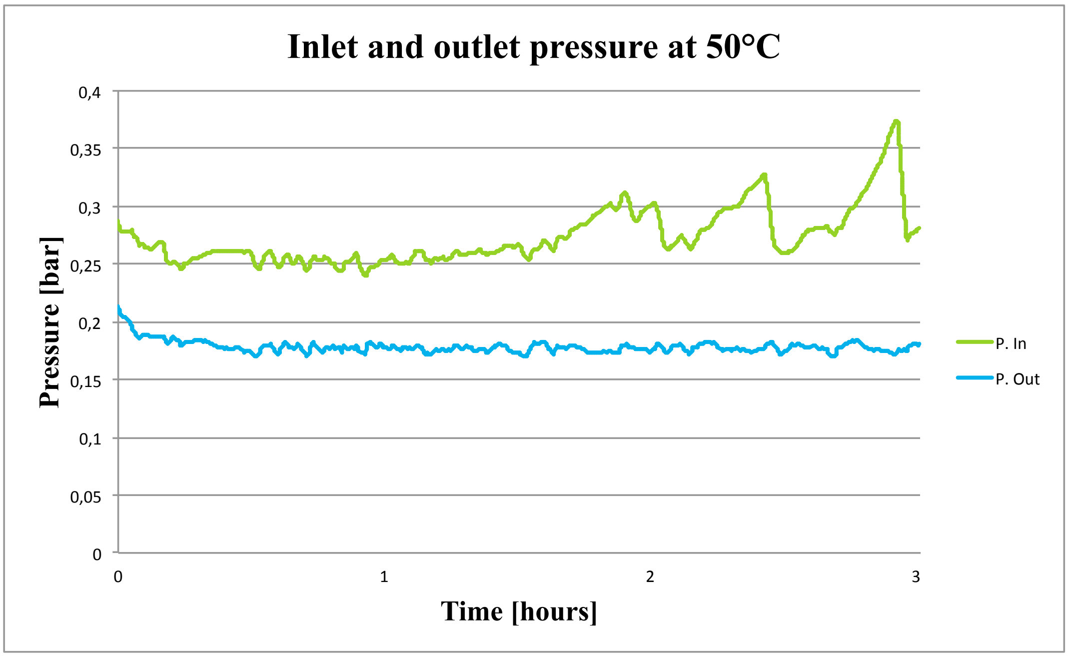

Figure 36: Inlet and outlet pressure at 50°C

From the graph one can see three pressure build-ups in inlet pressure during a time period of three hours. After 1.5 hours one can see an increase in the inlet pressure of 0.02 bar, before the wax particles are sheared off. This is repeated with a pressure build-up of 0.04 and 0.08 bar respectively.

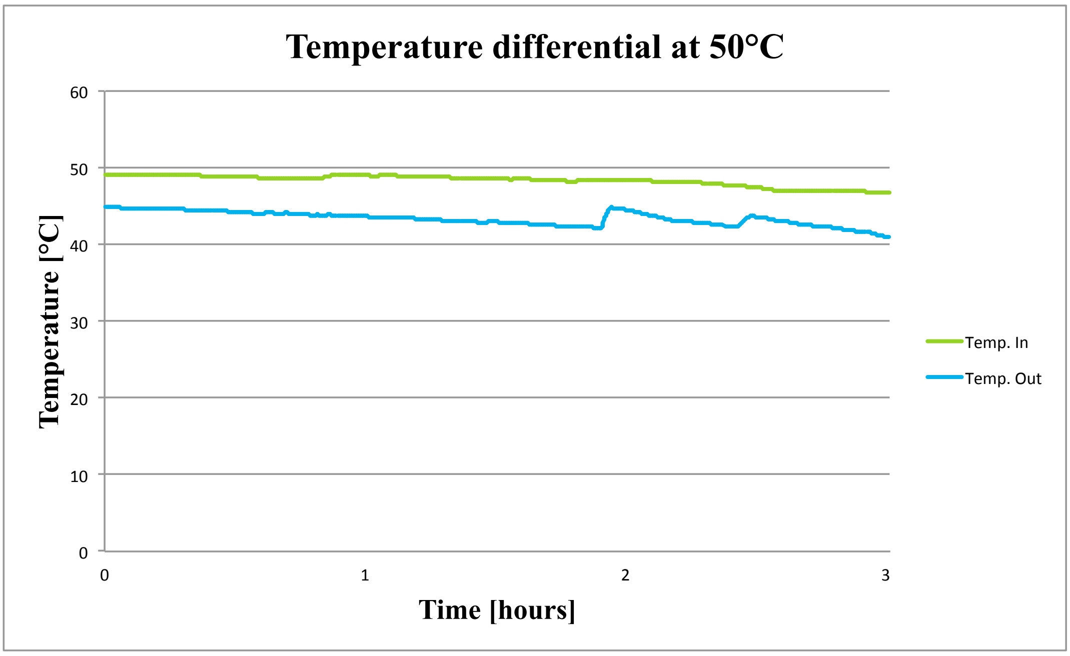

Figure 37: Temperature differential at 50°C

Initially, the inlet temperature is 49°C, which is very close to the set temperature of the test pipeline. One can see two increases in outlet temperature. This is caused by the fact that the test pipeline is insulated due to the wax deposition, which results in a reduced temperature differential along the test pipeline. The maximum temperature differential is 6°C.

4.5.2 Reducing the temperature of the thermostat and pre-heater

The pressure build-ups in inlet pressure seen in figure 36 were not that significant. In order to increase the inlet pressure build-ups the temperature of the thermostat was set to 45°C, which is 10°C below the WAT of crude D. This was successful, and one could see a significant increase in the inlet pressure build-ups. However, the initial temperature differential between the inlet of the test pipeline and the test pipeline was 5°C. Because of this the temperature of the pre-heater was reduced to 55°C, in order to reduce the thermal gradient between the inlet of the test pipeline and the test pipeline to a minimum. The adjustments with reducing the temperature of the thermostat and the pre-heater were done in two steps. It is important to adjust only one set value at a time, in order to see the effect of each individual parameter adjusted.

Stirrer	
Motor	100 rpm
Heating	80°C = WAT + 25°C
MTR pump	
Flow rate	20 ml/min
Heating	65°C = WAT + 10°C
Heaters	
Pre-heater	55°C = WAT
Post-heater	80°C = WDT + 15°C
Thermostat	
Heating	45°C = WAT – 10°C

Table 8: Final set values crude D

The following graph presents the final result after reducing the temperature of the thermostat and pre-heater:

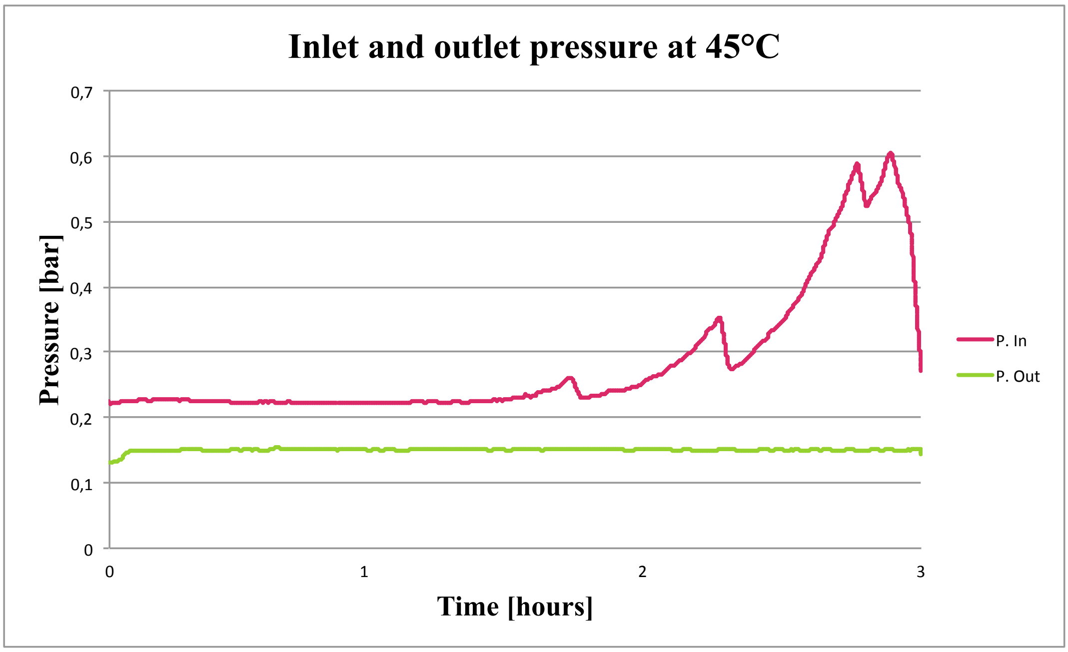

Figure 38: Inlet and outlet pressure at 45°C

From figure 38 one can see significant pressure build-ups in inlet pressure during a time period of three hours, which means that reducing the temperature of the thermostat was successful. A pressure build-up of 0.03 bar appears after 1 hour and 40 minutes, followed by pressure build-ups of 0.12, 0.35 and 0.37 bar respectively. At 0.6 bar the inlet pressure has reached its maximum, and the wax crystals are sheared off due to the high inlet pressure.

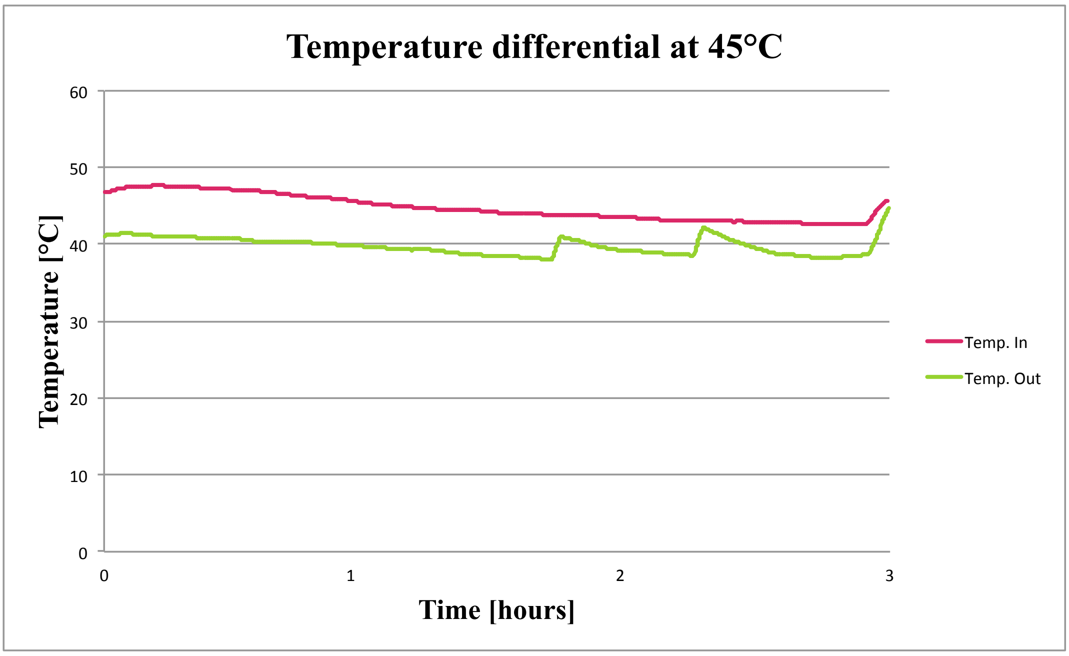

Figure 39: Temperature differential at 45°C

Reducing the temperature of the pre-heater resulted in an initial inlet temperature of 46.75°C, which is very close to the temperature of the test pipeline. One can see three increases in outlet temperature, which appears at the same time as the wax particles are sheared off due to the increasing inlet pressure. The maximum temperature differential is 6°C.

With the final set values presented in table 8 all the requirements were obtained: clear pressure build-ups, a pressure build-up of at least 0.1 bar, a laminar flow regime and a temperature differential between the inlet of the test pipeline and the test pipeline reduced to the minimum. This means that with the final set values for crude D, one has obtained wax deposition that is driven by shear dispersion rather than a thermal gradient.

4.5.3 Adding a dispersant to the crude

At this point, a new test with adding 500 ppm of dispersant 1 was performed in order to see if the dispersant did show a good performance on the crude. The reason for choosing dispersant 1 was that this dispersant did show a good performance on crude A, and it would have been interesting to see if one could see the same results when adding it to crude D. Dispersant 1 exceeded the inlet pressure of the blank sample from the beginning, and after approximately two hours both the inlet and outlet pressure dropped dramatically and the pump stopped. The reason for this was that the test pipeline was completely blocked causing the wax loop to automatically change to the bypass pipeline. The bypass pipeline was not heated, which caused the bypass pipeline to be blocked and the pump stopped. There was clearly no flow in the wax loop, and the crude inside the plastic tubes at the inlet and the outlet of the wax loop became solid due to the heat loss. The whole system stopped.

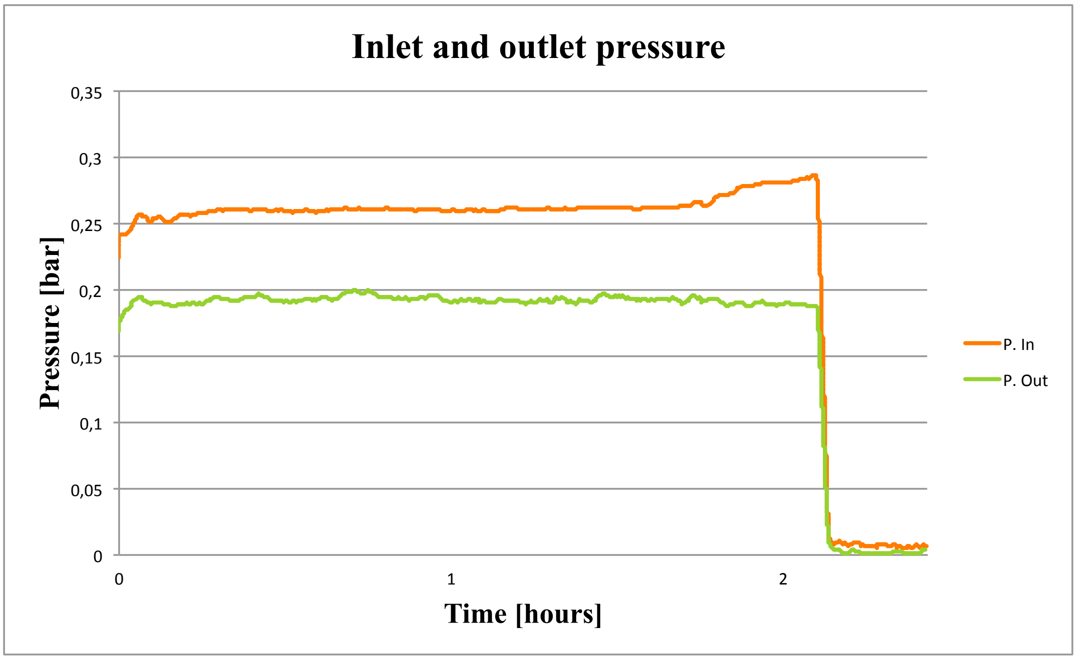

Figure 40: Inlet and outlet pressure dispersant 1

Since the exact same set values as presented in section 4.5.2 was used for this test, it was necessary to analyse what could be different with this crude oil sample. The crude oil sample used when performing this test was taken from the bottom of the crude oil container. When discussing the issue with the engineers at M-I Swaco, it appeared that this problem had been previously experienced. When a crude oil sample is taken out of the crude oil container, the container is shaken well and depressurized. When you repeat this over a longer time period, the last crude oil sample remained in the crude oil container may contain heavier components than a sample taken out when the crude oil container was full. Originally, the crude should be homogenous which means that this should not be a problem. However, this actually seemed to be a problem and one were not able to perform any further testing on the crude having a higher wax content.

When looking back at the procedures, it would have been beneficial to insulate the plastic tubes at the inlet and outlet of the wax loop. Then one can reduce the risk with the crude being solid inside the plastic tubes and prevent heat loss, in case of a blockage of the wax loop. It would also be beneficial to look at the procedures with handling the crude oil sample.

4.6 Wax crystal structure

In this section wax crystal structure is analysed. In order to see how different types of wax prevention chemicals are affecting the agglomeration of growing wax crystals, four different types of wax prevention chemicals were added to a blank sample of crude A. A concentration of 1000 ppm was used, which is a standard starting dosage rate used for inhibitors at M-I Swaco. The structure of the growing wax crystals was analysed at the microscope and compared to a blank sample of crude A, and the WAT was measured. During all tests the start temperature of the water bath was set to 80°C, and each sample was cooled down with a cooling rate of 1°C/min. A picture was taken when the crude oil sample reached a temperature of 25°C. In addition, the wax crystal structure of a blank sample of crude D was analysed and compared to a blank sample of crude A.

	Type of dispersant/inhibitor
Dispersant 4	Blend of polyacrylate and sulphonate surfactant/amine salt
Inhibitor 1	Hyperbranched polymer
Inhibitor 2	Ethylene vinyl acetate (EVA)
Inhibitor 3	Polyacrylate

Table 9: Types of wax prevention chemicals

Table 9 presents the different types of wax prevention chemicals that were added to a blank sample of crude A. One dispersant and three types of inhibitors were tested. All the chemicals were injected into crude A at a temperature above the WAT.

4.6.1 A blank sample of crude A

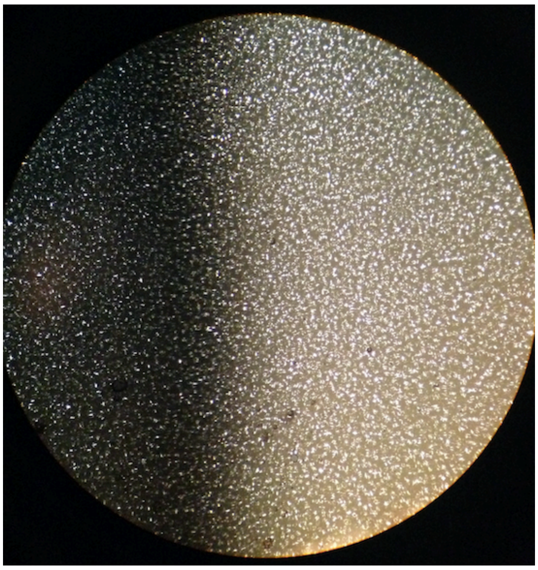

Figure 41: Wax crystal structure crude A

A blank sample of crude A was analysed at the microscope. The picture seen in figure 41 is taken at a temperature of 25°C, which is 13.5°C below the WAT of crude A. From the picture seen in figure 41 one can see that the crude is filled with a large amount of small elongated wax crystals, which have precipitated out of the crude oil sample. Even though the crude oil sample is filled with a large amount of small wax crystals, small wax crystals are much more easily transportable than larger wax crystals, seen later in this chapter.

4.6.2 Dispersant 4

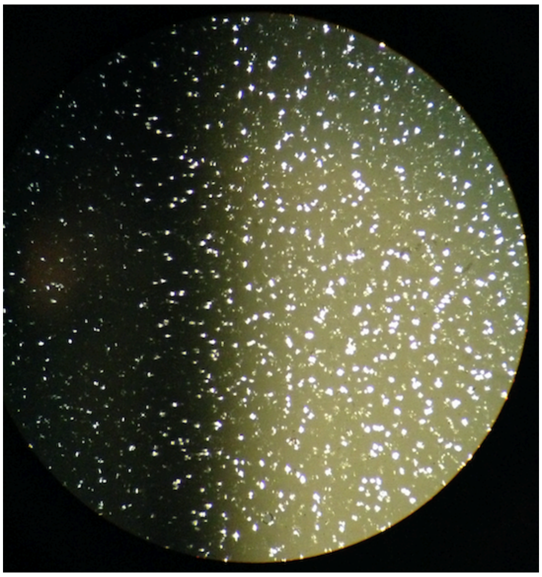

Figure 42: Wax crystal structure dispersant 4

Dispersant 4 is a blend of polyacrylate and a sulphonate surfactant/amine salt. Adding 1000 ppm of dispersant 4 resulted in a WAT of 36.5°C, which is 2°C below the WAT of the blank sample of crude A. A dispersant has the ability to coat growing wax crystals and decrease their tendency to agglomerate, which can be seen in the picture. The amount of wax crystals is reduced and the amount of black areas between the wax crystals has increased. Adding dispersant 4 to the crude oil sample resulted in wax crystals of different sizes with an elongated structure.

4.6.3 Inhibitor 1

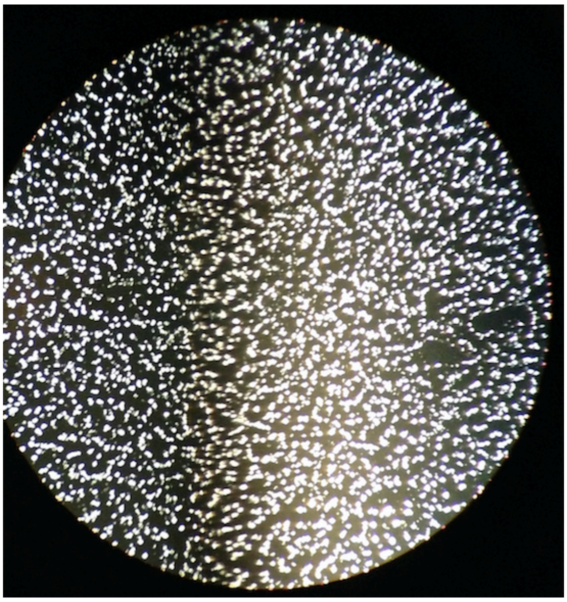

Figure 43: Wax crystal structure inhibitor 1

Inhibitor 1 is a hyperbranched polymer. Adding 1000 ppm of inhibitor 1 resulted in a WAT of 35.5°C, which is 3°C below the WAT of the blank sample of crude A. Paraffin inhibitors works by inhibit wax crystallization. From the picture one can see an increase in the size of the growing wax crystals, with wax crystals having an elongated structure. Larger wax crystals are not that easy transportable compared to smaller wax crystals. However, one can see that the amount of black areas between the wax crystals has increased. The black areas contain no wax crystals as the wax crystals have been attracted to the inhibitor itself.

4.6.4 Inhibitor 2

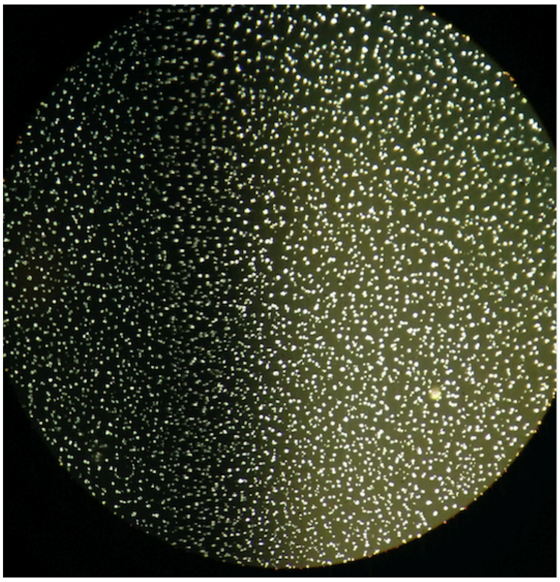

Figure 44: Wax crystal structure inhibitor 2

Inhibitor 2 is an EVA. Adding 1000 ppm of inhibitor 2 increased the WAT to 47°C, which is 8.5°C above the WAT of the blank sample of crude A. From the picture one can see medium sized wax crystals with a spherical structure. When comparing this sample with the blank crude oil sample the amount of black areas has increased, which means that inhibitor 2 does seem to inhibit wax crystallization even though the WAT increased.

4.6.5 Inhibitor 3

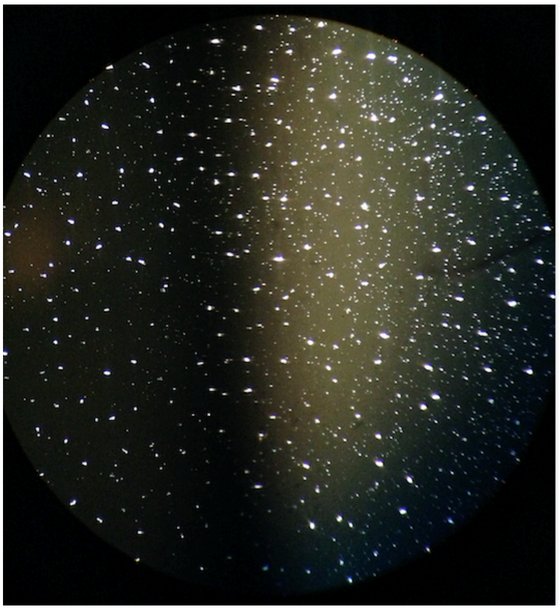

Figure 45: Wax crystal structure inhibitor 3

Inhibitor 3 is a polyacrylate. Adding 1000 ppm of inhibitor 3 resulted in a WAT of 35.5°C, which is 3°C above the WAT of the blank sample of crude A. From the picture one can see that inhibitor 3 did show a good performance in inhibiting wax crystallization and preventing agglomeration of growing wax crystals. One can clearly see a reduced amount of wax crystals compared to the blank sample of crude A, together with clear black areas between the wax crystals. This means that the wax crystals seen in this picture would be much more easily transportable than the wax crystals seen in figure 41. The wax crystals are of different sizes, seen as larger elongated wax crystals together with smaller spherical wax crystals.

4.6.6 A blank sample of crude D

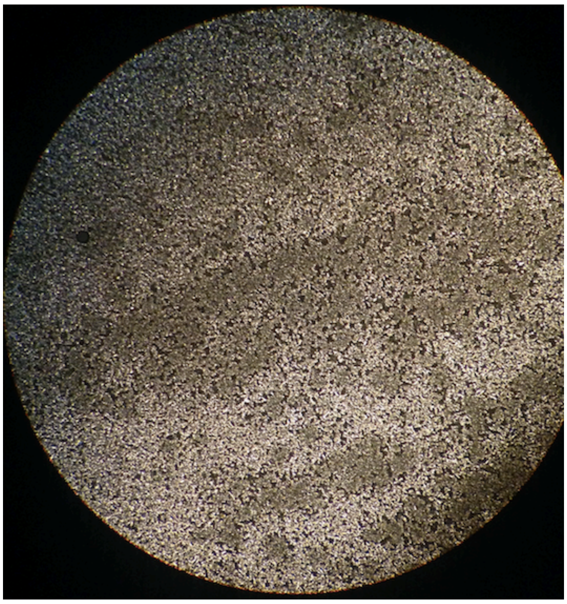

Figure 46: Wax crystal structure crude D

The picture seen in figure 46 is taken at a temperature of 25°C, which is 30°C below the WAT of crude D. From the picture one can see that the crude is filled with a large amount of small elongated wax crystals, with nearly no spaces between the wax crystals. It was earlier estimated that crude D did have a higher wax content than crude A. From the picture one can clearly see that crude D has a higher wax content, when looking at the amount of wax crystals that has precipitated out of the crude oil sample. Crude A did have some spaces between the wax crystals compared to Crude D, which means that the wax crystals that were precipitating out of crude A would be much more easily transportable than the wax crystals seen in figure 46.

Chapter 5 Conclusion

When developing a methodology for testing paraffin dispersants a number of tests were performed. Two different types of crudes were tested, with varying results. The aim of the development of methodology was to obtain wax deposition that was driven by shear dispersion rather than a thermal gradient, and to clearly differentiate between a good and bad performer of paraffin dispersants. When testing crude A having a wax content of 20.4%, this was obtained and one could clearly differentiate between a good and bad performer when adding different types of paraffin dispersants to the crude oil sample. However, the development of this methodology showed some limitations. This was clearly experienced when testing was performed on crude D, due to the large differences between the two crudes with respect to wax content, viscosity, pour point, WAT and WDT. When repeating the methodology on crude D having a higher wax content and WAT than crude A, it was possible to obtain wax deposition driven by shear dispersion rather than a thermal gradient. Despite of this it was not possible to perform any further testing on crude D due to the different properties mentioned, and the limitations of the current equipment setup made it difficult to control the temperature changes in the crude. The high wax content and viscosity made changes occur too rapidly to control, and hence made it difficult to differentiate between a good and bad performer of paraffin dispersants, when the system was changing so fast.

When looking at the structure of paraffin wax crystals at the microscope, the addition of different types of wax prevention chemicals did not result in a significant change in wax crystal structure. However, the addition of different types of wax prevention chemicals did influence the amount and size of wax crystals and the WAT of the crude. When comparing two different types of crudes, one could clearly see a difference in the amount of wax crystals and the visible matrix of the deposits.

Chapter 6 Future work

In this thesis it was not possible to differentiate between good and bad performance of a paraffin dispersant when testing the methodology on crude D type oils. In the future, the methodology should be repeated with testing several types of crudes. When having a wider range of crudes tested it would be easier to tune the set parameters in relation to the wax content, viscosity, pour point and WAT, and to classify the crudes into intervals in relation to the wax content. In order to manage to test a crude with a very high wax content on the wax loop, one should modify the test equipment and insulate the plastic tubes at the inlet and outlet of the wax loop and fully insulate the inlet pipework. Then one can reduce the risk with the crude being solid inside the plastic tubes and prevent heat loss, in case of a blockage of the wax loop. It would also be beneficial to look at the procedures with handling the crude oil sample, in order to obtain a homogenous sample of the crude oil at all times.

In addition, it would be interesting to test different dosage rates of paraffin dispersants, in order to see how different dosage rates affect the wax deposition. One could also test a wider range of flow rates in order to see how the flow rates affect the wax deposition.

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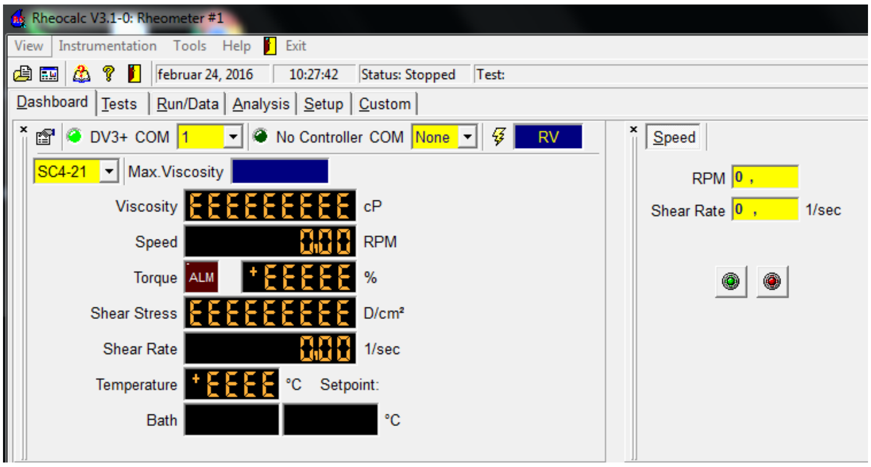
Appendix 1: Viscosity procedure

- Turn on the water bath and set the temperature to 60°C. Turn on the rheometer and press the "yes" button. Place the test container in the oven at 60°C.
- The rheometer is communicating with the computer. Open the software program named "Rheocheck32" on the computer. Open the file named "stand + visc" dated 05.11.2009.
- Connect the test container to the rheometer when the water bath reaches 60°C.
- Click on "dashboard". "DV3 + com" should be 1 and "no controller com" should be none. Make sure that the right spindle number corresponding to the spindle used is chosen.



februar 24, 2016 10:27:42 Status: Stopped Test:

DV3+ COM 1

No Controller COM None

SC4-21 Max.Viscosity

Viscosity EEEEEEEE cP

Speed 0.00 RPM

Torque ALM +EEEEE %

Shear Stress EEEEEEEE D/cm²

Shear Rate 0.00 1/sec

Temperature +EEEE °C Setpoint:

Bath °C

Speed

RPM 0 ,

Shear Rate 0 , 1/sec

Figure 47: Print screen of command window

- Click "run data" and →. The rheometer now has to be zeroed. It is important that the spindle is disconnected when the rheometer is being zeroed.
- Connect the spindle. Take the crude sample out from the oven and add crude to the test container using a plastic tube. The test container should be filled with crude to its upper line. Place a small plastic sample cap on top of the test container, using the channel allowing the spindle to move. This will help to reduce any evaporation.
- Take at least three constant measurements at 60°C before you set a lower temperature and a cooling rate. The viscosity readings will now be sent automatically to the computer and a graph will be made.

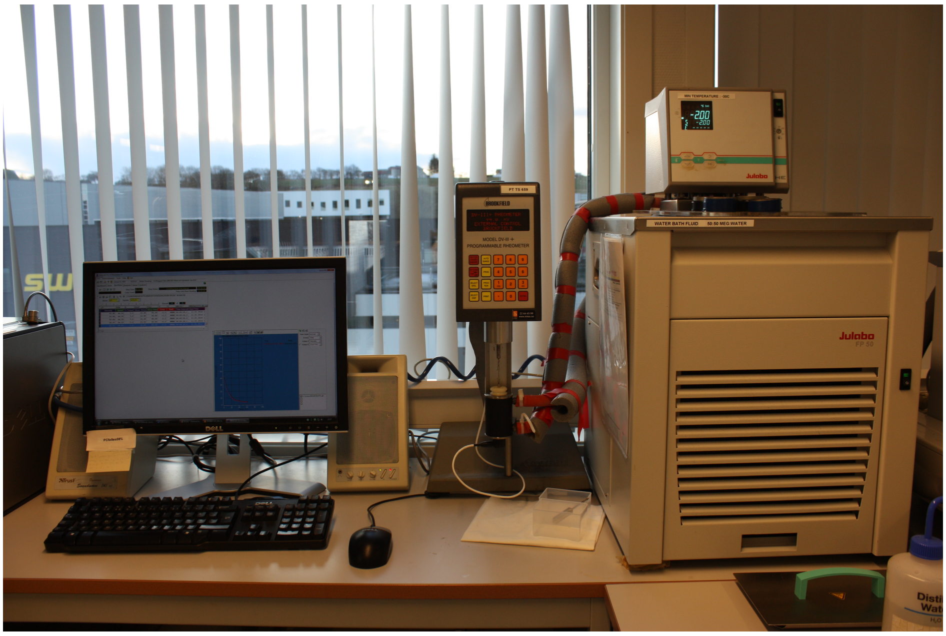


Figure 48: Rheometer connected to computer and water bath

- When the set temperature is reached: stop the test and export data. Exit the program.
- Set the water bath to 60°C and wait until the test specimen is pourable. Disconnect the cable, spindle and the test container. Pour the crude from the test container into the crude waste container. Clean the test container with xylene before cleaning it with soap and water. Flush it with deionized water.
- Turn off the rheometer and water bath.

Appendix 2: Pour point procedure

This procedure is developed from the D5853 ASTM standard test method for pour point of crude oils.

- Turn on the water bath and set the temperature to 0°C.
- Take the sample of crude out of the oven and fill the test jar with crude until it reaches the indication line for sample height. The indication line is 54 ± 3 mm above the inside bottom.
- Put the cork on the test jar and find a suitable thermometer. The thermometer should be placed in the test jar through a hole in the center of the cork. Let the test specimen cool down in room temperature.

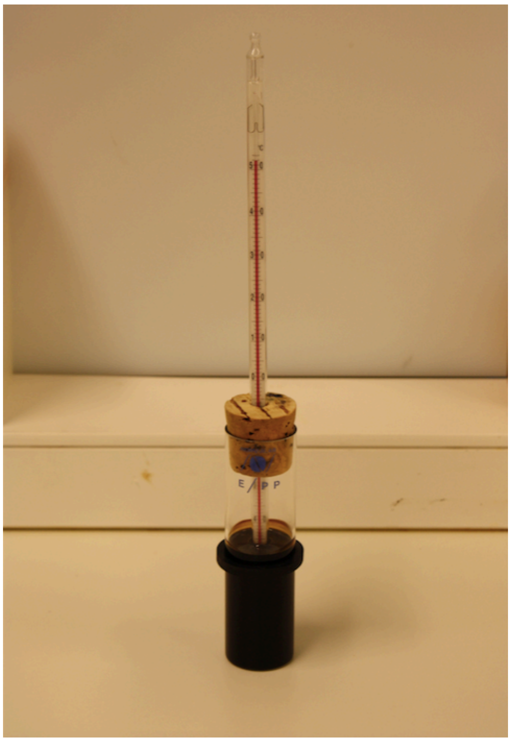


Figure 49: Test jar containing crude oil

- Place the test jar in the water bath when it reaches 45°C. At every third degree the test jar should be taken out of the water bath, and be tilted just enough to ascertain if there is movement of the test specimen. If there is still movement: place the test jar back in the water bath.

- If the test specimen is still pourable at +9°C, the water bath should be set to -18°C. If the test specimen is still pourable at -9°C, the water bath should be set to -33°C.
- The pour point is reached when the test specimen is no longer pourable. Record the reading of the test temperature.
- The final pour point is calculated by adding +3°C to the reading of the test temperature. Example: The test specimen stopped being pourable at 21°C. The final pour point is then 24°C.

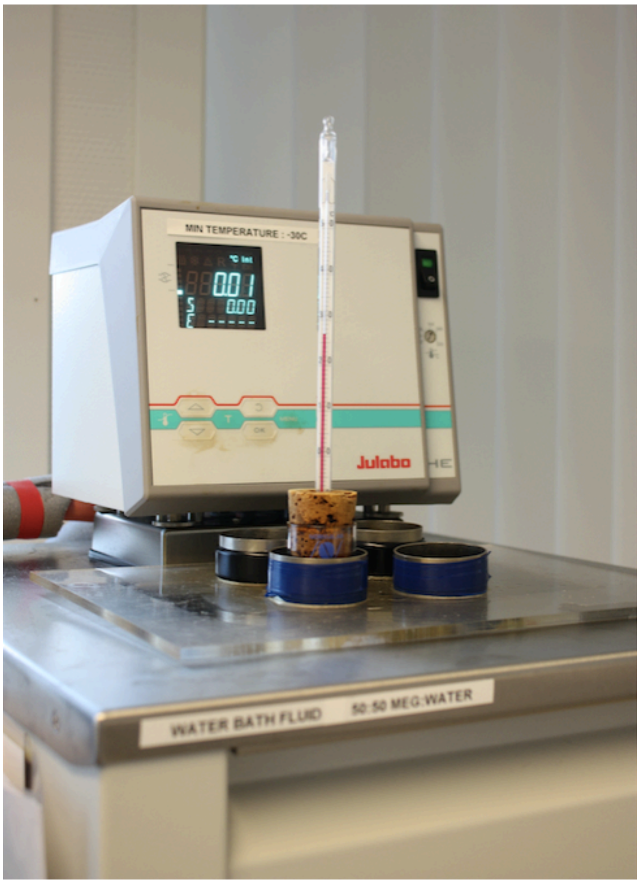


Figure 50: Test jar placed in water bath

When the test is done:

- Put the test jar back in the water bath and set the water bath to 60°C. Take the test jar out of the water bath when it is pourable. Turn off the water bath.
- Pour the crude into the crude oil waste container and clean it with xylene.

Appendix 3: WAT and WDT procedure

- Turn on the pump and the microscope.
- Take the crude out of the oven. Add a droplet of the crude to a transparent plastic slide. Place another transparent slide on top of the other, making the crude droplet "trapped" between the slides. NB! Make sure that the transparent slides are clean and free from dust before adding the droplet of crude. If dust is observed on the transparent slides one should use an air pistol to clean it.
- Place the transparent slides on the microscope
- Set a low temperature and cool the sample down quickly until a relatively high amount of wax crystals appears. Use the microscope to find the right focus.
- Set the temperature to 80°C to heat up the sample. This is to make sure that there are no visible wax crystals left in the sample.
- Set a cooling rate of 1°C/min to cool down the sample. Watch the sample through the microscope. The WAT is reached when the first visible wax crystal appears and can be seen through the microscope.
- Use the same cooling rate to heat up the sample, and watch the sample through the microscope. The WDT is reached when there are no visible wax crystals left.

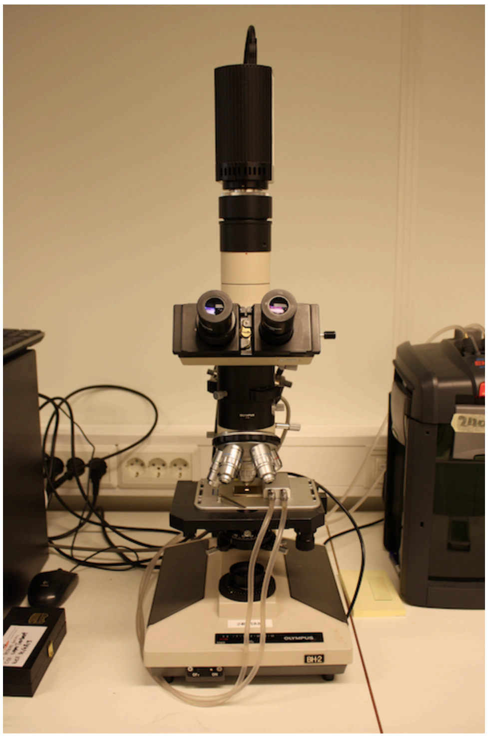
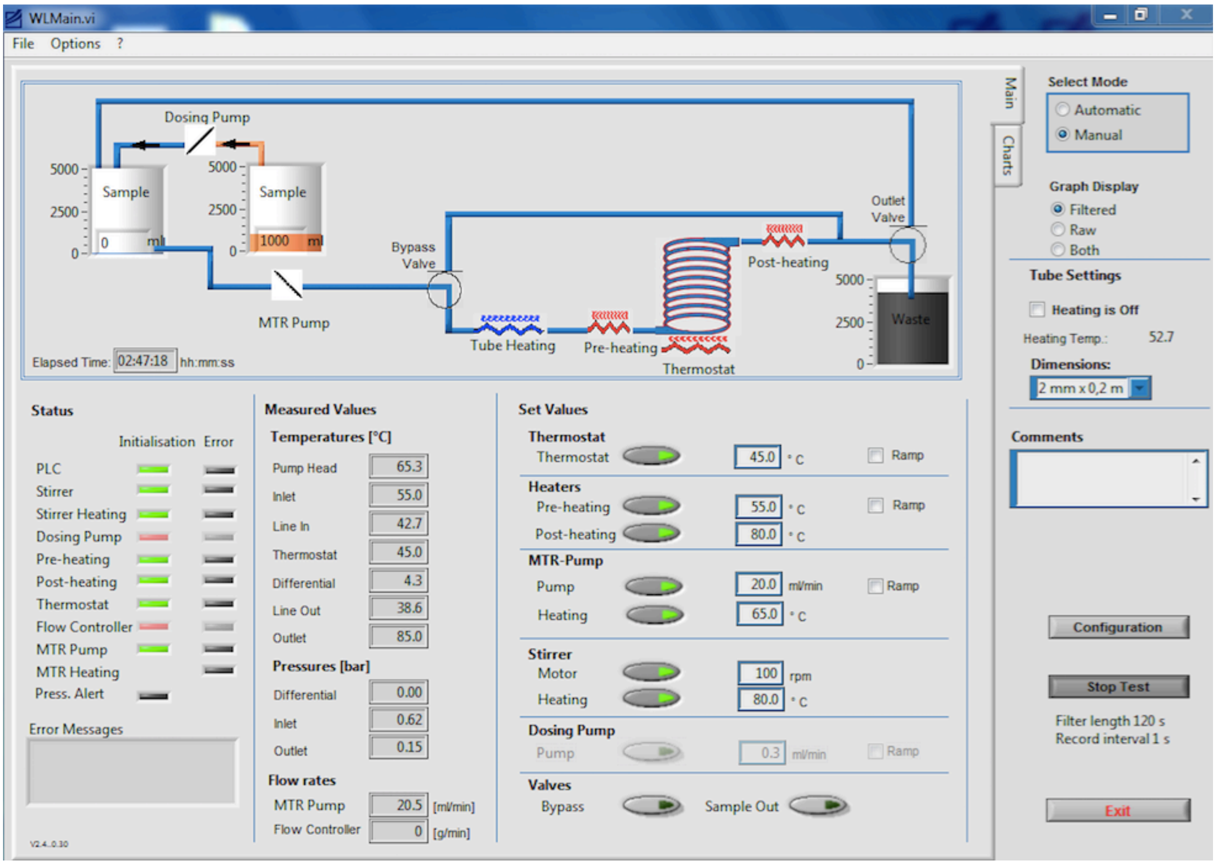


Figure 51: Microscope used during WAT and WDT procedure

Appendix 4: Wax loop procedure

- Make sure that the oxygen valve is open and connected to the wax loop. The oxygen valve is working as an emergency exit if the wax loop is exposed to a blockage. The oxygen valve will contribute to a pressure build up and remove the blockage in the system.
- Push the on-button for 3-4 seconds until the computer screen is on. Log in and start the WL program.
- Turn on the stirrer. Make sure that both switches are on.
- Check the status in the WL program and wait for the colour signals under "initialisation" to be green. Everything except "dosing pump" and "flow controller" should be green before continuing.
- Plot set values. Everything except the pump should be turned on.



Sample: 0 ml
Sample: 1000 ml
Elapsed Time: 02:47:18 hh:mm:ss

Status

	Initialisation	Error
PLC	🟩	▬
Stirrer	🟩	▬
Stirrer Heating	🟩	▬
Dosing Pump	🟥	▬
Pre-heating	🟩	▬
Post-heating	🟩	▬
Thermostat	🟩	▬
Flow Controller	🟥	▬
MTR Pump	🟩	▬
MTR Heating		▬
Press. Alert	▬	

Error Messages

V2.4..0.30

Measured Values

Temperatures [°C]

Pump Head	65.3
Inlet	55.0
Line In	42.7
Thermostat	45.0
Differential	4.3
Line Out	38.6
Outlet	85.0

Pressures [bar]

Differential	0.00
Inlet	0.62
Outlet	0.15

Flow rates

MTR Pump	20.5	[ml/min]
Flow Controller	0	[g/min]

Set Values

Thermostat

Thermostat 45.0 °C ☐ Ramp

Heaters

Pre-heating 55.0 °C ☐ Ramp
Post-heating 80.0 °C

MTR-Pump

Pump 20.0 ml/min ☐ Ramp
Heating 65.0 °C

Stirrer

Motor 100 rpm
Heating 80.0 °C

Dosing Pump

Pump 0.3 ml/min ☐ Ramp

Valves

Bypass
Sample Out

Select Mode
○ Automatic
● Manual

Graph Display
● Filtered
○ Raw
○ Both

Tube Settings

☐ Heating is Off
Heating Temp.: 52.7
Dimensions: 2 mm x 0,2 m

Comments

Filter length 120 s
Record interval 1 s

Figure 52: Print screen of command window in the WL program

- Fill a 600 ml beaker with 150 ml synthetic oil. The beaker with synthetic oil works as an insulation around the bottle of crude, and prevents heat loss. Place the beaker on the stirrer.
- Connect a 250 ml glass bottle of xylene or solvesso to the wax loop. Place it in the beaker containing synthetic oil. The tube named “line out” should be placed in the bottle of waste.
- Flush the system by turning on the pump. The pump rate should be the same as the pump rate that is used during the test. When the tube for line out is transparent and does not contain any air bubbles, the pump rate should be reduced to 1 ml/min. The wax loop is very sensitive, and the pump should not be stopped until the test is done.
- A glass bottle containing 300 ml crude oil should be placed in the oven at 80°C for at least 12 hours before starting the test. This is to ensure that all wax crystals are dissolved in the crude oil. Take the glass bottle of crude oil out of the oven, shake it well in the fume hood and release the pressure. Put a magnetic stirrer into the glass bottle.
- Disconnect the bottle of xylene or solvesso and connect the glass bottle containing crude oil to the wax loop, and place it in the beaker containing synthetic oil. This should be done very quickly in order to prevent heat loss from the crude oil.
- Set the pump rate and flush the system with crude. It takes about 100 ml of crude to flush the system. When the tube named “line out” is dark and completely filled with crude the pump rate should be reduced to 1 ml/min.
- Remove the line out from the bottle of waste and place it in the bottle of crude.
- Set the pump rate. Save and give the test a name and choose a location. Push the button for “start test”.

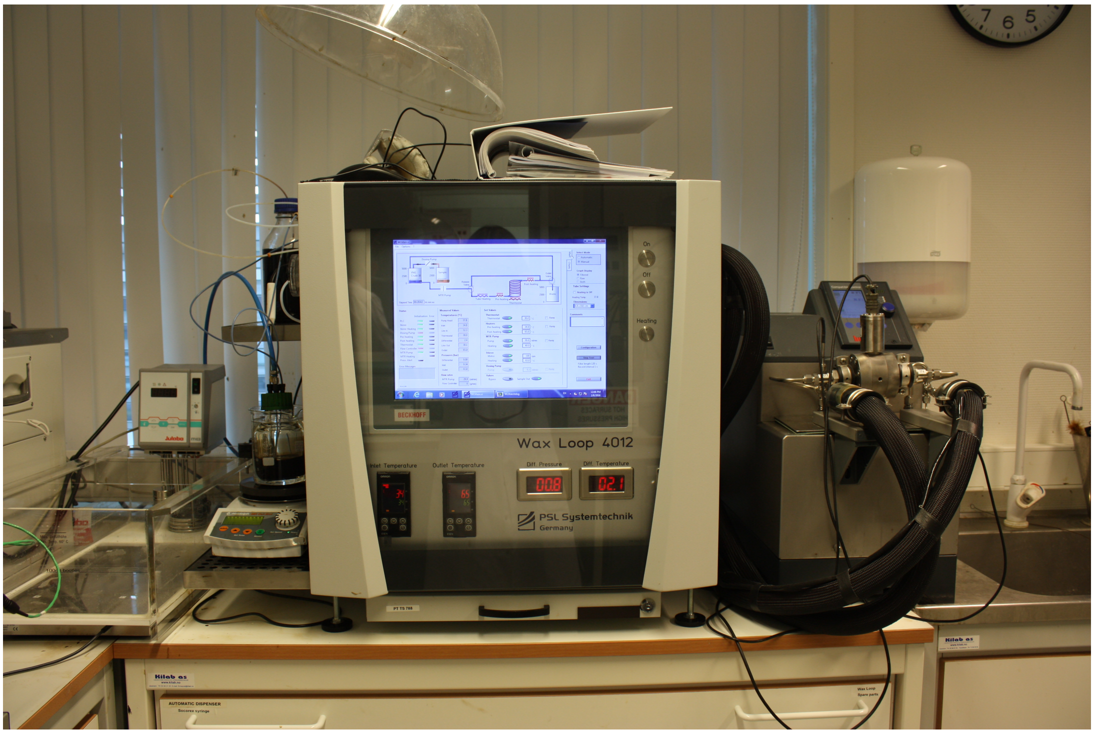


Figure 53: Wax loop equipment

When the test is done:

- Push the “stop test” button. Take a print screen of the graphs.
- Remove the tube named “line out” from the bottle of crude and place it in the waste bottle.
- Set all temperatures to a temperature of 60°C in order to heat up the system. Disconnect the bottle of crude and connect a bottle of xylene or solvesso to the wax loop. Wait until the temperature is reached. Flush the system with a flow rate of 90 ml/min until the tube named “waste” and “line out” is transparent. It is very important to flush the system with a solvent when the test is done. Sample deposits remaining in the pump can crystallize, stick together or lead to corrosion, which affects the functionality of the MTR-pump.
- Turn off the wax loop and stirrer, and close the oxygen valve.

Appendix 5: Calculating Reynolds number

The Reynolds number was calculated by the following equation:

$$Re = \frac{Inertial\ forces}{Viscous\ forces} = \frac{Du\rho}{\mu}$$

Re = Reynolds number
D = Hydraulic diameter of the pipe (m)
u = Average fluid velocity (m/s)
ρ = Density of the fluid (kg/m^3)
μ = Dynamic viscosity of the fluid (Pas)

Where

$$u = \frac{q}{A} = \frac{q}{\frac{\pi}{4}\ x\ D^2}$$

q = Volumetric flow rate (m^3/s)
A = Cross sectional area of flow (m^2)
D = Diameter of the test pipeline (m)

Testing crude A at 25°C

The following values were used when calculating the Reynolds number at a thermostat temperature of 25°C:

D = 0.004 m
u = Average fluid velocity (m/s) = x
ρ = 836 kg/m^3
μ = 82.15 cP = 82.15 x 10^{-3} Pas at 25°C

Flow rate (ml/min)	Calculated fluid velocity (m/s)	Reynolds number
20	0.026	1.058
40	0.053	2.157
60	0.079	3.216
80	0.106	4.315
100	0.133	5.414

Table 10: Calculated numbers at 25°C

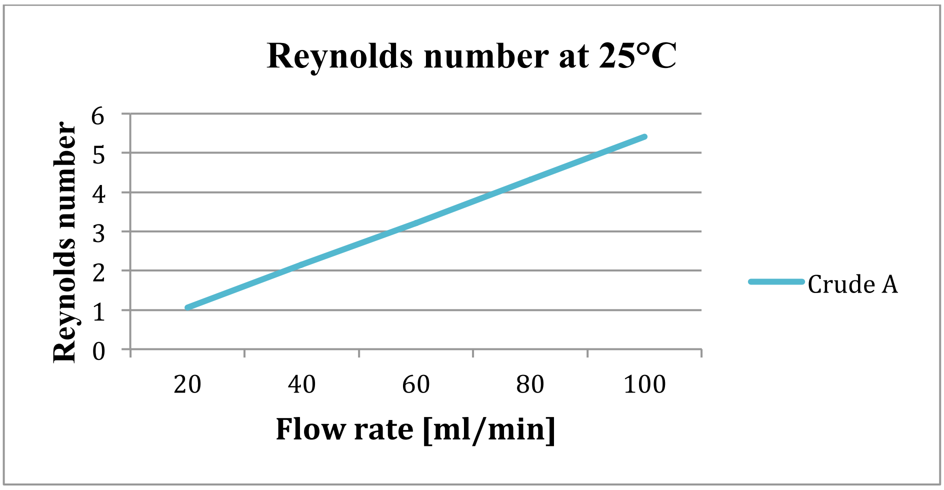


Figure 54: Reynolds number at 25°C

Flow rates of 20 ml/min and 30 ml/min were used when testing crude A at a thermostat temperature of 25°C. From the graph one can see that even with a flow rate of 100 ml/min the Reynolds number is as low as 5.414, which means that the flow regime is laminar.

Testing crude A at 20°C

The following values were used when calculating the Reynolds number at a thermostat temperature of 20°C:

D = 0.004 m
u = Average fluid velocity (m/s) = x
$\rho = 836 \text{ kg/m}^3$
$\mu = 191.425 \text{ cP} = 191.425 \times 10^{-3}$ Pas at 20°C

Flow rate (ml/min)	Calculated fluid velocity (m/s)	Reynolds number
20	0.026	0.454
40	0.053	0.926
60	0.079	1.380
80	0.106	1.852
100	0.133	2.323

Table 11: Calculated numbers at 20°C

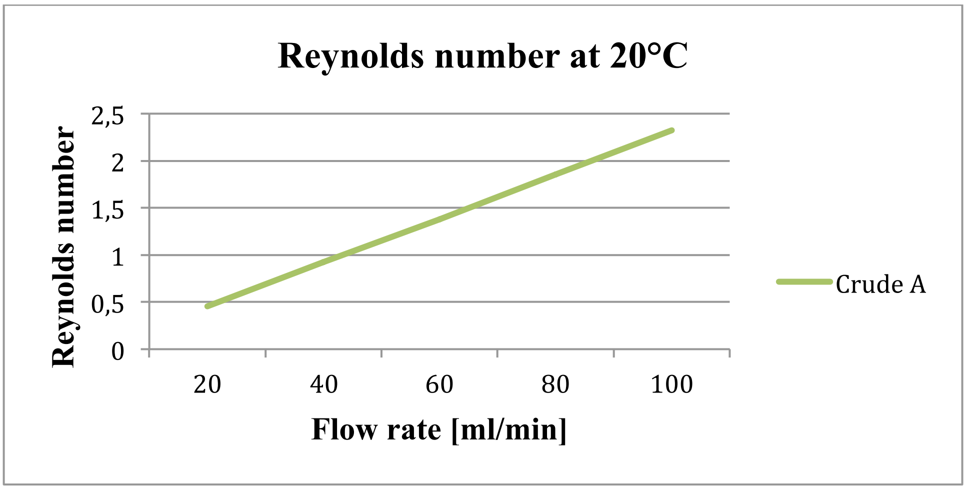


Figure 55: Reynolds number at 20°C

A flow rate of 20 ml/min was used when testing crude A at a thermostat temperature of 20°C. At 20 ml/min the Reynolds number is as low as 0.454, which means that the flow regime is laminar.

Testing crude D at 50°C

With a thermostat temperature of 50°C the following values were used when calculating the Reynolds number:

D = 0.004 m
u = Average fluid velocity (m/s) = x
$\rho = 855\ kg/m^3$
$\mu = 17.05\ cP = 17.05 \times 10^{-3}$ Pas at 50°C

Flow rate (ml/min)	Calculated fluid velocity (m/s)	Reynolds number
20	0.026	5.215
40	0.053	10.631
60	0.079	15.846
80	0.106	21.262
100	0.133	26.678

Table 12: Calculated numbers at 50°C

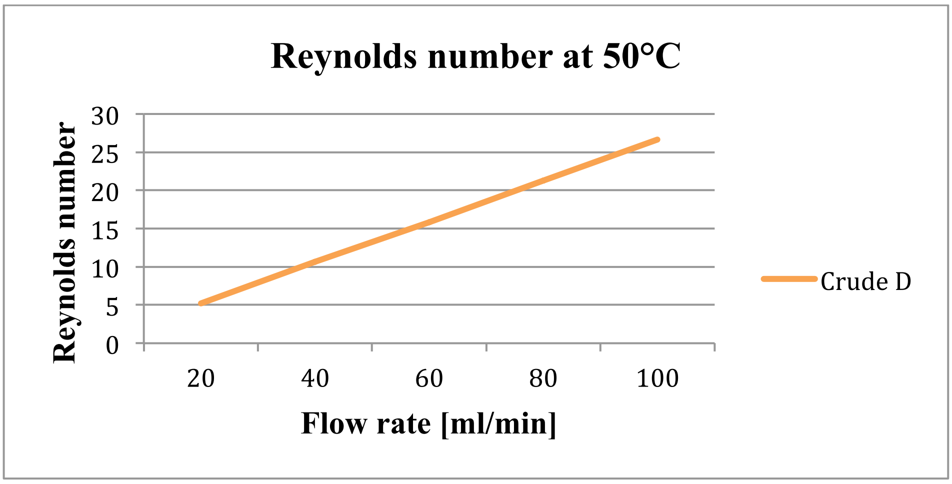


Figure 56: Reynolds number at 50°C

A flow rate of 20 ml/min was used when testing crude D at a thermostat temperature of 50°C. At 20 ml/min the Reynolds number is as low as 5.215, which means that the flow regime is laminar.

Testing crude D at 45°C

With a thermostat temperature of 45°C the following values were used when calculating the Reynolds number:

$D = 0.004$ m

u = Average fluid velocity (m/s) = x

$\rho = 855$ kg/m^3

$\mu = 20.15$ cP $= 20.15 \times 10^{-3}$ Pas at 45°C

Flow rate (ml/min)	Calculated fluid velocity (m/s)	Reynolds number
20	0.026	4.413
40	0.053	8.995
60	0.079	13.408
80	0.106	17.991
100	0.133	22.574

Table 13: Calculated numbers at 45°C

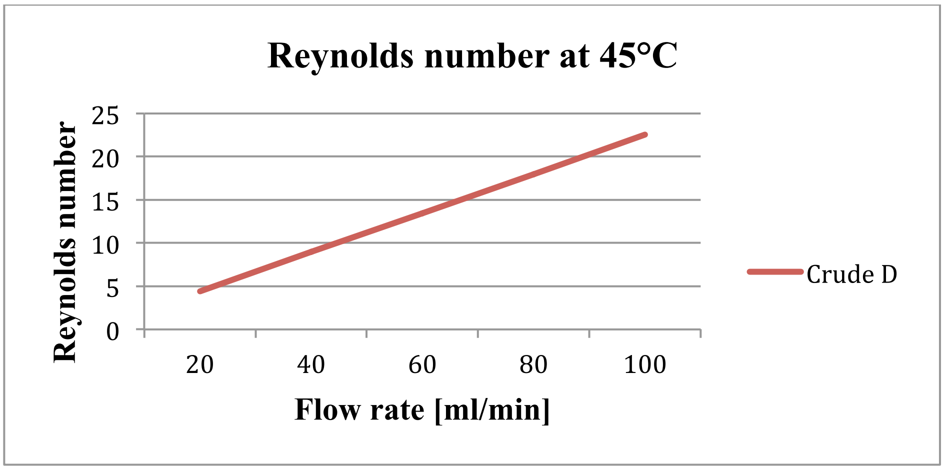


Figure 57: Reynolds number at 45°C

A flow rate of 20 ml/min was used when testing crude D at a thermostat temperature of 50°C. At 20 ml/min the Reynolds number is as low as 4.413, which means that the flow regime is laminar. From the graph one can also see that increasing the flow rate to 100 ml/min ensures a laminar flow regime. This is caused by the small diameter of the test pipeline.